

LNG Technology: The Weathering in Above-Ground Storage Tanks

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1. INTRODUCTION

Since the beginning of the new century, energy markets and their sustainability have been the focus of both public and private interest. Security of supply, economic efficiency, and environmental protection have become the main topics in the debate about energy and its future, promoting the collaboration of both engineers and economists, lawyers, and public spheres. In this work, the attention is strictly centered on the highly growing market of natural gas, i.e., the liquefied natural gas (LNG) state-of-art technology that will increase gas supply via sea transportation^{1,2} and also, although to a much lesser extent, via ground transportation (micro LNG plants).

According to the economic theory, economic growth and energy consumption are strictly correlated: indeed, the high growth rates expected from developing countries (i.e., China and India) are one of the main causes for the rising concern about the amount and portability of natural resources from production countries to new markets. Based upon International Monetary Fund and Asian Development Bank estimates, through 2035, China will be able to achieve an average growth rate of 5.6% annually.

However, although economic development has been nourished by coal, until recently, and coal consumption has been increasing by 8% per year for the past decade, increasing environmental burden of coal have moved the general interest up to other energy sources (i.e., natural gas), whose consumption doubled within a few years. Indeed, among fossil fuels, natural gas is projected, to 2030, to have up the highest growth rate (2.1% per year), mainly in non-OECD countries and in the Middle East. Continuing with the Chinese case, this country is expected to diversify its fuel mix away from coal, reaching a level of gas use estimated to be ~46 Bcf, which is the same level as that for the European Union in 2010.^{3,4}

Also, the natural gas supply, as gas demand, is expected to grow in the near future. A major contribution is certainly coming from the Middle East and the former Soviet Union (FSU), with 26% and 19% of the global growth, respectively.

However, new entrants are being projected to change the rule of supply and competition in the gas market. West Africa, North Western Australia, South America, Caribbean, Indonesia, Malaysia, and Alaska are opening a market that has been traditionally dominated by a maximum of three players—Russia, Algeria, and Norway—to competition, a hazardous monopoly to prices and security of supply.

The United States now plays a role apart: natural gas from shales is treated in micro LNG plants from which LNG for automotive applications is transported by train or other above-ground facilities to the final destination.

However, it is noteworthy to specify that such a diversification in importers' choice is mainly made possible by the introduction of LNG technology in the natural gas logistics and transportation system. Indeed, until the introduction of LNG, the low density of natural gas has made gas transportation costs higher than those of either oil or coal, limiting movements and connections to those allowed by a long-term fixed infrastructure (i.e., pipelines).⁵ However, since 1964, when the first LNG cargo was sent from Algeria to the United Kingdom, the number of participants and the number of routes in the gas market have increased significantly. Thanks to LNG, which currently accounts for 32.3% of the global gas trade,⁶ moving natural gas from low-cost/low-value resources to distant, high-value markets has become not only feasible, but also efficient, especially if the route is more than 1000 km long.

At the same time, this requires appropriate technologies for the transport and storage. This article proposes a model that allows to predict the dynamic behavior of the LNG contained in a storage tank with boiloff. This topic is fundamental in LNG technology for mainly two reasons: the necessity to meet quality specifications when blending LNGs from different

Received: July 2, 2013

Revised: January 27, 2014

Accepted: February 18, 2014

Published: February 18, 2014

sources and the safety requirement to avoid stratifications and possible roll-over phenomena inside the LNG tank.⁷

During its residence within a tank, LNG slowly changes in composition due to heat flux received from the surroundings: nitrogen is the first to escape, while methane vaporizes at a higher rate than ethane and propane. After a long period, that can last months or years in the case of a tank for peak shaving adjustments, LNG is warmer and denser, as confirmed by the results obtained in the present paper. This has important consequences when a cooler and lighter stock is mixed with the heel (i.e., the old LNG present in the tank). The resulting stratification can cause instability inside the tank with the sudden release of LNG vapors and rollover. At best, such a situation results in the loss of valuable fuel while, at worst, it can be dangerous. Therefore, a reliable tool for predicting the LNG time behavior is fundamental.

2. STATE OF THE ART

Many publications regarding facilities, safety, and atmospheric dispersion are available, often approaching LNG as a substance characterized by methane properties, and neglecting the influence of changes in chemical composition. However, in the literature, studies on the unsteady evolution of LNG during storage are limited.

Aspelund et al.⁸ developed a program for calculation of the gas quality in a small-scale LNG chain by considering a constant heat flow. The model, as well as the one by Kountz,⁹ is based on equilibrium between liquid and vapor phases, with good approximation of experimental data, as reported by Miana et al.¹⁰ Conrado and Vesovic¹¹ proposed a model to estimate the rate of vaporization of LNG and LPG cryogenic mixtures spreading on unconfined water surfaces, showing that the behavior of LNG can be very different from that of pure methane. Similar conclusions had been previously obtained by Boe¹² in 1997. Miana et al.¹⁰ proposed an algorithm for marine transportation, developed on the basis of two parameters that should be known: the boiloff rate (BOR) and the ship capacity. In general, then, it can be inferred that, in the majority of studies present in the literature, certain drastic simplifying assumptions are considered, in particular as for the boiloff gas (BOG) amount and the composition. These assumptions may be acceptable for preliminary evaluation, but they should be removed for detailed thermo-economic evaluations and optimization analysis. This is also remarked by Dimopoulos and Frangopoulos,¹³ who stated that “the handling of the boil-off gas during the LNG vessel operation and the assessment of its thermodynamic properties are key issues in the technical and economic assessment” of the energy system of LNG vessels.

The proposed model, then, aims at removing these simplifying assumptions, in order to best describe the evolution of the system during time.

3. DEVELOPMENT OF THE MODEL

LNG is stored in tanks at a pressure slightly higher than the atmospheric value; since the vapor–liquid equilibrium hypothesis is made, storage temperature is the bubble point temperature of the mixture.

Unlike other models that can be found in the literature,^{10,14} the proposed model does not require knowledge of the boiloff rate (BOR), which is the amount of evaporated gas in one day, in terms of the amount of liquid volume relative to the initial volume of LNG. As a matter of fact, the flow rate of gas that

leaves the tank is determined by knowing the heat flow to the tank, which can be calculated using generalized curves¹⁵ or a dedicated model of heat transfer through the insulations.

From the equilibrium relation

$$y_i = k_i x_i \quad (1)$$

the LNG boiling point conditions can be found computing the numerical root of

$$\sum_{i=1}^{NC} y_i = \sum_{i=1}^{NC} k_i x_i = 1 \quad (2)$$

Molar balances for LNG and for each of its components, coupled to the enthalpy balance, generate the following system of differential equations:

$$\frac{dM_{\text{tot}}}{dt} = -\dot{W} \quad (3)$$

$$\frac{d(x_i M_{\text{tot}})}{dt} = -y_i \dot{W} \quad (4)$$

$$\frac{d(\sum_{i=1}^{NS} (x_i H_i^L M_{\text{tot}}))}{dt} = -\sum_{i=1}^{NS} (y_i H_i^V \dot{W}) + \dot{Q} \quad (5)$$

Differentiating eq 2 with respect to time, the following correlation that expresses the temperature dependence on time is obtained:

$$\frac{dT}{dt} = -\frac{\sum_{i=1}^{NC} \left[k_i \frac{dx_i}{dt} \left(x_i \frac{\partial k_i}{\partial T} + k_i \right) \right] - \frac{dP}{dT} \left(x_i \frac{\partial k_i}{\partial P} \right)}{\sum_{i=1}^{NC} \frac{\partial k_i}{\partial T} x_i} \quad (6)$$

Introducing eqs 1 and 4 into eq 6 and then equating with (dT/dt) obtained from the energy balance (eq 5), an expression correlating the evaporated moles at the considered time with the heat loss at the same time is found:

$$\dot{W} = \frac{\dot{Q}}{\frac{(\sum_{i=1}^{NC} x_i C_{P,i}^L) \left[\sum_{i=1}^{NC} x_i \left(x_i \frac{\partial k_i}{\partial x_i} + k_i \right) (k_i - 1) \right] + \frac{dP}{dT} \sum_{i=1}^{NC} \left(x_i \frac{\partial k_i}{\partial P} \right)}{\left(\sum_{i=1}^{NC} \frac{\partial k_i}{\partial T} x_i \right)} + \sum_{i=1}^{NC} (k_i x_i \Delta \bar{H}_{\text{ev},i})} \quad (7)$$

where the first term in the denominator represents the contribution of sensible heat, which is much smaller than the second term, which represents the latent heat (and usually is not considered in the literature).^{16,17}

($\partial k_i / \partial x_i$) is, for LNG systems, usually negligible, compared to ($\partial k_i / \partial T$), while (dP/dt) has a non null value only for systems with variable pressure, in which case a trend of pressure over time must be assigned.

Equations 1, 3, 4, and 7 constitute a system of ordinary differential equations (ODEs) and algebraic equations that can be solved using a simple numerical method (i.e., fourth-order Runge–Kutta). At each time step, the total mass (M_{TOT}) and the molar fraction of the LNG components x_i are calculated by solving the differential equations of the total and component balances while the temperature and the boiloff are obtained by rooting eq 1 and directly from eq 7, respectively.

Alternatively, if the boiloff is assumed constant, $\dot{W} = n_{\text{ev}} / 86400$ (kmol/s), eq 7 is not needed. This alternative will be discussed in section 4.

4. EQUILIBRIUM AND DENSITY CALCULATION

An appropriate thermodynamic description of LNG cannot use an ideal scheme,^{18–20} because of the proximity to critical conditions at least for nitrogen, if present, and sometimes also for methane.

To calculate the equilibrium condition represented by the boiling point, eq 1, the Soave–Redlich–Kwong (SRK) Equation of State (EoS),²¹ has been used.

The same EoS can be used to predict density values, although it is well-known that, near critical conditions, cubic EoSs fail in predicting reliable values of volumetric properties. On the other hand, density requires accurate calculation, because it is the difference in densities that causes stratifications and, consequently, rollover in LNG plants.

In the literature, the Penélox correction²² is widely applied so that density can be calculated according to

$$\frac{1}{\rho} = v = v^{\text{SRK}} - c \quad (8)$$

with

$$c = 0.40768(RT_R)(0.29441 - Z_{RA})$$

where Z_{RA} is the Rackett compressibility factor²³, estimated as $0.29056 - 0.08775 \omega$.

A better prediction can be obtained by assuming²⁴

$$c(T_R) = AT_R^2 + BT_R + D \quad (9)$$

where A , B , and D depend on the reduced normal boiling point of the given compound (NBP_R), and are expressed as

$$A = a_1 NBP_R^2 + a_2 NBP_R + a_3 \quad (10)$$

$$B = b_1 NBP_R^2 + b_2 NBP_R + b_3 \quad (11)$$

$$D = d_1 NBP_R^2 + d_2 NBP_R + d_3 \quad (12)$$

After a long period inside the tank, LNG is warmer and denser, and the stratification resulting when a cooler and lighter stock is added can cause the sudden release of LNG vapors and roll-over. By considering an accurate thermodynamic method, the proposed model allows a reliable prediction of compositions and densities inside the tank during time. This helps in evaluating whether, when adding new LNG into the tank, the difference in composition and, consequently, the difference in density and temperature, can be so high to result in a dangerous scenario.

5. RESULTS AND DISCUSSION

The procedure illustrated in section 3 has been applied to two sample cases studied in the literature⁹ and reported also in another reference.¹⁰ A small tank containing 190 L of LNG receives a constant heat flow by means of a catalytic heater. Pressure is kept constant and equal to 7.7 bar, except during the last three days, when it is slightly reduced (to 7.397 bar). Such experimental conditions do not reproduce the usual operating conditions of above-ground tanks, where the pressure is almost atmospheric and the BOR is $\sim 0.5\%$ per day, but they have been assumed to accelerate the aging process by experimental researchers. Experimental data reproduced in the simulation are reported in Table 1. Because of the unavailability of the report by Kountz,⁹ which presented data for many cases, experimental values have been directly taken from Miana et al.,¹⁰ who reported data for only Case 5 and Case 6.

Table 1. Data of the Experimental Conditions of the Simulated Cases

property	Case 5	Case 6
tank pressure (bar)	7.7	7.7
heat flow (W)	14.64	11.71
initial tank filling (%)	81.42	91.44
time duration of the experiment (days)	21	27
boiloff rate, BOR (day^{-1})	4	3.1
composition		
methane	0.919	0.878
ethane	0.068	0.068
propane	0.013	0.01
nitrogen	0	0.044

Figures 1–4 respectively show the evolution over time for Case 5 of the mass in the tank, the boiloff, the temperature, and

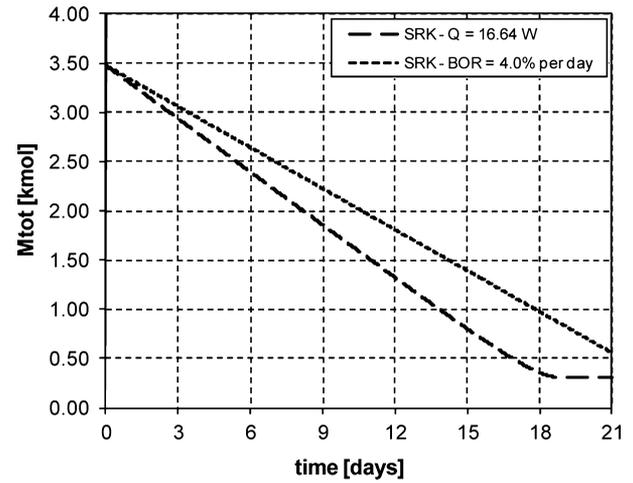


Figure 1. Evolution over time of the mass in the tank for Case 5.

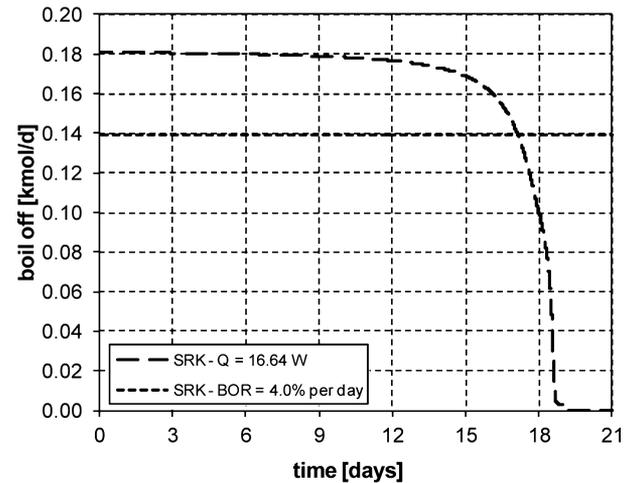


Figure 2. Evolution over time of the boiloff for Case 5.

the density results obtained from the software that implements the proposed model using SRK EoS with the correction factor for density calculation.

The dotted lines represent the results obtained using a constant value for BOR, instead of the value calculated with eq 7 for $Q = 16.64$ W. The value of BOR is 4%, which is the same

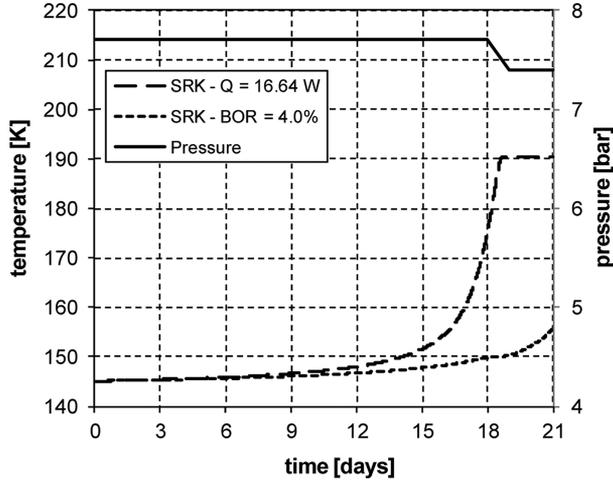


Figure 3. Evolution over time of the temperature and pressure for Case 5.

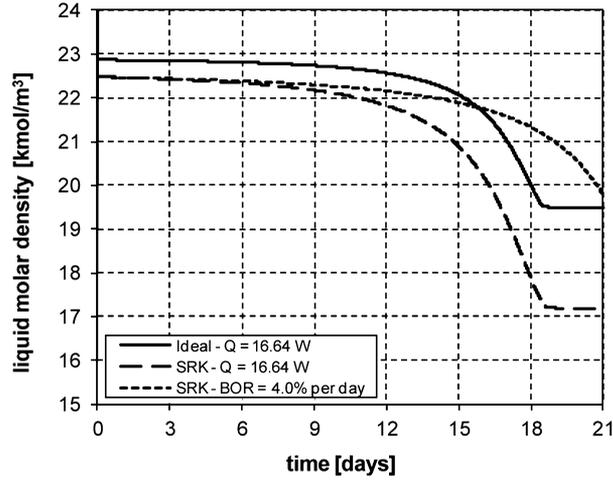


Figure 4. Evolution over time of the density for Case 5.

mean value used in the literature,¹⁰ where the simplifying assumption of a constant BOR is applied to all the simulations.

As shown in Figures 1 and 2, BOR can be assumed constant only in the first part of the transient since, for $t > 12$ days, the evolution of the variables characterizing the system becomes fully nonlinear. It is evident also that the assumption of constant BOR gives an incorrect representation of temperature and density for $t > 10$ days. This is obtained by employing the proposed model, which considers a BOR that varies with time and depending on the heat flux.

Moreover BOR, which is defined as

$$\text{BOR} = \frac{V_{\text{ev}}^L}{V_{\text{in}}^L} \quad (13)$$

can be assumed equal to $n_{\text{ev}}/n_{\text{in}}$ only at times far from those corresponding to the tank emptying when density cannot be considered constant, as shown in Figure 4.

In Case 5, nitrogen, which is the supercritical component, is not present; therefore, a comparison of densities can be made between the results obtained using SRK with the correction for density and the results obtained assuming an ideal thermodynamic model i.e., $k_i = (P_{\text{ev},i}(T))/P$ with $P_{\text{ev},i}(T)$ calculated from

the Antoine equation,²⁵ while the density is obtained from HBT correlation:^{25–27}

$$\frac{1}{\rho_s} = v_s = v_R^0 [1 - \omega_{\text{SRK}} v_R^\delta] v^* \quad (14)$$

$$v_R^0 = 1 + a(1 - T_R)^{1/3} + b(1 - T_R)^{2/3} + c(1 - T_R)^{1/3} + d(1 - T_R)^{4/3} \quad (15)$$

$$0.25 < T_R < 0.95$$

$$v_R^\delta = \frac{e + fT_R + gT_R^2 + hT_R^3}{(T_R - 1.00001)} \quad 0.25 < T_R < 1.0 \quad (16)$$

where values of the constants a – h and of the pure component characteristic volume (v^*) can be found in the literature.²³

The difference in the results from the two methods at the initial time corresponds to 1.74% while, near the emptying of the tank, it reaches 13.38%.

Figures 5–7 report the trends of molar fraction for methane, ethane, and propane, respectively. The results at constant duty

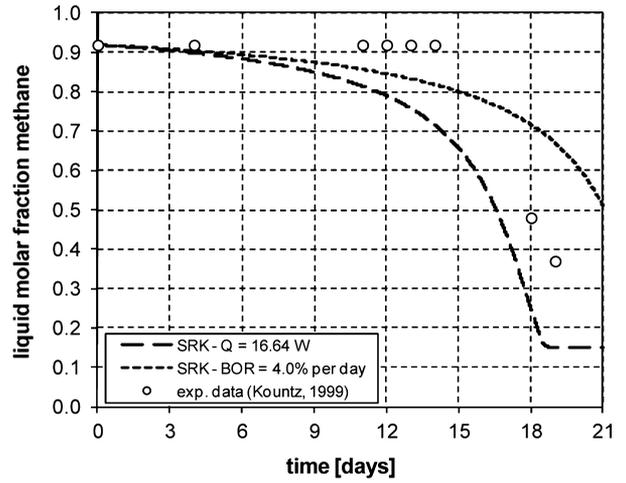


Figure 5. Evolution over time of the liquid molar fraction of methane for Case 5.

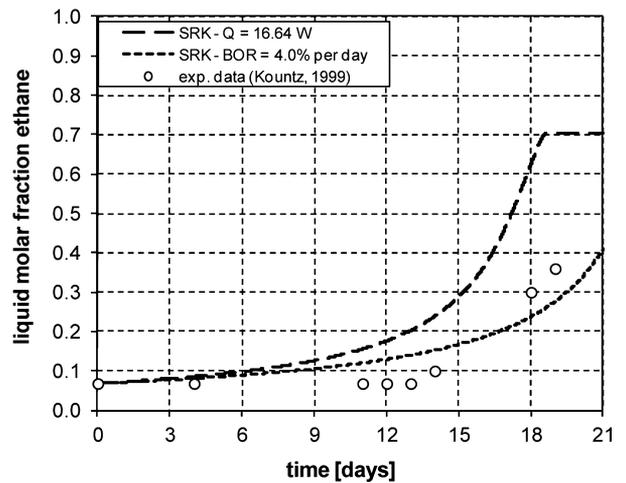


Figure 6. Evolution over time of the liquid molar fraction of ethane for Case 5.

and the ones based on a constant value of BOR show a clear deviation: analyzing Figure 2 again, it is clear that, in the former case, the boiloff is higher in the first days and, therefore, light components exit the tank earlier so that in the end the

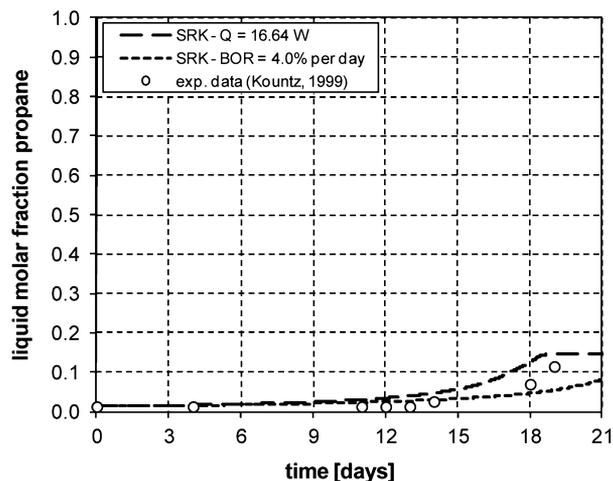


Figure 7. Evolution over time of the liquid molar fraction of propane for Case 5.

composition of heavy components is higher as well as the corresponding equilibrium temperature. It is worthwhile to note that, for $t \approx 19$ days, the time derivatives in eqs 3–7 become null and the system reaches the steady-state conditions (i.e., \dot{W} is null and the other state variables remain constant).

The results for both cases ($Q = \text{cost}$ and $\text{BOR} = \text{cost}$) are far from the experimental data. However, a careful analysis shows how, for Case 5, the experimental points do not fulfill the overall material balance: the sum of experimental molar fractions do not sum up to 1. The proposed model is consistent with material balance calculations: indeed, the experimental values could not be reproduced, but the resulted trend is plausible.

Figures 8–11 report the molar fractions evolution over time, based on Case 6. Simulations from Miana et al.¹⁰ are also

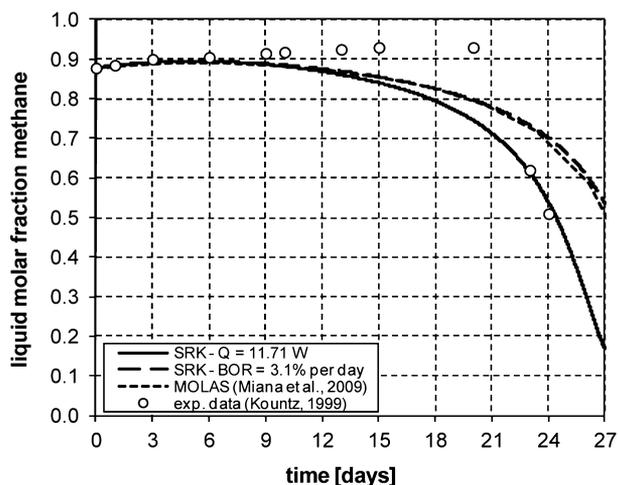


Figure 8. Evolution over time of the liquid molar fraction of methane for Case 6.

reported and compared with our simulations at the same BOR value of 3.1% per day and at $Q = 11.71$ W, as shown from Table 1. A comparison of results is shown also in Table 2, which reports the percent errors of the proposed model and of the model from literature.¹⁰

The proposed model shows the lowest deviation for the molar fractions of all compounds. In particular, a good

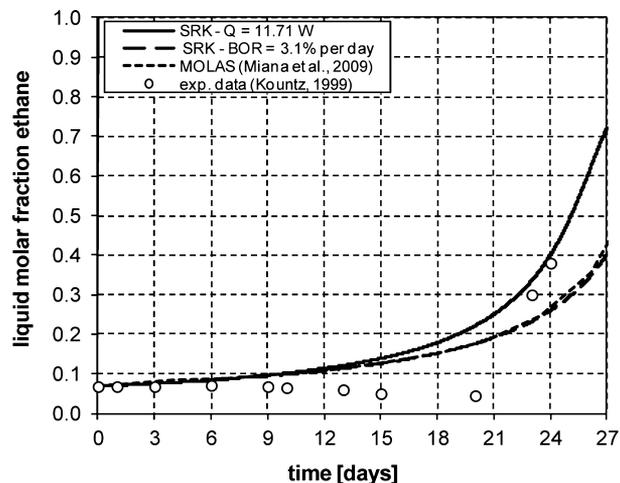


Figure 9. Evolution over time of the liquid molar fraction of ethane for Case 6.

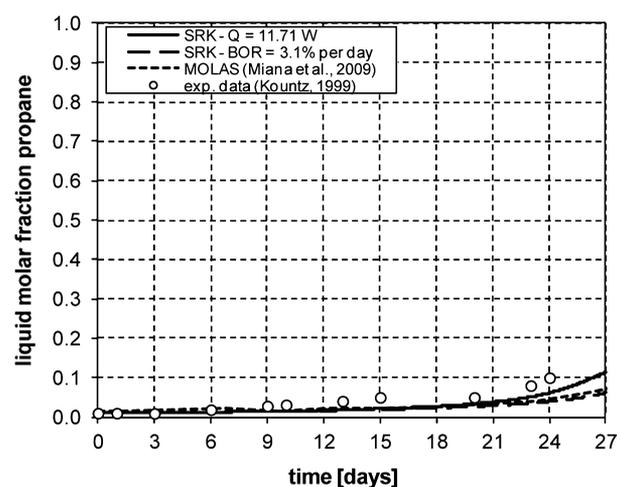


Figure 10. Evolution over time of the liquid molar fraction of propane for Case 6.

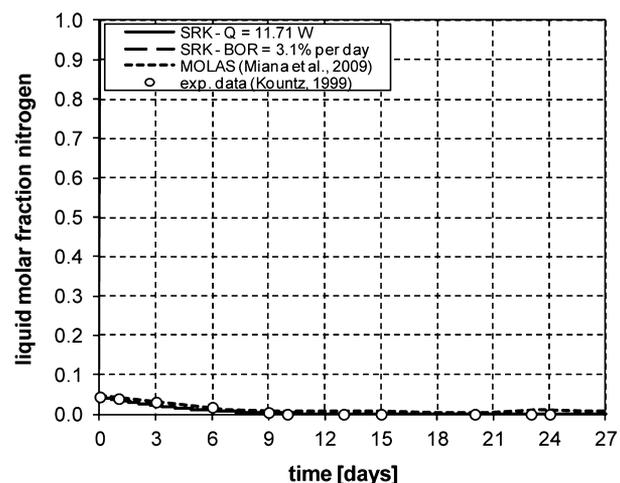


Figure 11. Evolution over time of the liquid molar fraction of nitrogen for Case 6.

representation of the amount of methane and ethane is fundamental, given the fact that these compounds are present in higher concentrations than the other ones.

Table 2. Percent Errors Resulting with the Proposed Model and with Another Model¹⁰ from the Literature, Which Analyzes the Same Experimental Cases, at the End of the Day, for Case 6

component	% Error	
	model from literature	proposed model
methane	41.01	5.59
ethane	35.73	5.44
propane	59.29	39.17
nitrogen	0	0

For Case 6, the experimental molar fractions are consistent and the proposed model with \dot{W} calculated according to eq 7 is in better agreement with experimental data at least in the first days and during the emptying of the tank.

In the initial composition nitrogen, which is above its critical point ($T_C = 126.2$ K) at Case 6 operating conditions, is present, so no simulation can be performed using an ideal thermodynamic approach.

It is interesting to notice that the molar fraction of liquid methane has a maximum in Case 6, unlike Case 5: this is due to the presence of nitrogen which is the first component leaving the tank. As the amount of N_2 lowers, methane becomes the most volatile compound and starts to significantly vaporize.

In the end the temperature results are compared in Figure 12: also in this case the best agreement is obtained from simulation with $Q = 11.71$ W, confirming the inaccurate prediction obtained when using an average value for the boiloff.

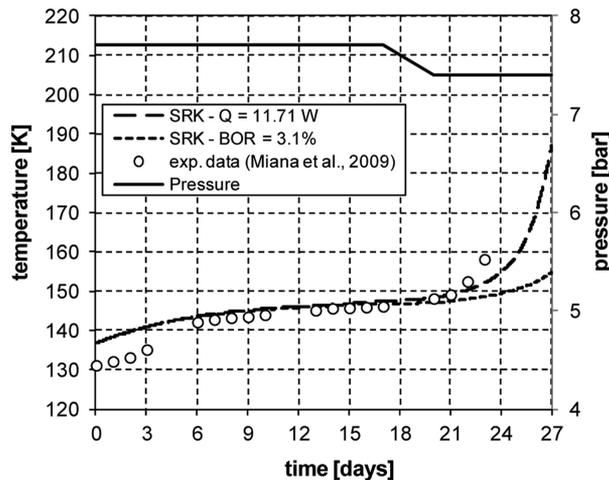


Figure 12. Evolution over time of the temperature and of the pressure for Case 6.

6. CONCLUSIONS

An introductory analysis has shown how natural gas is rapidly becoming an internationally traded commodity, because of the improvements in technology and costs.

This is made possible mainly by the introduction of liquefied natural gas (LNG) technology in the natural gas logistics and transportation systems: previously, the low density of natural gas made gas transportation costs higher than those of either oil or coal, limiting the movements and connections to those allowed by long-term pipelines.

One problem to be faced in LNG technology is the LNG aging (i.e., a change of composition during LNG transportation

and storage). Moreover, an accurate prediction of composition and density is necessary to perform blending operations and prevent accidents that are due to stratification and roll-over phenomena.

The method proposed in this paper for predicting aging in LNG above-ground tanks is based on the Soave–Redlich–Kwong cubic Equation of State (SRK EoS) with a density correction. It is capable to calculate the time evolution of temperature and composition inside the tank for an assigned value of the boiloff, as well as when the heat flow to the tank is assigned and the boiloff must be calculated.

The paper shows, by comparison with experimental data, the misleading results obtained using a mean value of the boiloff, as often assumed in previous literature works, instead of calculating it, as done in the proposed model, from the heat exchanged with the surroundings, which can be computed using generalized correlations or, better, by calculating all of the heat-transfer contributions.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

NOMENCLATURE

A = parameter for volume correction eq 10 ($m^3/kmol$) a_1 ,

a_2, a_3 = parameters in eq 10 ($m^3/kmol$)

$a-h$ = parameters in eqs 15 and 16

B = parameter for volume correction in eq 11 ($m^3/kmol$)

b_1, b_2, b_3 = parameters in eq 11 ($m^3/kmol$)

BOR = boiloff rate, defined as the amount of evaporated gas in one day, in terms of liquid volume, relative to the initial volume (%)

$c(T_R)$ = molar volume correction ($m^3/kmol$)

C_p^L = liquid specific heat ($J/(kmol K)$)

D = parameter for volume correction in eq 12 ($m^3/kmol$)

d_1, d_2, d_3 = parameters in eq 12 ($m^3/kmol$)

H = molar enthalpy ($J/kmol$)

k_i = vapor–liquid equilibrium constant of component i M_{tot} = total molar mass ($kmol$)

n = number of moles ($kmol$)

n_{ev} = number of moles evaporated in one day ($kmol/d$) n_{in}

= initial number of moles ($kmol$)

NBPR = reduced normal boiling temperature, defined as $NBPR = T_{NBPR}/T_c$

NC = number of components

P = pressure (bar)

P_{ev} = vapor pressure (bar)

Q = exchanged power (W)

R = gas constant ($(Pa m^3)/(kmol K)$)

t = time (days, s)

T = temperature (K)

v = molar volume ($m^3/kmol$)

v^* = characteristic molar volume ($m^3/kmol$)

v_R^δ = parameter for HBT correlation

v_R^0 = parameter for HBT correlation

V_{ev}^L = volume of evaporated gas in one day (m^3/d)
 V_{in}^L = initial volume (m^3)
 \dot{W} = boiloff (kmol/s)
 ω = acentric factor
 x = molar fraction in liquid phase (kmol/kmol)
 y = molar fraction in vapor phase (kmol/kmol)
 Z_{RA} = Rackett compressibility factor

Greek Symbols

$\Delta \tilde{H}_{ev,i}$ = molar enthalpy of vaporization (J/kmol)
 ρ = molar density ($m^3/kmol$)

Superscripts

i = component
L = liquid
V = vapor
SRK = Soave–Redlich–Kwong

Subscripts

C = critical value
ev = evaporated
in = initial
L = liquid
NBP = normal boiling temperature (K)
R = reduced value, i.e., divided by the critical value
s = saturation
SRK = Soave–Redlich–Kwong

Abbreviations

BOG = boiloff gas
EoS = equation of state
FSU = former Soviet Union
HBT = Hankinson–Brobst–Thomson equation
LNG = liquefied natural gas
OECD = Organisation for Economic Co-operation and Development
SRK = Soave–Redlich–Kwong

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