LNG AGEING DURING SHIP TRANSPORTATION

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ABSTRACT

International LNG trade has undergone a considerable increase in recent years, with a growth rate of 120% since 2000. This increment of LNG demand has generated a fast augmentation of LNG transport by sea.

The knowledge of LNG composition acquires special importance in long-duration trips and is essential for importers, exporters, shipments, etc., to know the 'quality' of the LNG that is to be unloaded in the Regasification Terminal, so that LNG meets quality specifications of each country.

In order to solve the existing lack of knowledge on the behaviour of LNG during ship transportation, a group of European gas companies led by Enagás has developed a useful tool called MOLAS for predicting changes in LNG composition at any time during the voyage and just at the end. MOLAS application contains two different approaches. A Physical Model based on mass balances and equilibrium state between liquid and vapour phases, and an 'intelligent' Model, based on Artificial Neural Networks that takes into account nonlinear relationship among the variables involved.

MOLAS has been tried out comprehensively and an average error in Wobbe Index and Gross Calorific Value less than 0.20% and 0.30% has been obtained respectively. The results provided by MOLAS, can help Terminal Operators to manage Regasification Plants in a more safe and efficient manner and can help Engineers and Technicians to take, in advance, necessary actions on natural gas so that it can comply with required Quality Specifications.

1 INTRODUCTION

Liquefied Natural Gas (LNG) is an energy source with a worldwide steady growth. This increment of LNG demand has generated a big augmentation of LNG transport by sea. The main LNG Exporters by Country are shown below. Qatar is the largest exporter followed by Malaysia, Indonesia, Australia and Nigeria.
The knowledge of LNG composition acquires special importance in long-duration trips and is essential for supporting terminal operators, shippers, dealers, surveyors, consulting, regulators and, in general, any company involved in the LNG field in order to know the ‘quality’ of the LNG that is to be unloaded in the Regasification Terminal.

The LNG is transported by ship at atmospheric pressure close to its boiling point. Although the cargo tanks are highly insulated, heat inputs from surroundings are unavoidable, vaporizing the liquid and producing boil-off gas (BOG).

LNG vaporization is not homogeneous because of the differences in the boiling points of each LNG component (ranging from -196 °C to +69 °C). Components with the lowest boiling point, mainly nitrogen and methane, are vaporized first (see table 1).

### Table 1: Boiling points of LNG components

<table>
<thead>
<tr>
<th>Component</th>
<th>Boiling point (atmospheric pressure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>-196 °C</td>
</tr>
<tr>
<td>Methane</td>
<td>-161 °C</td>
</tr>
<tr>
<td>Ethane</td>
<td>-89 °C</td>
</tr>
<tr>
<td>Propane</td>
<td>-42 °C</td>
</tr>
<tr>
<td>i-Butane</td>
<td>-12 °C</td>
</tr>
<tr>
<td>n-Butane</td>
<td>-1 °C</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>+28 °C</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>+36 °C</td>
</tr>
<tr>
<td>Hexane</td>
<td>+69 °C</td>
</tr>
</tbody>
</table>

This phenomenon, known as *ageing*, causes LNG composition changes in the course of the time. Therefore the composition and properties of LNG at the port of unloading (destination) will be slightly different from the port of loading (origin).
The input heat transferred to LNG is quantified by means of the Boil Off Rate (BOR) parameter, which is defined as the percentage of the vaporized volume respect to the initial LNG volume as is showed in equation 1. The BOR is calculated for a time period of 24 hours. A typical value is around 0.10%-0.15% and it depends on the type of container and the quality of its thermal insulation.

\[
\text{BOR} \, (\%) = \frac{\text{Volume evaporated per day}}{\text{Volume at origin}} = \left(\frac{V_{\text{ORIGIN}} - V_{\text{DESTINATION}}}{V_{\text{ORIGIN}}}\right)/\text{days} \times 100
\]  

(Equation 1)

2 MOLAS APPLICATION

In order to solve the existing lack of knowledge on the behaviour of LNG during ship transportation from loading port to unloading port, a group of European gas companies led by Enagás and within the GERG Organization have developed an useful software tool called MOLAS for predicting changes in LNG composition. MOLAS stands for MODELS OF LNG AGEING DURING SHIP TRANSPORTATION.

This software estimates the LNG composition at destination and, from this value, calculates the LNG main properties such as Gross Calorific Value (GCV), Net Calorific Value (NCV), Wobbe Index (WI) and LNG Density, according to international standards (ISO 6976 and GPA 2172) at different units and under different conditions.

The application offers two different modelling options: a Physical Model and an Intelligent Model (iModel). The Physical Model is based on mass balances and equilibrium state between liquid and vapour phases while the Intelligent Model, based on historical data, uses artificial neural networks to take into account nonlinearity resulting from the specific characteristics of the ships, LNG quality, routes, etc.

MOLAS application also includes a useful database loaded with basic information about LNG industry: Ships, exporters, ports, countries, etc. The aim of this database is to collect the most widely used data regarding LNG business.

3 PHYSICAL MODEL

The Physical Model is based on mass balances and the thermodynamic equilibrium state between liquid and vapour phases where the following hypotheses are assumed:

- The algorithm is independent of the shape and number of tanks in the ship
  Two parameters define the ship characteristics: Boil Off Rate (BOR) and ship capacity which is defined as the total LNG volume that can be carried by the ship.
• **LNG cargo is considered in equilibrium state**
  It is assumed thermodynamic equilibrium between liquid and vapor phases at boiling temperature during the trip. Subcooled or superheated states in tanks are not considered. As result, initial conditions are transformed into equilibrium conditions at the beginning of the first time step.

• **Constant time step size**
  The evolution of the ageing process is calculated in a discrete form where the total time is divided in steps of half hour. In each time step, the vaporization rate is calculated from BOR definition and it is used to find the new composition of the LNG mixture.

• **Linear evolution of pressure during the voyage**
  The evolution of the pressure is assumed to follow a linear relationship from the loading port to destination.

The algorithm of the physical model is composed of four blocks (see Figure 3). First a reading block is executed to get the input data that define the LNG ageing process to be simulated: LNG composition, pressure and temperature at origin port, ship characteristics (capacity and BOR), trip duration and initial filling percentage.

Next, input data are used to calculate the initial equilibrium conditions at the loading port. After that, the evolution of quality and parameters of LNG are calculated by means of an iterative loop. LNG equilibrium are calculated through two different equations of state: Lee-Erbar-Edmister or GERG2004. The first one is a general equation of state (EoS) while GERG2004 has been specially developed for natural gas.

Finally, at the end of execution, two different sets of results are stored (writing block):

- A summary of parameters at the origin and destination port: LNG composition, pressure, temperature, volume and relevant properties (Calorific Value, Wobbe Index and Liquid Density).

- Main variables evolution during trip duration.

![Figure 3: Algorithm of the Physical Model - Four blocks](image)

### 4 INTELLIGENT MODEL

Intelligent Model (iModel) is based on historical data stored in a specific database developed to handle the main information about LNG trading by ship and provides the same information than the Physical Model.
iModel works with Artificial Neural Networks (ANN). It is a very sophisticated technique capable of modelling extremely complex functions. ANN are nonlinear mathematical functions whose architecture is inspired in the brain. They consist of a high number of simple processing units which are wired together in a complex communication network. Each unit or node is a simplified model of a real neuron which sends a new signal if it receives a sufficiently strong input signal from the other nodes to which it is connected (See figure 4).

ANN are a powerful technique to solve many real world problems. They have the ability to learn from experience in order to improve their performance and to adapt themselves to changes in the environment. ANN are being successfully applied across an extraordinary range of problems in areas as finance, medicine, engineering, geology and physics.

5 GENERAL DATABASE

General database includes information about ships, countries, routes, trips, ports, exporters, charterers, basins, operators, builders, etc. The aim of this database is to collect the most widely used data regarding LNG business.

MOLAS application includes basic information about LNG industry\(^1\) that the user can add, delete or modify.

The whole database can be exported and imported. Moreover, in order to facilitate the database management, the most important information (shipments, ships, routes and ports) can be loaded automatically instead of introducing it by hand.

6 SOFTWARE DESCRIPTION

6.1 Input variables

The calculation of the LNG ageing requires the introduction of the data shown on the table 2. These input data are the same by using any model. Some of them are optional and it is not necessary to introduce their values to run the application.

\(^1\) Source: LNG Journal, April 2012
### Table 2: Input variables

<table>
<thead>
<tr>
<th>VARIABLE RELATED TO</th>
<th>VARIABLE</th>
<th>UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>LNG Composition: ( \text{N}_2, \text{C}_1, \text{C}_2, \text{C}_3, \text{iC}_4, \text{nC}_4, \text{iC}_5, \text{nC}_5, \text{nC}_6 )</td>
<td>%mole</td>
</tr>
<tr>
<td></td>
<td>Pressure</td>
<td>mbar</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>LNG Volume</td>
<td>m³</td>
</tr>
<tr>
<td></td>
<td>Filling percentage</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>Port name</td>
<td>-</td>
</tr>
<tr>
<td>Travel</td>
<td>Ship name</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>BOR</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>Duration</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>Trip number (optional)</td>
<td>-</td>
</tr>
<tr>
<td>Destination</td>
<td>Pressure (optional)</td>
<td>mbar</td>
</tr>
<tr>
<td></td>
<td>Port name</td>
<td>-</td>
</tr>
</tbody>
</table>

### 6.2 Output variables

As output data the software estimates the LNG composition at destination and, from this value, calculates the LNG main properties such as Gross Calorific Value (GCV), Net Calorific Value (NCV), Wobbe Index (WI) and LNG Density according to different standards, units and with several combustion and measuring conditions.

### Table 3: Output variables

<table>
<thead>
<tr>
<th>VARIABLE RELATED TO</th>
<th>VARIABLE</th>
<th>UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Destination</td>
<td>LNG Composition: ( \text{N}_2, \text{C}_1, \text{C}_2, \text{C}_3, \text{iC}_4, \text{nC}_4, \text{iC}_5, \text{nC}_5, \text{nC}_6 )</td>
<td>%mole</td>
</tr>
<tr>
<td></td>
<td>Properties (CV, WI, density)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>LNG Volume</td>
<td>m³</td>
</tr>
<tr>
<td></td>
<td>Pressure (if it is applicable)</td>
<td>mbar</td>
</tr>
</tbody>
</table>

### 6.3 Input and Output files

MOLAS application works with TSV files (Tab-Separated Values). These files are easily transferred into and out of a spreadsheet.

### 6.4 Main screens of MOLAS application

The main features of MOLAS application are shown on the figure 5:

- The menu *Ageing Model Approach* gives access to the Physical Model, the Intelligent Model, the generation of new iModels and the massive calculation.
- The menu *Database Management* shows all Database fields, including the importation / exportation of data.
MOLAS application has been developed in English and Spanish languages.

Figure 5: MOLAS application - Main menu

Both Physical and Intelligent Model show the same screens for input and output data. The properties of LNG at destination can be calculated according to ISO or GPA standards, in different units (MJ/m$^3$, MJ/kg, kWh/m$^3$ or BTU/scf) and with several combustion and measuring conditions. Table 4 shows all these possibilities.

Table 4: Standards, units, combustion and measuring conditions

<table>
<thead>
<tr>
<th>INDEX</th>
<th>STANDARD</th>
<th>UNITS</th>
<th>COMBUSTION TEMPERATURE</th>
<th>MEASURING TEMPERATURE</th>
<th>PRESSURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ISO 6976</td>
<td>MJ/m$^3$</td>
<td>0 °C</td>
<td>0 °C</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ISO 6976</td>
<td>MJ/m$^3$</td>
<td>15 °C</td>
<td>15 °C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>ISO 6976</td>
<td>MJ/m$^3$</td>
<td>20 °C</td>
<td>20 °C</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ISO 6976</td>
<td>MJ/m$^3$</td>
<td>25 °C</td>
<td>0 °C</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>ISO 6976</td>
<td>MJ/kg</td>
<td>0 °C</td>
<td>-</td>
<td>1.01325 bar</td>
</tr>
<tr>
<td>6</td>
<td>ISO 6976</td>
<td>MJ/kg</td>
<td>15 °C</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>ISO 6976</td>
<td>MJ/kg</td>
<td>20 °C</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>ISO 6976</td>
<td>MJ/kg</td>
<td>25 °C</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>ISO 6976</td>
<td>kWh/m$^3$</td>
<td>0 °C</td>
<td>0 °C</td>
<td>14.696 psia</td>
</tr>
<tr>
<td>10</td>
<td>GPA 2172</td>
<td>BTU/scf</td>
<td>60 °F</td>
<td>60 °F</td>
<td>1.01325 bar</td>
</tr>
<tr>
<td>11</td>
<td>GPA 2172</td>
<td>MJ/m$^3$</td>
<td>15 °C</td>
<td>15 °C</td>
<td></td>
</tr>
</tbody>
</table>
**Simulation: Output data**

After running the simulation LNG composition, temperature, volume and properties at destination are displayed on the screen (see Figure 6).

![Figure 6: Simulation - Output data](image)

In addition a summary file can be generated which includes the parameters both at the origin and destination port (see Figure 7). For the physical Model an evolution file is also generated (see Figure 8).

![Figure 7: Summary file](image)
To predict changes in LNG composition during the journey from loading port to destination, the user can choose between the Physical Model or Intelligent Model. Both models can be executed in manual or massive way. The first is performed introducing one by one all variables required for the simulation but massive calculation makes it possible to calculate several shipments at the same time, without limiting the number of cases.

The Physical Model can always be used and does not need any previous stage. However Intelligent Model requires the previous generation of iModels. MOLAS application includes a Default iModel but only works properly if the case simulated is similar to those shipments used to generate it. In order to obtain the best predictions it is recommended that the user creates his own iModel(s). This is summarized as follows (see Figure 9).

![Figure 9: How to select the model](image-url)
Default iModel has been generated from 700 cargoes provided by Enagás. Information about ships, routes, trip duration and others parameters included in the Default iModel is shown on the screen when this model is selected (see Figure 10).

The shipments Database is firstly empty since the trips used to generate the Default iModel are not included due to their privacy. Therefore it is possible to use the Default iModel but not to see its cargoes.

To carry out the generation of a new iModel is necessary to fill the database with own information about ships, countries, ports and shipments, being required a minimum of 10 shipments.

Figure 11 summarizes how MOLAS application runs.
MOLAS APPLICATION
Calculation of LNG Ageing during Ship Transportation

Step 1
Software Installation

Step 2
Creation of your own DB (Ships, Routes, etc.)
Optional

MOLAS is ready to use

Step 3
Calculation of LNG Ageing

Choose How
- Manual Calculation
- Massive Calculation

Choose Model Type
- Physical Model
  - This model can always be used
  - Choose EOS
    - Lee-Erbar-Edmister
    - GERG2004
- Intelligent Models
  - Shipments similar to those contained into the i-model
    - i-model default
    - User i-models
      - Introduction of shipments in DB
      - Creation of your own i-models

Choose Properties Conditions
- ISO 6976
- GPA 2172-09

Figure 11: Steps to run MOLAS application

8 RESULTS

MOLAS application is a user friendly, powerful and reliable tool that runs on a desktop and enables to know the LNG composition to be unloaded at destination and the most essential LNG properties: LNG Density, Heat Value and Wobbe Index, according to international standards (ISO 6976 and GPA 2172) at different units and under different conditions.

Two different modelling approaches have been developed to predict LNG ageing during ship transportation: a Physical Model and an Intelligent Model.

The performance of the tool has been cross checked against a large number of real cases, with an average error rate in the Wobbe Index and Calorific Value lower than 0.20 % and 0.30 % respectively, obtained from Physical Model (see figure 12).
In general, it is observed a better performance of the Intelligent Model using Default iModel. Therefore using own iModels lower errors can be found although, in any case, the Physical Model is always a valid option if the intelligent Model cannot be applied due to the lack of historical data for ships, routes or qualities.

9 APPLICATIONS

The predictive results provided by MOLAS application will really support terminal operators, shippers, dealers, surveyors, consulting, regulators and, in general, any company involved the LNG field, to take proactive actions on the LNG to achieve demanded quality by the applicable standards.

MOLAS application can be applied in different areas of LNG industry:

- **Operational Area.** Knowing, in advance, LNG density to be unloaded may help Terminal Operators to avoid that stratifications can be formed into ground tank and, as consequence, a future roll over incident. MOLAS application can help to manage regasification plants in a more safety and efficient manner.

- **Quality Area.** MOLAS application helps to take decisions about necessary actions (Blending & Mixing) to comply with Quality Specifications.

- **Economical Area.** Although MOLAS application is not intended for billing purposes, it may be also used to estimate the amount of energy to be transferred from ship to ground tank.

- **Administration Area.** By means of Database Management the users can obtained, in a rapid way, useful information about shipments, routes, ships, trips, dates, average composition, etc.
10 REFERENCES


