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Investigation of Factors Influencing NO_x Emissions in Gas Turbine Generators of a Natural Gas Liquefaction Facility

Soutenu le 29/06/2025

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This achievement is dedicated to those who lit the path for me.

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With my deepest gratitude
and love.

Abdel Rafik

Dedications

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This achievement is as much yours
as it is mine.

Ben Ali

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الملخص

يقدم هذا البحث دراسة تجريبية للعوامل المؤثرة على انبعاثات أكاسيد النيتروجين (NO_x) من التوربينات الغازية طراز Frame 6، المجهزة بأنظمة الاحتراق الجاف منخفض الانبعاثات(DLN) ، وذلك في مجمع لتسييل الغاز الطبيعي .تمثل هذه الملوثات تحديا” كبي“را لقطاع الطاقة، حيث يمكن أن تتجاوز انبعاثاتها الحدود التنظيمية على الرغم من استخدام تقنيات تحكم متقدمة .تجمع الدراسة بين مراجعة نظرية لآليات تكوين أكاسيد النيتروجين وحملة تجريبية دقيقة، تستخدم تحليلات الغاز في الموقع، والتحليل الكروماتوغرافي لغاز الوقود، وجمع بيانات التشغيل اللحظية .تظهر النتائج أن لكثافة وتركيب غاز الوقود، وخاصة مستويات النيتروجين والإيثان، تأثي“را حاس“ما على إنتاج أكاسيد النيتروجين يفوق تأثير القيمة الحرارية الإجمالية للوقود .تؤكد هذه النتائج على ضرورة اتباع نهج نظامي متعدد المتغيرات للتحكم في الانبعاثات، وتفتح المجال لتطوير نماذج تنبؤية متقدمة لتحسين الأداء البيئي للتوربينات الغازية الصناعية.

Summary

This thesis presents an experimental investigation into the factors influencing nitrogen oxide (NO_x) emissions from Frame 6 gas turbines equipped with Dry Low NO_x (DLN) systems within a natural gas liquefaction complex. These pollutants represent a major challenge for the energy industry, as their emissions can exceed regulatory limits even with advanced control technologies in place. The study combines a theoretical review of NO_x formation mechanisms with a rigorous experimental campaign, utilizing in-situ gas analysis, fuel gas chromatography, and real-time operational data collection. The results demonstrate that fuel gas density and composition, particularly the levels of nitrogen and ethane, have a more decisive influence on NO_x production than the fuel's overall calorific value. These findings underscore the need for a systemic, multi-parameter approach to emissions control and open pathways for developing advanced predictive models to optimize the environmental performance of industrial gas turbines.

Résumé

Ce mémoire présente une étude expérimentale des facteurs qui influencent les émissions d'oxydes d'azote (NO_x) des turbines à gaz de type Frame 6 équipées de systèmes de combustion à faibles émissions (DLN) au sein d'un complexe de liquéfaction de gaz naturel. Ces polluants représentent un défi majeur pour l'industrie énergétique, car leurs émissions peuvent dépasser les seuils réglementaires malgré l'utilisation de technologies de contrôle avancées. L'étude associe une revue théorique des mécanismes de formation des NO_x à une campagne expérimentale rigoureuse, combinant des analyses de gaz in situ, la chromatographie du gaz combustible et la collecte de données opérationnelles en temps réel. Les résultats démontrent que la densité et la composition du gaz combustible, notamment les teneurs en azote et en éthane, ont une influence plus déterminante sur la production de NO_x que son pouvoir calorifique global. Ces conclusions soulignent la nécessité d'une approche systémique et multi-paramètres pour le contrôle des émissions et ouvrent la voie au développement de modèles prédictifs avancés afin d'optimiser la performance environnementale des turbines à gaz industrielles.

General introduction

GENERAL INTRODUCTION

Nitrogen oxide (NO_x)is one of the primary air pollutants produced by industrial and energy activities. In a natural gas liquefaction complex, NO_x emissions from Gas Turbine Generators (GTG) represent a significant challenge, so strict environmental regulations and reducing their health and ecological impact are essential. NO_x is a key in creating tropospheric ozone and acid rain while contributing to air pollution and the indirect greenhouse effect. Consequently, the effective control of NO_x is a top priority goal in the latest energy industries.

In this case, General Electric's Frame 6 gas turbines, which were equipped with Dry Low NO_x (DLN) systems, have been developed to reduce NO_x formation in the combustion process. These systems use the most recent airflow control and combustion temperature management to reduce pollutant emissions. Despite this, measurements of NO_x emissions during operating conditions frequently give results above anticipated values, which implies that some influential or poorly managed factors affect the performance of DLN systems.

These excessive emissions are most likely associated with multiple parameters, including:

- The air quality at the intake might be contaminated due to the release of pollutants, thus affecting the combustion process.
- The composition of the fuel gas, with its varying proportions of components such as methane, ethane, and impurities, can influence the kinetics of NO_x formation.
- Non-optimum airflow, which is due to mechanical or design issues.
- Combustion conditions below the optimum level can be either high temperatures or non-evenly distributed reactants.

The interaction of these variables in complex atmospheres is a challenge of sorts when predicting and controlling NO_x production. So, a detailed study to find the exact sources of these emissions is a prerequisite for formulating the necessary operational optimization strategies.

The primary purpose of this study is to carry out an NO_x emissions investigation in the Gas Turbine Generators (GTG) of a natural gas liquefaction complex by focusing on the interactions between operational parameters and NO_x formation mechanisms. The study is based on a thoroughly scientific process, blending the foremost analytical approaches with the most thorough analysis of the emissions-impacting factors. The primary methods used here are the NO_x measurements with the TESTO analyzer and the gas chromatography (GC) for the fuel gas composition and intake air. This data will be compared to the turbines' operating conditions so that valid inferences can be drawn and implementable suggestions can be made.

To address these different aspects, the present paper is structured into two major parts:

Part I: Theoretical Framework

- Chapter 1: Introduction to the complex and the laboratory. This chapter presents the gas liquefaction complex by emphasizing the Gas Turbine Generators (GTG) and the laboratory installations used for the analysis. Particular attention will be given to the DLN systems of the Frame 6 turbines and their operation.
- Chapter 2: Theoretical Review of NO_x Formation and Impacts. This chapter will describe the chemical mechanisms responsible for NO_x and their environmental and health consequences.
- Chapter 3: Analytical techniques for the measurement of NO_x. The analytical tools used to measure the NO_x and to analyze the chemical composition of the gas (i.e., intake air and fuel) will be explained in detail here.

Part II: Experimental Study and Recommendations

- Chapter 4: Experimental procedures. This chapter describes the sampling protocols for taking and measuring samples, including the methods used to analyze them.
- Chapter 5: Results and discussions. The results of the NO_x measurement and chemical analyses will be presented, followed by a comprehensive discussion to interpret the observed variations and identify the critical factors.

In conclusion, this study aims to provide good comprehension and practical information to enhance the turbine's performance, reduce NO_x emissions, and promote environmentally sustainable management of the natural gas liquefaction complexes. The wrok will conclude with practical recommendations for operational improvements and suggestions for future studies.

CHAPTER I.

DESCRIPTION OF LNG (LIQUEFIED NATURAL GAS)

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CHAPTER I. DESCRIPTION OF LNG (LIQUEFIED NATURAL GAS)

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I.1. INTRODUCTION

The LNG-3Z complex, known as the Arzew Mega Train, is a central industrial facility that produces liquefied natural gas (LNG) from Hassi R'Mel gas reserves. The complex integrates several key operational areas - utilities, process/manufacturing, and terminal - and implements sophisticated processes to treat, purify, refrigerate, and liquefy natural gas. Rigorous end-product quality control relies on advanced analytical equipment, including gas chromatography and various physico-chemical measuring instruments. In addition, Frame 6 gas turbines equipped with DLN systems ensure the energy production required for the continuous operation of the complex, guaranteeing both performance and compliance with environmental standards.

I.2. DESCRIPTION OF LNG (LIQUEFIED NATURAL GAS)

SONATRACH is committed to developing these structures to exploit the gas reserves of the Hassi Berkine field:

The position of the site is as follows:

This site extends over 54.6 h and is located along the Mediterranean coast at BETHIOUA, east of ARZEW, in the industrial port of ARZEW El Djedid, as shown in Figure I.1.

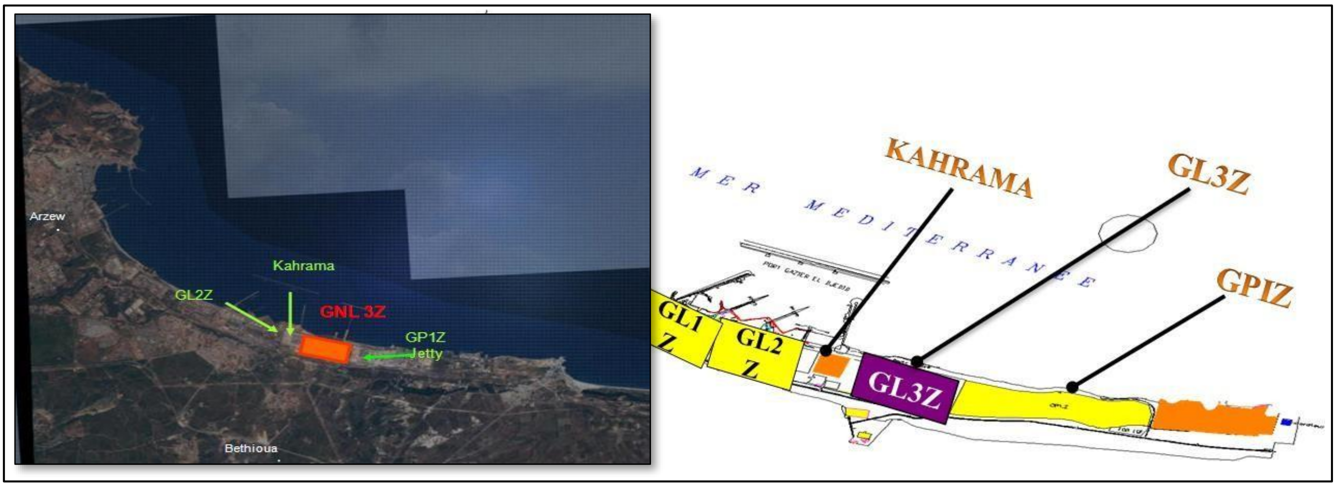

Figure I.1. Position of the complex [1].

LNG is natural gas cooled to a liquid state. The liquefaction process considerably reduces the volume of natural gas by around 1/600, enabling it to be transported over long distances, particularly by sea. LNG sampling is necessary to obtain a representative sample for laboratory analysis. The purpose of LNG analysis is to determine its composition and, consequently, its calorific value. The product must comply with specific compositional limits defined in sales contracts on the global LNG market. The LNG 3/Z sampling station is designed to take samples with a precision that depends on the parameters specified by the manufacturer. The accuracy of these analyses, linked to the control laboratory, relies mainly on the retention factor determined by gas chromatography (GC) [2,3,4].

I.3. LNG-3Z COMPLEX: ZONES AND PROCESSES

The LNG-3Z complex is designed with three key operational zones:

- Utilities Zone
- Process/Manufacturing Zone
- Terminal Zone (Jetty, Storage, and Flares)

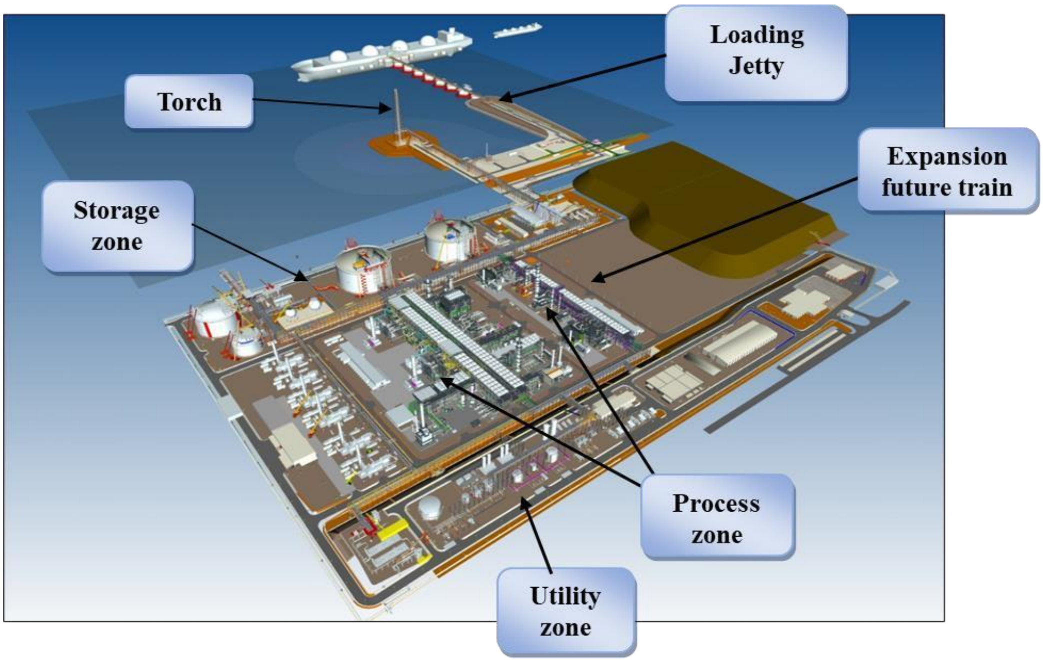

Figure I.2. GL3/Z complex [1].

I.3.1. OVERALL PROCESS

Feed gas arrives at the complex at a pressure of 42 bar and a temperature of 38°C. It undergoes several treatments through the following units:

- Mercury Removal
- Acid gas removal/Decarbonization (CO_2 removal)
- Dehydration (removal of H_2O)
- Cooling
- Fractionation
- Propane refrigeration circuit
- Mixed refrigerant circuit
- Liquefaction

I.4. COMPLEX EQUIPMENT

The complex comprises an LNG train and all the necessary infrastructure, including *utilities*, storage facilities, and a jetty for ship loading. The plant has a design life of 30 years [1].

I.4.1. UTILITIES ZONE

- **Unit 01**:

Feed gas inlet installation with measurement skid, analysis shelter, and control cabinet.

- **Unit 02**:

Amine storage (activated AMDEA) for acid gas removal.

- **Unit 08**:

Hot Oil storage for combined reheating systems.

- **Unit 51**:

Power generation via gas turbines (4 × 42 MW) - primary source for LNG train, utilities, and ancillary areas.

- **Unit 53**:

Emergency diesel generator set (fuel storage and distribution).

- **Unit 55**:

Common Fuel Gas system - HP (24.5/26 bar) and BP (5/6 bar) gas distribution in case of unavailability of dedicated systems.

- **Unit 56**:

Instrument and Plant Air - undried compressed air (general use) and dry air (instrumentation), designed for two trains.

- **Unit 57**:

Nitrogen System: The distribution network is designed for two trains, but the current equipment is for one train. Liquid nitrogen is supplied by tanker trucks and stored in cryogenic tanks.

- **Unit 58**:

Drinking Water System: Storage and distribution of drinking water, safety showers, and supply to the demineralized water system.

- **Unit 59**:

Demineralized and Service Water system - centralized management.

- **Unit 64**:

Wastewater and Effluent Treatment - design adaptable to a future second train.

I.4.2. PROCESS ZONE

- **Unit 11:**

Feed Gas Conditioning includes feed gas compression and mercury removal sections.

- **Unit 12:**

Acid Gas Removal (Decarbonation) is specifically for carbon dioxide removal.

- **Unit 13:**

To prevent freezing in downstream cryogenic units, Gas dehydration removes water from feed gas using a three-bed configuration (adsorption/regeneration/standby). Regeneration uses fuel gas.

- **Unit 17:**

LNG Recovery and Fractionation, comprising the Demethanizer, Deethanizer, Depropanizer, and Debutanizer sections. Prepares gas for liquefaction by removing heavy hydrocarbons, produces ethane, propane, butane, pentane, and gasoline for export, adjusts the heating value of LNG, and provides refrigerant make-up.

- **Unit 15:**

Liquefaction**,** including the LNG liquefaction section, the helium recovery section, the nitrogen rejection section, and the final flash gas system.

- **Unit 16:**

Refrigeration is divided into the Propane Circuit and the Mixed Refrigerant Circuit.

- **Unit 14:**

A fuel gas system (Train 1) supplies HP (26 bar) and BP (6 bar) fuel gas to train users.

- **Unit 18:**

Hot Oil System providing heat at two temperature levels (260°C and 160°C).

- **Unit 19:**

A Cooling Water System removes heat from machines using tempered cooling water.

I.4.3. TERMINAL AREA (STORAGE & EXPORT)

- **Unit 71:**

LNG Product Loading and Storage, providing product storage and export facilities for continuous production with intermittent ship loading. Storage tanks have a capacity of 160,000 m^3.

- **Unit 72:**

LPG Product Loading and Storage provides storage and export capacity for Propane (C3) and Butane (C4), designed to accommodate the products of two future trains. Propane is stored in 56,000 m^3 tanks and butane in 12,000 m^3 tanks.

- **Unit 73:**

Refrigerant storage is designed to support the LNG train, providing storage and transfer capacity for ethanol used in the MR system and propane used in the propane and MR refrigeration circuits.

- **Unit 75:**

A flare system was installed and sized for two trains to safely remove hydrocarbon vapors and light liquids from emergencies, disturbances, start-ups, blowdowns, and equipment drainage.

- **Unit 76:**

The Gasoline Storage System is designed to receive and store gasoline produced by LNG recovery and fractionation. The gasoline is stored in a 1800 m^3 spherical tank and pumped in batch mode for export.

I.5. PRESENTATION OF THE LABORATORY AND MEASURING INSTRUMENTS

The laboratory is fundamental to the complex's efficiency, playing a critical role in quality assurance. It plays a crucial role in ensuring the smooth operation of raw material processing units and analyzing finished products for marketing and export. The laboratory's function is to constantly monitor and control the quality of finished products in the chemical and petrochemical industry.

Sonatrach's laboratory is divided into several sections, including Oil, Water, and Gas Analysis, each equipped with specific instruments:

I.5.1. GAS CHROMATOGRAPHY (GC)

I.5.1.1. Gas chromatography (GC)

This separation analysis method applies to molecules naturally in the gaseous state, or to those that can be volatilized by heating without decomposition. It is a form of partition chromatography. Schematically, the apparatus comprises a gas source (carrier gas), an injection chamber, an oven containing the column, a detector, and a recorder/PC-integrator. The principle involves the injection of a volatilized sample into a gaseous mobile phase; the components separate according to their different affinities with the stationary phase as they pass through the column, emerging at various times as detected and recorded concentration peaks. The carrier gases typically used are nitrogen (N_2), hydrogen (H_2), and helium (He), which must be pure, dry, oxygen-free, and inert. The furnace maintains a controlled column temperature. Detectors detect substances in the carrier gas as they elute, transforming a change in gas property into amplified electrical signals and transcribing them as a chromatogram. Sampling valves can replace injectors, allowing a gas sample loop to be rinsed and inserted into the carrier gas stream. The chromatogram shows a series of peaks, each representing a component of the analyzed mixture. GC analysis is fundamental for checking each unit's correct operation in each train. It is used to determine the various gaseous constituents. The accuracy of LNG analysis, linked to the control laboratory, relies significantly on the retention factor determined by GC. Incorrect operating conditions in fractional distillation can lead to discrepancies between the measured and actual compositions of the liquid products, underlining the importance of GC analysis.

Figure I.3. Gas chromatography.

Principle:

- Separating volatile compounds by equilibrium between a gaseous mobile phase (helium, hydrogen) and a stationary phase (capillary column).
- Detection via mass spectrometry (GC-MS) or specific detectors (FID, TCD) [5,6,7,8,9].

I.5.2. WATER SECTION

I.5.2.1. Spectrophotometry

Spectrophotometry is a quantitative analysis technique that measures the absorption or transmission of light by a chemical substance dissolved in a solution. The device (spectrophotometer) is used to determine the concentration of a specific compound.

Principle of operation:

- Based on Beer-Lambert's Law (absorbance is proportional to concentration).
- A beam of light of a specific wavelength passes through the sample.
- The instrument measures the light absorbed to calculate concentration [10,11].

Figure I.4. Image representing the used spectrophotometer.

I.5.2.2. Determination of free chloride in water

This is a portable colorimeter, such as the Hach Pocket Colorimeter II shown in the picture, designed to quickly measure the concentration of free chlorine in water in the field. It's a lightweight, easy-to-use device, ideal for spot checks on water quality.

Principle of operation:

- Uses the DPD colorimetric method.
- Free chlorine reacts to produce a pink/red color.
- The instrument measures color intensity to determine concentration [12,13].

Figure I.5. Hach portable colorimeter for free chlorine.

I.5.3. OIL SECTION

I.5.3.1. Viscosimeter

The Lauda Proline PV 36 is a high-precision thermostatic circulation bath designed to maintain an extremely stable and homogeneous temperature. It is mainly used to immerse viscometers to ensure accurate fluid viscosity measurements.

Principle of operation:

- Fluid viscosity is highly sensitive to temperature variations.
- The bath actively controls the temperature of its internal liquid with great accuracy.
- The bath ensures that the sample contained in the immersed viscometer is at the exact temperature required for reliable viscosity measurement [14,15].

Figure I.6. Lauda proline PV 36: thermostated bath for viscosimetry.

I.5.3.2. Flash point tester

The Anton Paar PMA 500 is an automatic Pensky-Martens flash point tester. It is designed to determine the lowest temperature at which a liquid forms flammable vapors sufficiently to ignite temporarily in the presence of an ignition source.

Principle of operation:

- The sample is heated at a controlled rate in a closed cup.
- An ignition source is periodically introduced into the atmosphere above the liquid.
- The flash point is the temperature at which the device detects a brief flame (flash) [16,17].

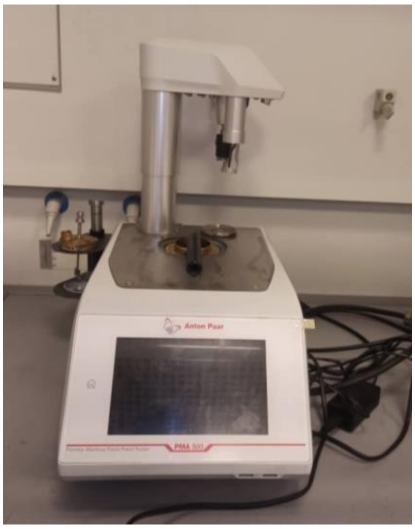

Figure I.7. Anton Paar PMA 500: Pensky-Martens Flash Point Tester.

I.6. HOW THE TESTO 350 XL ANALYZER WORKS FOR NO_X MEASUREMENTS

The Testo 350 XL is a portable flue gas analyzer for precise industrial measurements, particularly nitrogen oxides (NO_x). Its operation is based on the following features:

Figure I.8. Testo 350 XL analyzer.

I.6.1. MEASUREMENT TECHNOLOGY

- **Electrochemical sensors**:

- Measure NO (0-3,000 ppm) and NO_2 (0-500 ppm) with a 0.1 ppm resolution.

- Calculation of total NO_x ($NO + NO_2$) to assess emissions by standards.

- **Dilution system**:

- Adjustable dilution factors (2 to 40×) to extend the CO measurement range and protect sensors in high concentrations.

- **Sample preparation**:

- Integrated cooler to prevent condensation of corrosive gases.
- Automatic rinsing with fresh air to minimize interference.

I.6.1.1. Industrial applications

- Emissions monitoring of gas turbines, industrial engines, and burners via simultaneous measurements before/after gas treatment.

  Extended measurements (up to 24 hours) with 250,000 data records in internal memory [18,19].

I.7. FRAME 6 GAS TURBINES WITH DLN TECHNOLOGY

I.7.1. TECHNICAL SPECIFICATIONS

- **Model**: GE Frame 6B (50-60 Hz)
- **Power**: 42-70 MW (depending on configuration)
- **Efficiency**: 34-38% (simple cycle)
- **Turbine inlet temperature**: 1,100-1,300°C
- **Role in liquefaction**: Drives the compressors of the propane and mixed refrigerant refrigeration circuit [20,21].

I.7.2. FRAME 6 TURBINES WITH DLN AND THEIR ROLE IN THE LIQUEFACTION PROCESS

Frame 6 turbines, like other industrial models, are equipped with advanced combustion systems to meet stringent emission requirements. In liquefaction processes, these turbines provide reliable, flexible power, essential for the continuous operation of refrigeration compressors and other process equipment. The integration of DLN (Dry Low NO_x) technology enables these turbines to operate efficiently while limiting NO_x emissions, even during load variations or frequent start-ups, which is crucial in sensitive industrial environments [22,23].

I.7.3. DESCRIPTION OF GAS TURBINE GENERATORS (GTG)

Gas turbine generators (GTGs) are power generation systems that use gas combustion to drive a turbine and turn an alternator. They are widely used in industrial plants, notably in natural gas liquefaction processes, providing the energy needed to drive compressors and other critical equipment [24,25].

I.7.4. DLN SYSTEMS AND THEIR PRINCIPLES FOR LIMITING NO_X EMISSIONS

DLN (Dry Low NO_x) systems are based on lean premixed combustion, where fuel and air are carefully mixed before ignition. This lean mixture reduces the flame temperature, thus limiting the formation of NO_x, which is favored by high temperatures.

- **Lean mixture**: Fuel is premixed with excess air, lowering combustion temperature and reducing NOx formation.
- **Fuel staging**: Multiple fuel feed circuits adjust fuel distribution according to load, optimizing flame stability and minimizing emissions at different engine speeds.
- **Dynamic control**: Modern DLN systems incorporate advanced controls to maintain combustion stability and limit emissions, even during rapid load variations or start-ups [26,27].

I.8. CONCLUSION

In summary, the LNG-3Z complex illustrates the harmonious integration of state-of-the-art technologies in natural gas liquefaction. The complex treatment and refrigeration processes are supported by a robust infrastructure, including gas turbines with low NO_x emissions thanks to DLN technology, and a high-performance analytical laboratory guaranteeing the conformity and quality of the LNG produced. This technical synergy optimizes production over the long term and meets the environmental and commercial requirements of the global liquefied natural gas market.

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CHAPTER II.

NO$_x$ FORMATION AND ITS IMPACT

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CHAPTER II.

NO_x FORMATION AND ITS IMPACT

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II.1. INTRODUCTION

Nitrogen oxides, or NO_x, include nitrogen dioxide, NO_2, and nitric oxide, NO. They are the primary air pollutants responsible, generated mainly through industrial activities and combustion processes, especially gas turbine engines. The impact of NO_x on public health and the environment is well established; hence, it is essential to understand precisely how they are produced and the different species that cause these effects.

II.2. DEFINITION AND CLASSIFICATION OF NO_x

Nitrogen oxides, NO_x, are a mixture of two primary gases: nitric oxide, NO, and nitrogen dioxide, NO_2. They are made when nitrogen N reacts with oxygen gas (O_2) in the air. While both are commonly grouped under the term NOx, these two nitrogen oxides are chemically different and have various characteristics, activities, and environmental effects.

II.2.1. NITRIC OXIDE

NO is a colorless, odorless, and non-reactive gas at room temperature. However, at high temperatures, such as those found in gas turbine engines, it plays a central role in the chemical reactions that lead to the formation of NO_2, a much more reactive and harmful gas. NO is generally produced in the initial stages of combustion, often in the form of free radicals that subsequently react with oxygen to form NO_2.

II.2.2. NITROGEN DIOXIDE

NO_2 is an irritating, highly reactive brownish gas often associated with urban air pollution. It is generated through the oxidation of NO in the upper parts of the atmosphere and the outlets of combustion systems. NO_2, which is especially harmful to human health, causes lung inflammation and asthma aggravation, among other things. In addition, it plays a key role in forming ground-level ozone and acid rain [1,2].

II.2.3. MAIN TYPES OF NO_x

Various mechanisms can produce NO_x depending on the combustion conditions. NO_x is generally divided into two categories: thermal NO_x and combustion NO_x (fuel NO_x). These two types of NO_x differ in their processes, but both are typically generated when the fuel burns in a turbine.

II.2.3.1. Thermal NO_x

Thermal NO_x is generally produced within the combustion flame at high temperatures. At elevated temperatures (over 1200°C), the nitrogen N_2 in the air reacts with oxygen O_2 to form nitric oxide NO. This process results from the chemical reaction described by the Zeldovich mechanism, which models nitrogen and oxygen molecules at high temperatures. This reaction is the primary stage in generating thermal NO_x.

The formation of thermal NO_x can be considered as follows:

$$N_2 + O \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

In gas turbines, where combustion temperatures are particularly high, a significant amount of thermal NO_x is generated through this process. NO_x formation through thermal processes depends not only on temperature-related factors but also on pressure, the availability of oxygen, and the time of gas exposure to extreme combustion conditions.

High-temperature zones inside the combustion chamber usually produce thermal NO_x. Their form is directly affected because the combustion temperature increases. Most notably, gas turbines within natural gas liquefaction facilities produce substantial amounts of thermal NO_x, making their reduction a very active challenge [3].

II.2.3.2. Combustion of NO_x

It involves directly reacting nitrogen from the air with oxygen under combustion conditions. This process typically occurs at lower temperatures than those required for thermal NO_x formation, but it is nevertheless essential in gas turbines and other industrial installations.

The formation of combustion NO_x can be represented by the following reaction:

$$N_2 + O_2 \rightarrow 2NO$$

This reaction is facilitated by the heat from combustion, which enables nitrogen molecules (N_2) to dissociate into reactive nitrogen atoms (N). These atoms can then react with oxygen (O_2) in the air to form nitric oxide (NO). Depending on combustion conditions and the composition of the fuel gas, this formation can occur at temperatures significantly lower than those required to generate thermal NO_x.

Oxygen concentrations within the combustion chamber influence the formation process of combustion-generated NO_x. Oxygen-lean mixtures can reduce the formation of combustion NOx, but this trade-off may compromise the system's energy efficiency.

However, although the term NO_x generally refers to nitric oxide, NO, and nitrogen dioxide, NO_2, it is essential to understand the different mechanisms by which they are formed. Thermal

NO_x and combustion-generated NO_x originate from distinct but interconnected processes in gas turbines. Thermal NO_x is primarily formed at high temperatures within the combustion flame. In contrast, combustion-generated NO_x is produced by reacting nitrogen from the air with oxygen at more moderate temperatures. Both types of NO_x contribute significantly to NO_x emissions in gas turbines, and their effective management is essential to reduce their impact on public health and the environment. Understanding the differences between these two categories of NO_x is crucial for developing emission reduction strategies in modern energy industries [4,5,6].

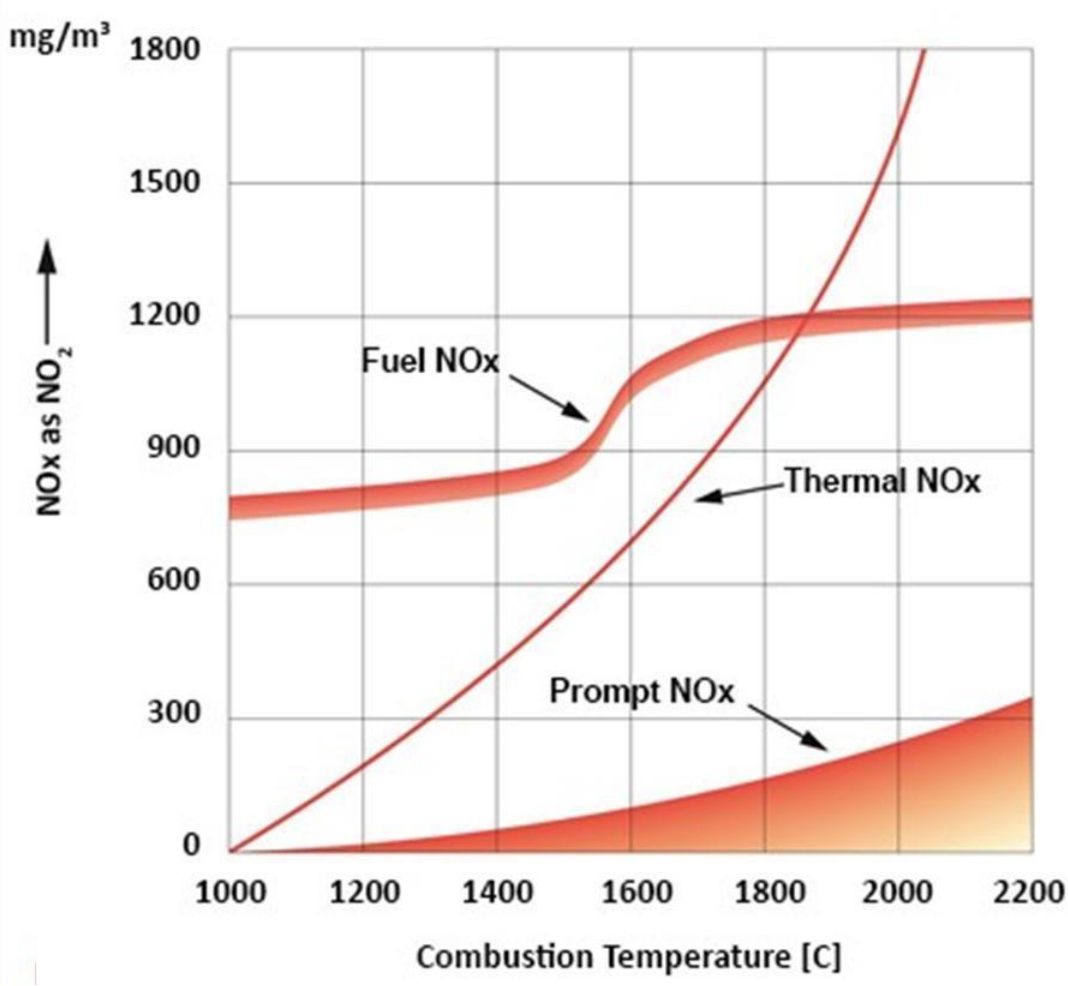

Figure II.1. Mechanism of NO_x in terms of temperature [30].

II.3. MECHANISMS OF NO_x FORMATION IN TURBINES

Nitrogen oxides NO_x are undesirable byproducts of combustion in gas turbines. They are produced by complex chemical reactions involving atmospheric nitrogen or nitrogenous compounds in the fuel. Understanding the mechanisms of NO_x formation is crucial for designing effective reduction strategies, especially in industrial turbines used for energy production. The two main mechanisms responsible for NO_x in these systems are thermal formation and combustion-related formation.

II.3.1. FORMATION OF THERMAL NO_x

Thermal NO_x is formed when molecular nitrogen N_2 from the intake air reacts with oxygen O_2 at high temperatures. This mechanism is described by the Zeldovich reactions, which provides the theoretical basis for thermal NO_x formation. The three primary steps are:

1. Dissociation of Molecular Nitrogen N_2

$$N_2 + O \rightarrow NO + N$$

This reaction requires significant energy to break the strong triple bond of molecular nitrogen (9.76 eV), explaining why it is favored at temperatures exceeding 1200°C.

2. Oxidation of Atomic Nitrogen N

$$N + O_2 \rightarrow NO + O$$

This step is rapid but depends on the oxygen concentration within the flame.

$$N + OH \rightarrow NO + H$$

These reactions accelerate with increasing temperature, making thermal NO_x formation proportional to an exponential function of temperature. This explains why gas turbines operate at temperatures up to 1500–1600°C to maximize efficiency and are particularly prone to this type of pollution [3,4,5,7].

II.3.1.1. Parameters influencing the formation of thermal NO_x

Combustion temperature: Thermal NO_x production increases exponentially with temperature. A rise of 100°C can nearly double emissions.

Residence time of hot gases: Prolonged exposure of hot gases in the combustion zone allows more time for Zeldovich reactions to occur, directly increasing NO_x concentrations.

Pressure: High pressure in the combustion chamber elevates reactant density and accelerates chemical reaction rates, further amplifying NO_x formation.

These dependencies make thermal NO_x challenging to control without compromising turbine energy efficiency [3,4,8].

II.3.2. FORMATION OF COMBUSTION NO_x

Combustion-generated NO_x, also known as fuel-bound NO_x, primarily originates from nitrogen-containing compounds in the fuel. When subjected to combustion conditions, these compounds are oxidized to form NO and NO_2. This mechanism is less temperature-dependent than thermal NO_x but is heavily influenced by fuel composition and mixing conditions.

1. Chemical Reactions Involved:

Nitrogenous compounds in the fuel (e.g., NH_3, CN^-) undergo complex reactions during combustion. For example:

$$R{-}NH_2 + O \rightarrow NO + H + R$$

Where R represents the carbon chain of the organic compound.

2. Excess oxygen:

Excess oxygen promotes complete oxidation of nitrogenous compounds, thereby increasing NO_x formation. Conversely, an oxygen-lean mixture can limit this formation but raises the risk of unburned pollutant emissions (e.g., CO, hydrocarbons).

3. Air-Fuel Mixing:

Uneven air and fuel distribution in the combustion chamber can lead to localized high-temperature zones or incomplete combustion, favoring the formation of NO_x [9].

II.3.3. TECHNOLOGIES DLN

Modern gas turbines often have DLN (Dry Low NO_x) systems to limit NO_x formation. These technologies rely on innovative combustion management principles:

Air/Fuel Mixture Stratification: DLN systems maintain a lean mixture (excess air) in the primary combustion zone, which lowers flame temperature and reduces thermal NO_x formation.

Reduced Residence Time: DLN systems minimize the time available for Zeldovich reactions by increasing gas velocity through the combustion chamber.

Combustion zone management: DLN chambers separate combustion into several stages. There is a primary zone where the temperature is controlled (lean combustion), and a secondary zone where the mixture is enriched to complete the combustion and reduce emissions of CO and unburned hydrocarbons [10,11,12].

II.3.3.1. Limitations of DLN systems

Despite their effectiveness, DLN systems can encounter operational difficulties:

Fuel variability sensitivity: Changes in the composition of natural gas can disrupt the air/fuel balance, leading to unexpected increases in NO_x.

Unstable combustion: Lean mixtures increase the risk of flame instabilities, which may affect the turbine's overall performance.

Increased maintenance: DLN systems require regular monitoring and maintenance to ensure optimal performance.

However, NO_x formation mechanisms in gas turbines are complex and influenced by numerous factors, including temperature, fuel composition, and operating conditions. A detailed understanding of thermal and combustion NO_x is essential to design appropriate reduction strategies, such as DLN technologies. Nevertheless, optimizing operational parameters remains challenging, requiring a balanced approach between energy performance and emission control [10,11,13].

II.4. FACTORS INFLUENCING NO_x FORMATION IN FRAME 6 TURBINES

Frame 6 gas turbines, widely used for their energy performance and efficiency in natural gas liquefaction plants, face significant challenges in controlling NO_x emissions. While partially regulated by advanced technologies like Dry Low NO_x (DLN) systems, these emissions are heavily influenced by various operational factors. These factors interact in complex ways to determine the amount of NO_x produced in combustion chambers.

II.4.1. INTAKE AIR QUALITY

The quality of air entering the turbine plays a fundamental role in combustion processes and, consequently, in NO_x formation. Contaminants in the air can have direct and indirect effects on combustion:

Presence of Contaminants: Solid particles, hydrocarbons, and metal oxides in the intake air can disrupt flame stability and promote secondary reactions, increasing NO_x emissions.

Intake Air Temperature: Higher intake air temperature reduces air density, decreasing the oxygen available per unit volume. This can create hotter combustion conditions, favoring Zeldovich reactions responsible for thermal NO_x formation.

Filtration and cooling systems for intake air are key tools to mitigate these impacts, but their effectiveness heavily depends on local conditions and maintenance cycles [14,15].

II.4.2. FUEL GAS VARIABILITY

Natural gas, the primary fuel for Frame 6 turbines, is mainly composed of methane but can contain variable fractions of other hydrocarbons (ethane, propane) and impurities (sulfur, nitrogen, carbon dioxide). This variability has significant effects:

Chemical composition: High levels of ethane or propane increase heat release during combustion, raising flame temperatures and intensifying thermal NO_x formation.

Impurities: Nitrogen-containing compounds in the fuel contribute directly to fuel NO_x formation, independent of Zeldovich reactions.

Calorific value: Fluctuations in calorific value affect the air/fuel ratio, causing combustion imbalances and localized temperature spikes.

Regular analysis of fuel gas composition is essential to adjust combustion parameters and reduce emissions [14].

II.4.3. AIR FLOW AND COMBUSTION CONDITIONS

Air flows within the combustion chamber directly influence the efficiency of the air/fuel mixture, heat distribution, and turbulence in the combustion zone, which are critical for controlling NO_x emissions.

Air distribution: Uneven air distribution leads to localized zones of oxygen-rich (lean combustion) or oxygen-poor (rich combustion) conditions. Oxygen-rich zones favor thermal NO_x formation, while oxygen-poor zones increase CO and unburned hydrocarbon emissions.

Turbulence and flame stability: Excessive turbulence can disrupt flame stability, creating temperature variations that intensify NO_x formation reactions.

The residence time of hot gases: Poor air flow management can prolong the residence time of hot gases in the combustion chamber, promoting the chemical reactions responsible for thermal NO_x formation.

Optimizing these parameters requires precise modeling of air flows and temperatures and rigorous maintenance of combustion systems [16].

II.5. THE IMPACT OF NO_x ON HEALTH AND THE ENVIRONMENT

Nitrogen oxides, especially nitrogen dioxide, can harm the environment and health. These gases can travel deep into our lungs and help create other dangerous pollutants, like ground-level ozone and fine particles. Because of this, NO_x is connected to various breathing and heart problems.

II.5.1. RESPIRATORY EFFECTS

NO_x acts as a powerful respiratory irritant, affecting special vulnerable groups such as children, the elderly, and those with chronic diseases.

Chronic obstructive pulmonary disease (COPD): Prolonged exposure to NO_x can exacerbate COPD symptoms, reduce lung function, and increase the risk of hospitalization.

Asthma and bronchitis: Many epidemiological studies have shown the correlation between exposure to saturated concentrations and increased asthma attacks, especially in children living in urban or industrial areas.

Respiratory tract infections: NO_x causes lung inflammation, increases sensitivity to respiratory diseases, and worsens before birth [17,18].

II.5.2. CARDIOVASCULAR EFFECTS

Although the cardiovascular impacts of NO_x are less examined than their respiratory impacts, they are increasingly recognized.

Heart Disease: Due to the systemic irritation it causes, the persistent introduction of NO_x is related to an increased risk of atherosclerosis.

Hypertension:1NO_x contributes to oxidative stress inside the vascular framework, disabling endothelial function and raising blood pressure.

Untimely Mortality: Longitudinal studies have appeared that have shown delayed introduction to NO_x is connected to expanded cardiovascular mortality, especially in zones with high mechanical contamination [19,20].

II.5.3. ENVIRONMENTAL IMPACTS OF NO_x

Nitrogen oxides, NO_x, especially nitric oxide, NO, and nitrogen dioxide, NO_2, have critical natural impacts through chemical reactivity within the air. These compounds contribute to phenomena such as the formation of tropospheric ozone, acid rain, and, indirectly, global warming [21,22].

II.5.3.1. Formation of tropospheric ozone

Tropospheric ozone, formed in the lower atmosphere, results from photochemical reactions involving NO_x and volatile organic compounds (VOCs) in the presence of solar radiation.

Unlike stratospheric ozone, which protects against reactions involving NO_x, tropospheric ozone could be a harmful pollutant.

II.5.3.2. Chemical mechanisms

The formation of tropospheric ozone begins with the photodissociation of NO_2 under ultraviolet radiation:

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

The released atomic oxygen O rapidly reacts with molecular oxygen O_2 to form ozone O_3:

$$O(^3P) + O_2 \rightarrow O_3$$

However, ozone can be destroyed when NO reacts with it:

$$NO + O_3 \rightarrow NO_2 + O_2$$

Volatile organic compounds (VOCs) disrupt this cycle by reacting with radicals to produce peroxides. These peroxides oxidize NO into NO_2 without destroying ozone, thereby promoting accumulation.

II.5.3.3. Effects on air quality and biodiversity

Tropospheric ozone is a potent irritant to the respiratory tract, contributing to increased respiratory diseases such as asthma. Its oxidizing effect can damage crops, reduce their yield, and compromise forest ecosystems by impairing photosynthesis. Furthermore, tropospheric ozone accelerates the degradation of organic and inorganic materials, thereby reducing the durability of infrastructure.

II.5.3.4. Acid rain

NO_x also plays a central role in the formation of acid rain by converting into nitric acid, HNO_3, in the atmosphere.

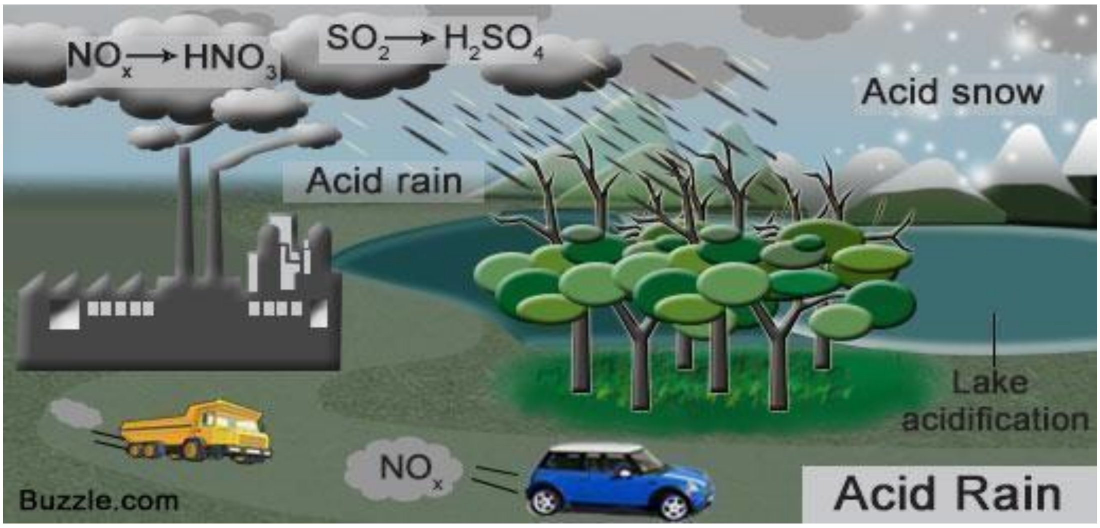

Figure II.2. Acid Rain [31].

II.5.3.5. Chemical conversion of NO_x into nitric acid

After being emitted, NO_x undergoes a series of chemical reactions. NO_2 is oxidized in the gas phase to form HNO_3:

$$NO_2 + OH \rightarrow HNO_3$$

The HNO_3 thus formed dissolves in atmospheric water droplets, increasing their acidity. The resulting precipitation has a lower-than-normal pH (often < 5.6) in rain, snow, or fog.

II.5.3.6. Environmental impacts

Soil and water acidification: Acid rain alters soil PH, disrupting essential biogeochemical cycles and reducing the availability of nutrients for plants. In waterways, acidification leads to declining biodiversity, particularly for sensitive aquatic organisms such as fish and amphibians.

Damage to terrestrial ecosystems: Forests exposed to acid rain suffer from foliage loss, slower growth, and increased susceptibility to disease and pests.

II.5.3.7. Long-term consequences

The effects of acid rain are not limited to the immediate vicinity of NO_x emissions. Atmospheric winds transport Acid compounds over long distances, which explains the cross-border pollution observed in certain industrial regions.

II.5.3.8. Contributions to greenhouse gases

Although NO_x is not a significant greenhouse gas, its indirect role in global warming is crucial.

II.5.3.9. Formation of ozone, a secondary greenhouse gas

As mentioned above, NO_x contributes to the formation of tropospheric ozone. Ozone is a potent secondary greenhouse gas that absorbs infrared radiation emitted by the Earth. Although it has a relatively short lifespan, its contribution to radiative forcing remains significant, particularly in areas with high NO_x and VOC emissions.

II.5.3.10. Interference with nitrogen and carbon cycles

NO_x also influences global biogeochemical cycles. Promoting ozone formation reduces terrestrial ecosystems' capacity to capture CO_2, thereby exacerbating the effects of global warming.

II.5.3.11. Amplification of local and global effects

The impacts of NO_x on the climate are not limited to the local scale. Industrialized regions, the primary sources of emissions, amplify global climate imbalances by increasing ozone levels and disrupting marine and terrestrial ecosystems on a large scale [22,23,24].

II.6. NO_x REDUCTION STRATEGIES

Reducing NO_x in gas turbines relies on a combination of advanced technologies and optimization of operating conditions.

II.6.1. PRIMARY TECHNOLOGIES

DLN (Dry Low NO_x) systems: Frame 6 turbines are equipped with DLN systems designed to limit NO_x emissions by controlling combustion temperature and promoting lean fuel combustion. These systems reduce thermal NO_x production by maintaining the flame below 1500°C.

Modifying fuel composition: Alternative fuels with low nitrogen content, such as biogas or hydrogen, can significantly reduce emissions—for example, partial substitution of methane with hydrogen limits NO_x formation thanks to lower flame temperatures.

II.6.2. SECONDARY TECHNOLOGIES

Selective catalytic reduction (SCR): This post-combustion technology uses a catalyst, ammonia, or urea to convert NO_x into molecular nitrogen N_2 and water H_2O. SCRs are highly effective, achieving up to 90% NO_x reduction, but their installation and maintenance represent a significant cost.

Selective non-catalytic reduction (SNCR): Although less effective than SCR, this method uses reducing agents injected directly into the hot gases to reduce NO_x.

Optimization of operating parameters: Adjustments to turbine operating conditions, such as precise control of the air-fuel mixture, reduction of excess oxygen, and maintenance of uniform temperatures in the combustion chamber, help to limit emissions.

Recent innovations: Emerging research explores hybrid technologies combining DLN systems with renewable fuels or advanced catalysts. These innovations aim to reduce emissions further while improving turbine energy efficiency [25,26,27,28,29].

II.7. CONCLUSION

This chapter details the formation of nitrogen oxides (NO_x), distinguishing between thermal NO_x, which is highly dependent on combustion temperature, and fuel-bound NO_x, which originates from nitrogenous compounds in the fuel. The significant impacts on human health, including respiratory and cardiovascular issues, and the environment through acid rain and tropospheric ozone, necessitate robust control measures. While advanced primary and secondary reduction strategies like DLN and SCR systems are effective, their optimal performance hinges on a deep understanding of the complex operational factors in gas turbines.

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CHAPTER III.

ANALYTICAL TECHNIQUES FOR NOx MEASUREMENT

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CHAPTER III.

ANALYTICAL TECHNIQUES FOR NOx MEASUREMENT

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III.1. INTRODUCTION

Nitrogen oxides (NO_x), comprising mainly nitric oxide (NO) and nitrogen dioxide (NO_2), are major air pollutants. Accurate measurement is essential to assess their impact on the environment and human health and to ensure compliance with environmental regulations. In an industrial context, such as natural gas liquefaction complexes, NO_x must be controlled at source to limit emissions. This chapter examines the analytical techniques commonly used to measure NOx, their basic principles, and practical applications.

Key criteria for choosing a measurement technique include sensitivity, accuracy, speed, robustness, and ability to operate under industrial conditions. These techniques range from portable devices like the TESTO analyzer to more complex methods like gas chromatography (GC).

III.2. TESTO ANALYZER

III.2.1. DETAILED OPERATING PRINCIPLE

The TESTO analyzer is a portable device designed to measure NO_x directly on site. It is generally based on two fundamental principles:

1. Chemiluminescence: This method measures the light intensity produced during the reaction between NO and ozone (O_3), forming excited NO_2, emitting light when it returns to its ground state. This light is directly proportional to NO concentration.
2. Non-dispersive infrared absorption (NDIR): Used for NO_2, this technique relies on the absorption of infrared radiation at specific wavelengths by NO_2. Attenuation of infrared energy is proportional to gas concentration.

III.2.2. LIMITATIONS AND CONSTRAINTS OF TESTO ANALYZERS

Despite their effectiveness, these instruments have certain limitations:

- Sensitivity to interference: Other compounds, such as CO_2, or ammonia, can interfere with measurements.
- Maintenance requirements: Sensors must be regularly calibrated to maintain accuracy.
- Environmental conditions: Measurements can be influenced by temperature, humidity, and pressure fluctuations.

III.2.3. INNOVATIONS IN PORTABLE ANALYZERS

The latest innovations include integrating advanced sensors, connected systems for remote data management, and improvements to reduce interference. These advances enhance the reliability and versatility of TESTO analyzers, making them essential for industrial applications [1,2,3,4].

III.3. GAS CHROMATOGRAPHY

III.3.1. PRINCIPLE AND INSTRUMENTATION

Gas chromatography (GC) is a powerful technique for analyzing NO_x and other gases in complex mixtures. It separates gaseous compounds based on their interaction with a stationary phase, while a gaseous mobile phase transports the molecules through a chromatographic column.

A specific detector, such as an electron capture detector (ECD) or a mass spectrometer (MS), accurately identifies NO_x. GC is particularly useful for analyzing complex samples,

III.3.2. SAMPLE PREPARATION

Samples must be conditioned before analysis to remove water and solid particles. Devices such as sorption traps, zeolite dryers, or filters are commonly used.

III.3.3. ADVANCED COUPLING FOR GC

Combinations with other techniques enhance analytical capabilities:

- GC coupled to a mass spectrometer (GC-MS): Provides qualitative and quantitative NO_x data with enhanced sensitivity.
- Photoionization detectors (PID): Suitable for trace volatile compounds.

III.3.4. PRACTICAL APPLICATIONS

In this thesis, GC is used to:

- Analyze the composition of fuel gases (CH_4, C_2H_6, CO_2).
- Identify impurities responsible for high NO_x emissions [5,6,7,8].

III.4. COMPARISON OF ANALYTICAL TECHNIQUES FOR NO_x

III.4.1. COMPARATIVE MATRIX OF TECHNIQUES

Selection of the proper analytical method for NO_x measurement depends on various criteria, such as sensitivity, robustness, cost, and specific applications. These criteria are compared in Table III.1.

Table III.1. Criteria for selecting a suitable analytical method for measuring NO_x.

Technique	Sensitivity	Robustness	Cost	Applications
TESTO	Medium	High	Low	Rapid on-site measurements
GC	Very high	Medium	High	In-depth laboratory analysis
UV Spectroscopy	High	High	Medium	Continuous measurements
Electrochemical Sensors	Medium	Medium	Low	Portable monitoring

III.4.2. SELECTION CRITERIA

The choice of technique depends on requirements:

- High sensitivity: GPC or spectroscopy.
- Speed and portability: TESTO or electrochemical sensors.
- Multi-gas analysis: GC coupled with GC-MS [9,10,11,12].

III.5. INNOVATIONS AND EMERGING TECHNIQUES FOR NO_x MEASUREMENT

The constant evolution of analytical technologies aims to improve the accuracy, speed, and portability of NO_x measurement systems. These advances respond to the growing need for real-time emissions monitoring in complex industrial environments, such as gas turbines in natural gas liquefaction complexes.

III.5.1. ADVANCED OPTICAL SENSORS

Optical sensors have gained popularity for NO_x detection thanks to their high sensitivity and ability to operate in harsh environments. These sensors use principles such as:

- Fourier Transform Infrared Spectroscopy (FT-IR): This technique detects NO_x by analyzing the specific molecular vibrations of gases at infrared wavelengths. Modern FT-IR systems can measure several gases simultaneously, making them a versatile tool.
- Tunable Diode Laser Absorption Spectroscopy (TDLAS): This method uses tunable diode lasers to detect specific concentrations of NO and NO_2. It is particularly useful for high-precision in situ measurements under variable combustion conditions.

III.5.2. NEW-GENERATION ELECTROCHEMICAL SENSORS

Although in use for decades, electrochemical sensors have undergone significant improvements in terms of stability, lifetime, and sensitivity. Recent models incorporate advanced materials, such as nanostructured electrodes, which offer improved selectivity for NO_x while reducing interference with other gases.

III.5.3. SURFACE PLASMON RESONANCE (SPR) TECHNOLOGY

SPR is an innovative technique that uses metal surfaces to detect specific interactions between NO_x molecules and sensitive layers. This technology is still in the research phase but promises fast, accurate detection under industrial conditions.

III.5.4. INTEGRATION OF ARTIFICIAL INTELLIGENCE (AI)

Analysis systems equipped with artificial intelligence algorithms significantly advance NO_x measurement. AI can be used to:

- Process data in real time, reducing errors due to gas interference or environmental fluctuations.
- Predict variations in NO_x emissions based on operational conditions.
- Optimize combustion system settings to minimize emissions [13,14,15,16].

III.6. INTERNATIONAL STANDARDS AND PROTOCOLS FOR NO_x MEASUREMENT

III.6.1. ENVIRONMENTAL REGULATIONS

NO_x measurements must comply with strict standards laid down by international organizations, such as:

- The U.S. Environmental Protection Agency (EPA): The EPA establishes standardized methods for NO_x measurement, notably method 7E for flue gases.
- European Union (EU): European directives, such as the Industrial Emissions Directive (IED), impose emission limits and continuous monitoring requirements.
- International Organization for Standardization (ISO): Standards such as ISO 10849 define methods for measuring gas turbine emissions.

III.6.2. IMPORTANCE OF INSTRUMENT VALIDATION

Regular validation of analytical instruments is essential to ensure compliance with standards. This includes:

- Periodic calibration: using standard gases to adjust sensor sensitivity.
- Cross-audits: Comparison of results obtained with different techniques to ensure measurement reliability [17,18,19].

III.7. CHALLENGES AND PROSPECTS IN NO_x MEASUREMENT

III.7.1. TECHNICAL CHALLENGES

Despite technological progress, several challenges remain:

- Extreme conditions: High temperatures and pressures in turbine combustion chambers complicate direct measurements.
- Gas interference: Other gases, such as CO_2, or hydrocarbons, can interfere with results.
- Instrument maintenance: Sensors must be regularly cleaned and calibrated, which can lead to downtime.

III.7.2. FUTURE PROSPECTS

Current research is aimed at overcoming these limitations through:

- Miniaturization of sensors: Development of portable devices for rapid on-site measurements.

- Use of advanced materials: For example, selective membranes to improve NO_x detection in complex mixtures.
- Integration with industrial control systems: Real-time measurement technologies can be coupled with automatic controls to optimize combustion parameters [20-21-22-23].

III.8. CONCLUSION

This chapter has explored analytical techniques for NO_x measurement, highlighting their operation, advantages, and limitations. Emerging innovations, such as optical sensors and AI-enabled systems, represent a significant advance for emissions monitoring. However, challenges remain, particularly in complex industrial environments such as Frame 6 turbines. A combination of proven technologies and innovative solutions is essential to meet the growing demands for accuracy, durability, and regulatory compliance.

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CHAPTER IV.

EXPERIMENTAL PROCEDURE

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CHAPTER IV. EXPERIMENTAL PROCEDURE

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IV.1. INTRODUCTION

The experimental campaign conducted as part of this study aims to characterize and understand the NO_x emissions generated by Frame 6 gas turbines equipped with low NO_x emission (DLN) combustion systems in a natural gas liquefaction complex. These emissions are a critical indicator of the environmental performance and efficiency of the combustion system. Based on in site measurements and laboratory analyses, the main objective is identifying the operating, environmental, and chemical factors influencing NO_x formation. More specifically, the goals of this campaign are:

- To quantify NO_x emission levels at different turbine operating conditions (partial load, full load) by taking repeated and comparable measurements over time.

- Correlate NO_x emissions with turbine operating parameters (intake temperature, pressure, mechanical load, excess air ratio), based on the thermal mechanisms of NO_x formation described in the literature (Zeldovich thermal formation, Fenimore prompt formation, etc.) [1].

- Study the impact of fuel gas composition (proportion of methane, heavy hydrocarbons, nitrogen, etc.) on observed emissions using standardized chromatographic analyses (ASTM D1945).

- Evaluate the influence of local environmental conditions, in particular the temperature and humidity of the intake air, on NO_x production, by experimental observations of thermal NO formation in industrial turbines.

Validate the DLN system's performance by comparing the measured emission levels with regulatory thresholds (200 mg/Nm3) and manufacturer data, and identifying any deviations due to operational drifts or component degradation.

This experimental part is part of an integrated approach combining field measurements, analytical diagnostics, and physical-chemical interpretation to formulate technical recommendations for reducing NO_x emissions under real industrial conditions.

IV.2. GAS TURBINE POWER GENERATION SYSTEM

The Gas Turbine Power Generation System provides the electrical power required for the entire complex. It comprises four Gas Turbine Power Generators, 51-MJ01-A/B/C/D-GT.

During regular operation, the gas turbines are the sole source of electricity for the LNG trains, their off-site facilities, and utilities. They are designed to burn fuel gas, usually supplied by the

LNG Trains, and feed gas during start-up operations. This electrical energy is produced by Frame 6 Gas Turbine Generators (GTGs).

The plant's electrical loads have been analyzed regarding current and future configurations (one Process Train and two Process Trains, respectively). The standard configuration during plant operation includes all turbines operating in static mode, sharing the plant's power requirements [2].

IV.3. SAMPLING AND MEASUREMENT OF NO_x EMISSIONS

Nitrogen oxide NO_x measurements were taken using a TESTO 350-XL portable analyzer, designed explicitly for emissions diagnostics in high-temperature industrial installations. Sampling was carried out at the end of the exhaust pipes of the Frame 6 gas turbine, under conditions representative of steady-state operation. According to the recommendations of EPA Method 7E for stationary sources, the measuring point is downstream of the combustion chamber. The TESTO 350-XL analyzer uses electrochemical sensors to measure the concentrations of nitrogen monoxide NO and nitrogen dioxide NO_2 separately, thus enabling the calculation of total NO_x. The measurements are expressed in mg/Nm^3 and are automatically corrected by the device according to the residual oxygen O_2 content, to normalize the values to a standard dry basis of 15% O_2. The equipment also has a heated probe that prevents condensation in the sampling line, thus ensuring the sample's integrity.

Under current Algerian regulations, the maximum permissible concentration of NO_x in exhaust gases from a petroleum refining and processing plant must not exceed 200 $^{mg/Nm3}$ [3]. This regulatory threshold is a critical reference for data interpretation and enables the results to be classified according to compliance. In Chapter 5, the experimental data collected using the TESTO will be compared with this threshold to diagnose the conditions favorable or unfavorable to NO_x formation and assess the effectiveness of the DLN system in different turbine operating configurations.

IV.4. SAMPLING AND ANALYSIS OF FUEL GAS COMPOSITION

Fuel gas for the Frame 6A gas turbine was sampled from a dedicated sampling point upstream of the turbine, identified under reference 51-S-001. This sampling point is connected to a purge line to the flare, enabling complete renewal of the dead volume before each sampling operation. This purge ensures that the sample taken is representative of the instantaneous composition of the gas injected into the combustion chamber.

Samples were collected in stainless steel cylinders that had been evacuated and pressurized with fresh gas, following a rigorous double-rinse protocol. The sampling line is maintained at constant pressure (27 barg) and at a temperature of around 110°C to prepare the fuel gas before it enters the combustion chamber.

Chromatographic analysis was conducted in the complex's laboratory using a Clarus 580 gas chromatograph (PerkinElmer), equipped with a thermal conductivity detector (TCD). Constituents are separated by a packed column thermostat at 110°C, enabling simultaneous detection of light gases (He, N_2, CO_2, CH_4, C2, C3...) following the precision requirements of ASTM method D1945. The system is calibrated using a certified multi-component standard gas, and the reproducibility of results is checked daily by duplicate analysis.

The analytical results obtained were compared with the limit values specified by the turbine manufacturer, as presented in Table IV.1. These limits include, among others:

- A methane content (C1) of between 60 and 98 mol%;
- Thresholds for higher hydrocarbons (C2 to C6+) to avoid excessive combustion temperature rise;
- Limits on carbon dioxide ($CO_2 < 2$ mol%) and nitrogen ($N_2 < 38$ mol%) to avoid dilution of the higher calorific value;
- A maximum moisture content of 0.35 mol%, measured according to ASTM D5454.

The data obtained were integrated into the cross-analysis with NO_x emissions measured by the TESTO 350-XL. In particular, they were used to calculate the HCV and estimate the stoichiometric air/gas ratio, essential parameters for interpreting the mechanisms of thermal NO_x formation. Any significant deviation from the manufacturer's specifications is thus identified as a critical factor in increasing pollutant emissions, particularly during fluctuating natural gas quality periods.

Table IV.1. Combustible gas sampling on turbine 51-MJ01A.

Sampling point	Ref.	T (°C)	P (barg)	Parametre	Values min - max	Unit	Method
Towards the GTG A/B/C/D system	51-S-001	110	27	He	0 – 1	mol%	ASTM D1945
				N_2	0,02 – 38		
				CO_2	0 – 2		
				C_1	60 – 98		
				C_2	0 – 15		
				C_3	0 – 7		
				n-C_4	0 – 0,30		
				i-C_4	0 – 0,10		
				n-C_5	0 – 0,05		
				i-C_5	0 – 0,05		
				C_6+	0 – 0,01		
				Humidity	0,01 – 0,35		ASTM D5454
				Density	—	—	—
				MW (Molecular weight)	—		

IV.5. CHARACTERIZATION OF INTAKE AIR

Intake air is fundamental to combustion performance and nitrogen oxide NO_x formation in gas turbines. In this study, the air admitted into the Frame 6A turbine is characterized using measurements provided by the complex's DCS (Distributed Control System) monitoring system. Sensors installed along the air intake circuit continuously monitor several critical parameters affecting combustion quality and pollutant emission levels.

The absolute air pressure at the compressor inlet is measured by the PI (Pressure Indicator) sensor, with a typical value of 1006 mbar, reflecting local atmospheric conditions (coastal environment and close to sea level). This pressure is an essential reference point for calculating the mass flow rate of incoming and excess air, two variables that directly influence flame temperature and NO_x formation.

The TI (Temperature Indicator) sensor, installed near the air intake, records the ambient temperature. This temperature affects the density of the intake air and the combustion temperature. Higher air temperatures can reduce compressor efficiency and increase NO_x in hot weather, as shown in the technical literature on Brayton cycles and GTG emission profiles [4].

The pressure differential indicator (PDI) measures the pressure drop across intake filters, showing a typical pressure drop of 1.5 mbar. This data can be used to assess filter clogging and its effect on adequate airflow. Partially clogged filters can cause less uniform combustion and alter the air/gas ratio, influencing the local formation of hot spots responsible for thermal NO_x.

A system of cartridge filters placed in line significantly reduces the relative humidity of the intake air, ensuring effective drying to a target value of 0.1%. This operation aims to minimize combustion variability by maintaining stable humidity levels. Several studies have shown that air humidity reduces NO_x formation by lowering the flame temperature and modifying the kinetics of oxidizing radicals (OH•, O•, H•), particularly in lean-burn DLN systems [5].

In this context, accurate characterization of the intake air is essential for interpreting fluctuations in emissions measured by the TESTO analyzer and for assessing the robustness of the DLN system in response to variations in actual environmental conditions. These parameters will be incorporated into the cross-correlations presented in Chapter V to establish statistical links between ambient conditions and the turbine's ecological performance.

IV.6. COLLECTION AND ORGANIZATION OF OPERATIONAL DATA

Operational data was extracted from the complex's DCS industrial supervision system to supplement the on-site experimental measurements. This information provides context for each NO_x emission measurement campaign and allows the results to be interpreted in light of the actual operating conditions of the Frame 6A turbine.

The following parameters were collected daily, at the time of each fuel gas sample and each NO_x recording:

- Turbine load (MW): This represents the mechanical power produced at the shaft, which is directly linked to the combustion temperature and the formation of NO_x. The load is an essential indicator for differentiating between operating modes (partial, nominal, maximum).

- Fuel gas flow rate (Nm3/h): This value, measured continuously by a vortex flow meter, evaluates the energy flow injected. Combined with gas composition from the GC, the calorific value injected and the air/gas ratio are calculated.

- Flame temperature (°C): indirectly deduced from the temperature at the combustion chamber outlet and corrected according to standard thermodynamic models. This temperature is a key determinant of the thermal formation of NO_x.

Air and gas intake temperatures are measured before compression and injection into the chamber, respectively. These temperatures influence flow density, mixing dynamics, and the combustion regime.

- Residual oxygen content (O_2, in vol%): Measured in the exhaust gases, this allows the excess air to be estimated and the NO_x concentrations to be corrected to a standard (often 15% dry O_2), as required by environmental standards [6].

- Combustion chamber pressure (barg): a valuable parameter for characterizing flame stability conditions and interpreting any increases in NO_x associated with transient regimes.

Each measurement point is time-stamped and linked to the ambient weather conditions, enabling complete traceability. This data is then exported from the DCS system in digital format, verified, and synchronized with the analytical results from the TESTO and GC instruments. This approach allows for cross-analysis of data (multivariate) to identify correlations between operational variables and NO_x emission levels, as will be presented in Chapter V.

IV.7. CONCLUSION

The experimental study on Frame 6 gas turbines equipped with low NO_x emission (DLN) combustion systems in a natural gas liquefaction complex provided a better understanding of the mechanisms influencing nitrogen oxides' formation. In situ measurements made with the TESTO 350-XL analyzer and chromatographic analyses of fuel gas composition highlighted the joint impact of operational parameters, gas composition, and environmental conditions on NO_x emissions. The results confirm the effectiveness of DLN systems in keeping emissions below regulatory thresholds, while underlining the importance of rigorous control of combustion conditions and gas quality. Combining on-site diagnostics and physico-chemical analysis, this integrated approach provides a solid basis for optimizing turbines' environmental and operational management in LNG complexes, contributing to more sustainable production in line with current requirements.

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CHAPTER V.

RESULTS AND DISCUSSIONS

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CHAPTER V. RESULTS AND DISCUSSIONS

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V.1. INTRODUCTION

This section presents the raw data collected during thirteen campaigns to measure emissions of atmospheric pollutants generated by the Frame 6A gas turbine, operating in a natural gas liquefaction complex. These data concern the concentrations of NO (nitrogen monoxide), NO_2 (nitrogen dioxide), total NO_x, and CO (carbon monoxide) measured directly in the combustion gases, as well as the chemical composition of the fuel gas analyzed in the laboratory. Additional operational information from the DCS control system, such as flame temperature, mechanical load, and air intake conditions, supports the environmental analysis.

CO, NO, and NO_2 concentrations were measured in situ using a TESTO 350-XL portable analyzer at the turbine stack outlet. These values were corrected for reference conditions (dry gas at 15% O_2) and expressed in mg/Nm^3, per Algerian regulations, which impose a 200 mg/Nm3 limit of total NO_x for industrial combustion plants. Table V.1 summarizes the results recorded over 13 consecutive days.

Table V.1. Measurement of NO_x and CO emissions (mg/Nm^3 at 15% dry O_2).

Sampling	NO (mg/Nm^3)	NO_2 (mg/Nm^3)	NO_x total (mg/Nm^3)	CO (mg/Nm^3)	Temperature (°C)
1	25.439	9.852	35.291	2.499	27.4
2	22.761	7.184	29.945	8.748	28.1
3	20.083	4.926	25.009	4.999	29.0
4	21.422	6.568	27.99	6.248	29.7
5	28.117	8.415	36.532	3.749	30.5
6	194	66,6	260.6	6	31.8
7	214	11.7	225.7	204	32.6
8	285	49.5	334.5	65	33.4
9	289	27.5	316.5	59	34.2
10	383	50.5	433.5	60	35.5
11	199	13.8	212.8	836	36.7
12	173	10.4	183.4	101	37.4
13	160	9.5	169.5	98	38.9

At the same time, fuel gas samples were taken daily at sampling point 51-S-001, located at the inlet to the turbine feed line. Gas chromatography (GC) analyzed each sample using a PerkinElmer Clarus 580, equipped with a TCD detector and a column heated in an oven to 110°C. The major components (CH_4, C_2H_6, N_2, CO_2, etc.) were quantified, and the following thermodynamic properties were calculated:

- Higher Calorific Value (HCV), expressed in kWh/Nm³;

- Gas density, expressed in kg/Nm³.

Table V.2 shows the results of this analysis during the 13-day campaign.

Table *V*.2. Measurement of NO_x and CO emissions (mg/Nm³ at 15% dry O_2).

N°	He	N_2	CO_2	C_1	C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	C_6^+	HCV (kWh/Nm³)	ρ (kg/Nm³)
	(%mol)												
1	0.076	14.662	0.330	71.370	12.958	0.446	0.050	0.075	0.012	0.012	0.009	8.532682	0.8215
2	0.049	14.734	0.281	70.899	13.470	0.430	0.042	0.063	0.011	0.011	0.010	8.580473	0.8348
3	0.063	17.587	0.136	68.753	13.121	0.247	0.028	0.043	0.007	0.008	0.007	8.255255	0.8416
4	0.041	16.144	0.214	69.561	13.640	0.293	0.032	0.049	0.009	0.009	0.008	8.455321	0.8408
5	0.047	17.323	0.458	67.306	14.395	0.346	0.037	0.058	0.010	0.011	0.009	8.351168	0.8555
6	0.077	19.101	0.212	66.720	13.312	0.420	0.049	0.073	0.012	0.013	0.011	8.135554	0.8569
7	0.107	15.435	1.240	67.568	14.343	0.931	0.105	0.166	0.035	0.039	0.031	8.737688	0.8439
8	0.053	17.480	0.200	68.814	12.943	0.371	0.041	0.064	0.012	0,013	0.009	8.255345	0.8471
9	0.284	18.380	0.261	66.202	14.075	0.565	0.069	0.105	0.019	0.021	0.019	8.296695	0.8590
10	0.065	15.187	0.397	67.741	15.839	0.563	0.063	0.096	0.016	0.018	0.015	8.717453	0.8557
11	0.167	19.470	0.135	68.816	10.890	0.381	0.044	0.068	0.010	0.011	0.008	7.988812	0.8389
12	0.243	19.756	0.055	70.381	9.034	0.384	0.048	0.070	0.010	0.011	0.008	7.806038	0.8302
13	0.380	25.138	0.066	61.881	12.207	0.239	0.029	0.043	0.006	0.007	0.004	7.504705	0.8722

V.2. INFLUENCE OF HCV ON NO_x EMISSIONS

A fuel gas's Higher Calorific Value (HCV) represents the maximum thermal energy that can be released by its complete combustion, considering the condensation of the water vapor produced. It is expressed in MJ/Nm3 or kWh/Nm3. In this work, HCV values were determined using in-house software called SYSPRO, which is based on the formula (Eq. V.1) taken from ISO 6976: 2016 [1]:

$$\mathrm{GCV} = \sum_{i=1}^{n} y_i \,.\, \mathrm{HCV} \qquad \text{(Eq. V.1)}$$

Where:

Yi: molar fraction of component i;

HCV_i: gross calorific value of component i, expressed in MJ/Nm³ or kWh/Nm³ (at 0°C, 101.325 kPa, dry gas).

Studying the relationship between HCV and NO_x emissions provides a better understanding of how fuel energy quality influences the reactions that form nitrogen oxides. Theoretically, a high HCV fuel favors a higher flame temperature, which can increase thermal NO_x production via Zeldovich reactions. Figure V.1 illustrates this relationship for the 13 sampling days studied.

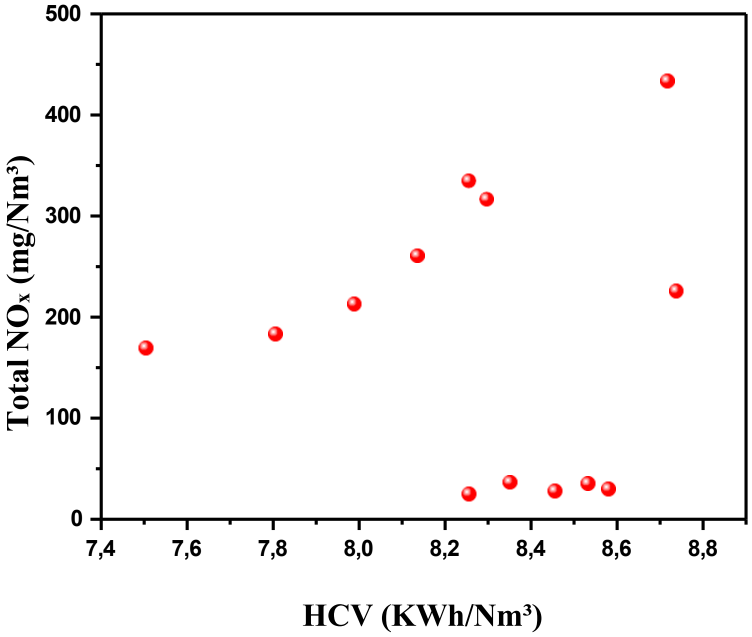

Figure V.1. Relationship between fuel gas HCV and NO_x emissions.

The scatterplot analysis reveals a moderate inverse trend between HCV and total NO_x concentration. Indeed, some of the most energy-rich days (HCV ≈ 8.7 kWh/Nm3) paradoxically show relatively low NO_x emissions (day 7), while lower HCV (around 7.5-7.9) are associated with NO_x peaks (days 10-13). This observation suggests that HCV alone cannot predict NO_x formation intensity. Despite a high theoretical HCV, other parameters such as mixture richness, turbulence, secondary air flow rate, and dilution ratio modify the effective flame temperature. On days with a high HCV, thermal control strategies (via DLN systems) may enable the peak temperature to be controlled, thus limiting NO_x formation. On the other hand, some days with a lighter gas may have resulted in locally hotter combustion, especially in the event of mixture imbalance or high load conditions.

Furthermore, several studies confirm that flame temperature is the determining factor in forming thermal NO_x, more so than HCV per se. Aliyu et al. indicated that the effect of HCV is secondary as long as combustion remains complete and well-mixed [2]. Funke et al. noted that in DLN burners, control of mixture stratification takes precedence over gas energy richness [3]. Thus, in modern low-NO_x industrial systems, the effect of HCV is non-linear and needs to be analyzed in conjunction with other operating conditions, notably excess air and flame temperature control mode [4].

However, the relationship between HCV and NO_x emissions in the Frame 6A turbine studied does not show a direct monotonic trend. This indicates that HCV cannot be considered an isolated factor, and that thermal control strategies, combustion conditions, and combustor architecture strongly influence NO_x formation kinetics.

V.3. INFLUENCE OF FUEL GAS DENSITY ON NO_x EMISSIONS

Fuel gas density, expressed in kg/Nm^3, is a fundamental physical property that conditions mass flow, the air/fuel mixture profile, and, consequently, flame characteristics. Although often ignored in simplified empirical approaches, it directly influences the maximum temperature reached in the combustion chamber, which plays a central role in forming thermal nitrogen oxides (thermal NO_x). The latter are highly temperature-dependent according to Zeldovich mechanisms, which are very active above 1200°C. Figure V.2 illustrates the variation of NO_x as a function of fuel gas density.

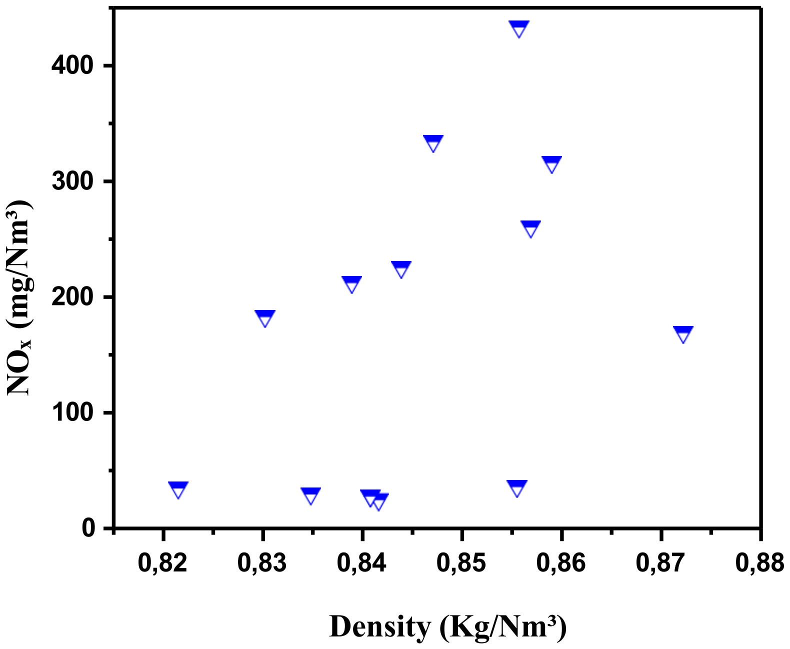

Figure V.2. NO_x variation as a function of density.

Gas density is directly influenced by the presence of nitrogen (N_2), an inert component often used as a natural diluent, as well as by the proportion of heavier hydrocarbons such as ethane (C_2H_6), propane (C_3H_8), and butanes. In the 13 samples analyzed, N_2 content ranged from 14.6% to 25.1% mol, with higher values systematically associated with increased density. A relative lowering of calorific value accompanies this increase in density and may lead to a shift in optimal mixing and combustion conditions. Nevertheless, the ethane content (C_2H_6) is mainly within the range recommended by the manufacturer (0 to 15% mol). This component is an important energy carrier: it has a higher calorific value than methane and generates a hotter, straighter flame. However, an excess of C2 associated with high density accentuates the peak temperature in combustion zones, aggravating the formation of thermal NO_x if the air/fuel mixture is not perfectly homogeneous. Thus, experimental analysis indicates that days when gas density exceeds 0.855 kg/Nm^3 correspond to NO_x peaks (often > 300 mg/Nm^3), linked to compositions rich in N_2 and C2. These days illustrate a complex interaction between density, chemical composition, and combustion regimes.

According to Ma et al, or gas density affects flame dynamics and premixing efficiency in low NO_x (DLN) chambers. High density shortens the flame length, increases the local temperature in the combustion core, and reduces the efficiency of internal cooling of the flame front by inert gases [5]. Similarly, Schiffer et al. point out that turbines fuelled by C2-rich nitrogen-rich gases require active regulation to compensate for non-linear effects on NO_x formation [6]. However, this analysis reveals that gas density, nitrogen, and ethane content are critical factors in NO_x regulation [6]. A higher density, reflecting a more complex composition, is systematically associated with increased emissions in the Frame 6 turbine.

Therefore, it is imperative to monitor the density and composition of the feed gas in real time. Dynamically adjust air flows and combustion regimes, and integrate these parameters into predictive NO_x formation models, considering recommended safety thresholds (e.g., 12-15% C2). This factor offers a significant operational opportunity to fine-tune the environmental strategy of GTGs and reduce NO_x-related impacts in natural gas liquefaction complexes.

V.4. INFLUENCE OF (CO) ON NO_x EMISSIONS

Carbon monoxide (CO) is a product of incomplete combustion, resulting from local oxygen deficiency or rapid cooling of reactive gases. In low-emission gas turbines like the Frame 6 equipped with DLN systems, CO is a critical tracer of the quality of the combustion process. Joint analysis of NO_x and CO emissions allows for exploring the thermochemical competition between complete oxidation of carbon and formation of nitrogen oxides. Indeed, conditions that favor NO_x production - high temperature, excess air, hot, homogeneous flame - often tend to reduce CO levels... and vice versa.

Experimental measurements carried out using the TESTO 350-XL analyzer show significant daily variations in CO and total NO_x concentrations. Figure V.3 shows the relationship between these two pollutants over the 13 sampling campaigns.

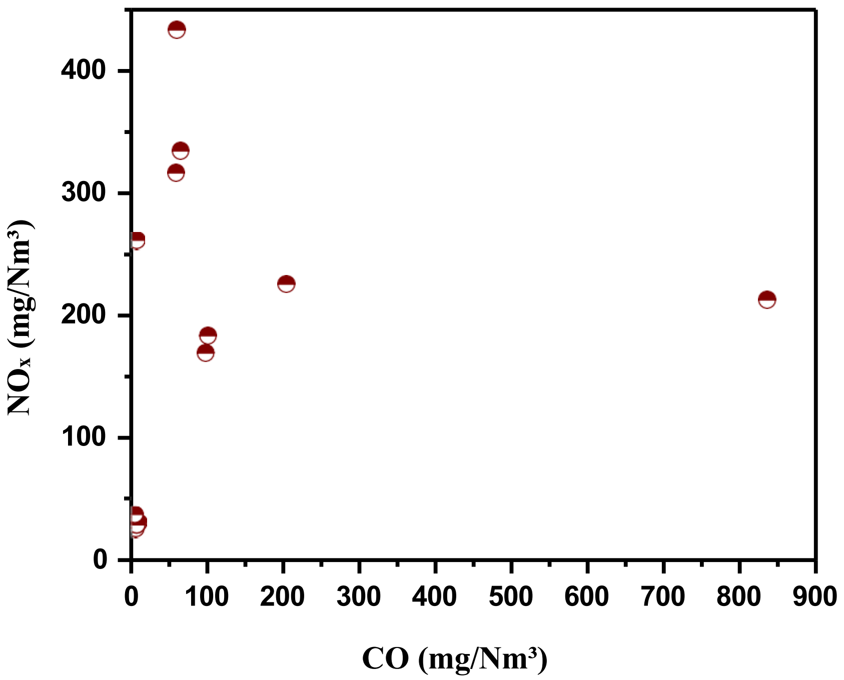

Figure *V*.3. Correlation between CO and total NO_x emissions.

The observed trend reveals a partial inverse relationship. For CO values < 50 mg/Nm^3, NO_x emissions often exceed 200 mg/Nm^3. On the other hand, high CO levels (notably > 800 mg/Nm^3, as on day 11) are associated with reduced NOx levels, sometimes close to the regulatory threshold. This phenomenon is explained by the thermochemical compromise inherent in combustion. A hot, well-oxygenated flame promotes the complete oxidation of carbon ($CO \rightarrow CO_2$) but generates thermal NO_x via the Zeldovich mechanism. Conversely, lean or unstable combustion, less oxygenated or locally cooled, produces more residual CO while limiting peak temperature and NO_x.

It is important to note that not all high CO levels correspond systematically to low NO_x (see Day 7). This partial decorrelation may be linked to compositional factors, such as a high ethane (C2) content, which increases flame temperature, or a high N_2 content, as observed on some days (> 18 mol%). N_2, although inert, acts as a thermal diluent in the gas mixture. It lowers the effective flame temperature and slows down the kinetics of complete carbon oxidation, thus contributing to CO formation. At the same time, this same nitrogen is also the primary precursor of thermal NO_x, making its effect ambiguous and highly dependent on combustion conditions.

Furthermore, at temperatures close to 1038°C - typical of the flame core in a Frame 6 - it is possible that some CO production is linked to rapid incomplete kinetics in rich zones, known as “prompt” combustion zones. This phenomenon manifests itself in transient or unstable regimes, when the air/gas distribution is not perfectly homogeneous, favoring the presence of CH and H radicals, which accelerate combustion while generating residual CO and NO prompt in small quantities. Wang and Sohn demonstrate the existence of an optimum zone in premixed combustions, where NO_x and CO emissions are simultaneously minimized [7]. Mardani et al. point out that inert compounds such as N_2 reduce flame temperature but slow down complete oxidation, favoring CO formation in some cases [8].

This study highlights a significant inverse correlation between CO and NO_x emissions, reflecting the thermal, kinetic, and chemical trade-offs specific to DLN systems. The influence of N_2 as a thermal modulator and the possibility of transient prompt combustion reinforce the idea that CO is a valuable indicator of combustion imbalances, especially in the transition phase.

V.5. INFLUENCE OF INTAKE AIR TEMPERATURE AND HUMIDITY ON NO_x EMISSIONS

Intake air temperature is a key parameter in the combustion process of low-emission gas turbines such as Frame 6 equipped with DLN systems. The intake air directly influences the air/gas mixture, the maximum flame temperature, and, therefore, the thermal reactions that produce NO_x.

This study recorded daily ambient intake air temperatures from the DCS control system. These showed moderate variability but were sufficient to assess their influence on NO_x production. The relative humidity of the intake air remained relatively constant at around 0.1% by mass, thanks to the action of desiccant cartridge filters installed upstream of the air compressor.

A higher air temperature increases the enthalpy of the mixture input, which raises the flame peak temperature and accelerates the kinetics of radical reactions [9], particularly the formation of NO via the Zeldovich thermal mechanism.

However, water vapour in the air acts as a thermal buffer. It absorbs part of the heat of combustion (thanks to its specific and latent heat), reduces flame temperature, and dilutes oxidizing radicals (O•, OH•), slowing NO_x production [10]. Moderate humidity, such as that observed in this campaign (~0.1%), has a mild but measurable attenuating effect on NO_x. Figure V.4 shows the relationship between intake air temperature in the Frame 6 gas turbine and the nitrogen oxides (NO_x) concentration measured in mg/Nm3 (corrected to 15% dry oxygen).

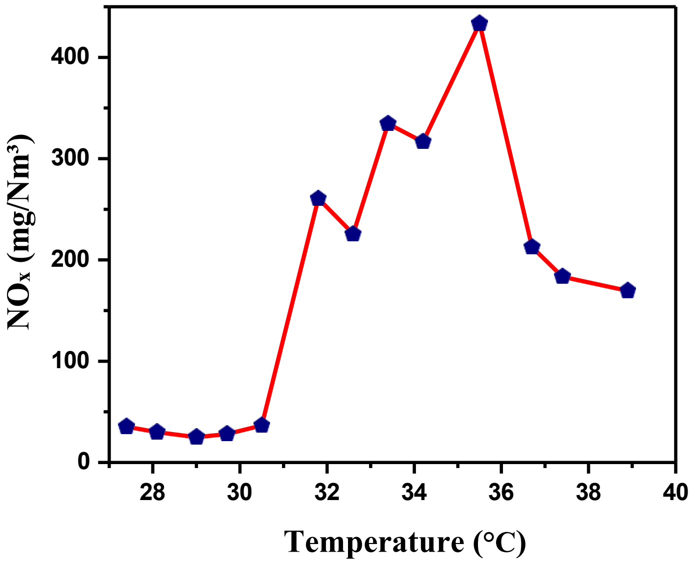

Figure V.4. NO$_x$ as a function of intake air temperature.

A clear upward trend is observed between ~30°C and 35°C, suggesting that the rise in air temperature at the compressor inlet helps to amplify the conditions for thermal NO$_x$ formation in the combustion chamber. This behavior is consistent with Zeldovich's mechanism, in which the rate of NO$_x$ formation increases exponentially with flame temperature, which is itself influenced by the initial temperature of the reactants. Indeed, a higher intake temperature increases air enthalpy, reduces the energy effort of ignition, and causes a greater thermal peak in the flame. However, above 35-36°C, an inflexion in the curve is observed, with NO$_x$ concentrations beginning to fall slightly despite the still-rising temperature (up to ~39°C). Several combined hypotheses can explain this behavior:

- <u>The DLN system has a self-regulating effect:</u> Automatic turbine control could detect NOx overproduction and adjust air/gas ratios or premix conditions.

- <u>Effect of humidity (0.1%):</u> although modest, this constant humidity plays a mitigating role by locally lowering the flame temperature through its specific heat, thus slowing the kinetics of oxidizing radicals (O-, OH-).

- <u>Dilution phenomena:</u> At very high temperatures, the air becomes less dense, which could indirectly reduce the mass of oxygen available per unit volume, affecting NO$_x$ kinetics.

Moreover, this evolution suggests that the temperature-NO$_x$ relationship is not strictly linear in DLN regimes. Still, it presents a zone of saturation or active regulation, beyond which the increase in temperature no longer leads to a proportional rise in NO$_x$. An intake temperature >

30°C contributes to NO_x formation, promoting hot, homogeneous combustion. Temperatures > 36°C and slight humidity can partially moderate NO_x emissions, probably through thermal dilution or system adjustment.

This analysis shows that ambient air temperature is a lever for environmental optimization of industrial turbines: it must be integrated into intelligent control (based on weather, seasons, or air-cooling systems).

V.6. CONCLUSION

The detailed analysis of experimental data collected over thirteen days at the Frame 6A gas turbine outlet has enabled us to critically examine the key factors influencing NO_x emissions in a real industrial environment. This study highlighted the intrinsic complexity of NO_x formation mechanisms. It demonstrated that their intensity cannot be reliably predicted from a single isolated parameter but results from the dynamic interaction between fuel gas characteristics, internal combustion conditions, and environmental parameters.

Although the gross calorific value (HCV) indicates the gas's energy richness, it did not prove decisive in predicting NO_x emissions. This result calls into question conventional models based on a linear relationship between energy richness and the production of nitrogenous pollutants. In contrast, gas density, as an integrating parameter of chemical composition (particularly in C_2 and N_2), showed a more direct influence. The highest values are associated with NO_x peaks, reflecting altered flame characteristics and less controlled combustion.

Carbon monoxide (CO) measurements provided crucial additional insight. A partial inverse trend with NO_x was observed, validating the well-known thermochemical trade-off between complete oxidation and nitrogen oxide formation. However, some specific cases showed simultaneously high levels of CO and NO_x, suggesting prompt combustion phenomena in unstable regimes. This highlights the limits of standard kinetic models applied to DLN systems. These observations are reinforced by the gas composition on the days in question, where high N_2 and C2 contents accentuate the instability of the flame front.

Finally, the influence of intake air temperature and humidity was examined. A gradual temperature rise favored NO_x formation, consistent with Zeldovich's mechanism. However, emissions were attenuated beyond a certain thermal threshold, probably due to the slight residual humidity of the air (~0.1%) and automatic compensation mechanisms of the DLN system. This illustrates the importance of considering environmental conditions, often neglected in conventional predictive approaches, as significant input variables in emission control strategies.

This study reveals that NO_x management in gas turbines cannot be based on simple indicators such as HCV or excess air rate. It requires a systemic approach, integrating physico-chemical, kinetic, and environmental parameters, and cross-referencing in real-time data from fuel composition, combustion conditions, secondary emissions (CO), and climatic variables. These results pave the way for developing advanced control tools and multidimensional predictive models capable of driving combustion while minimizing NO_x and CO emissions while maintaining the turbine's energy performance. By their integrated nature and based on real industrial data, these findings represent a methodological and scientific advance likely to significantly enrich the literature on low-emission combustion systems in the energy sector.

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General Conclusion

GENERAL CONCLUSION

Reducing atmospheric emissions from energy production systems represents a significant strategic challenge in a global context marked by tightening environmental regulations. Among the most worrying pollutants, nitrogen oxides (NO_x) occupy a central position, both for their role in forming tropospheric ozone and acid rain, and for their direct effects on human health and biodiversity. In this context, industrial gas turbines, particularly those used in natural gas liquefaction complexes, represent a significant source of NO_x emissions, even when equipped with advanced combustion systems such as Dry Low NO_x (DLN).

This work aimed to experimentally investigation of the factors influencing NO_x emissions in Frame 6 turbines at an Algerian natural gas liquefaction complex. The study was designed as a rigorous field study, combining actual sampling campaigns, in situ measurements using the TESTO 350-XL portable analyzer, chromatographic analysis of fuel gas (ASTM D1945 standard), and operational data collection from the Distributed Control System (DCS). Combining process engineering, environmental analysis, and applied combustion, this multi-disciplinary approach enabled us to address the subject from a technical, energy, and environmental standpoint, considering practical industrial realities.

The results obtained in this work are multiple and complementary. The study provided an accurate picture of NO_x emissions in a GTG Frame 6 turbine. Over thirteen consecutive sampling days, measured NO_x concentrations showed wide variations, ranging from 25 mg/Nm^3 to over 430 mg/Nm^3 (reference corrected to 15% dry O_2), with several exceedances of the Algerian regulatory threshold set at 200 mg/Nm^3. These fluctuations highlighted significant variability in operation, necessitating a detailed analysis of the causes.

Secondly, a cross-analysis of several parameters was carried out. Four main factors were systematically studied:

The Higher Calorific Value of fuel gas (HCV) was analyzed to explore its ability to predict emissions. It has been found that the HCV, expressed in kWh/Nm^3, although an indicator of chemical energy, was not directly predictive of NO_x production, particularly in optimized DLN systems. This finding calls into question certain simplified modeling practices that equate energy richness with emission levels.

On the other hand, fuel gas density proved to be a decisive parameter. A clear correlation was observed between density (expressed in kg/Nm^3) and an increase in NO$_x$, particularly above 0.85 kg/Nm^3. This relationship was attributed to the simultaneous presence of heavy components (C2, C3) and nitrogen (N_2), altering flame characteristics and reducing the stability of the air/gas mixture. This is an original result that is rarely experimentally discussed in industrial literature.

Simultaneous analysis of carbon monoxide (CO), the product of incomplete combustion, identified unstable thermochemical regimes, marked by complex trade-offs between complete oxidation and NO$_x$ formation. A partial inverse relationship was verified, but some days showed simultaneous peaks of NO$_x$ and CO, suggesting prompt combustion conditions due to mixing imbalances, turbulent injections, or high N_2 presence. This behavior highlights the value of simultaneous, rather than isolated, NO$_x$/CO monitoring in DLN control.

In addition, the influence of intake air temperature and humidity was evaluated. Increasing air temperature, measured at the compressor inlet, strongly impacted NO$_x$ production via the Zeldovich thermal mechanism. However, saturation or regulation was observed above a certain temperature threshold (above 35-36°C), probably moderated by humidity (0.1%), which acts as a thermal buffer. This section highlights the importance of considering ambient climatic conditions when modeling and regulating emissions.

By integrating these four axes of analysis, this work represents an original contribution to the experimental study of NO$_x$ emissions in DLN turbines, based on real industrial data. Unlike purely numerical or simulated approaches, it highlights complex multi-parameter interactions that conventional linear models cannot describe. The richness of this approach provides a better understanding of the real - and sometimes counter-intuitive - behavior of industrial systems under variable operating conditions.

This work also opens up new avenues for research and optimization. These include:

Developing a multi-variable predictive model (multivariate regression or artificial intelligence) to anticipate emissions as a measured parameter function.

Implement a dynamic control system based on air density, CO, and temperature, to adapt air/gas premix ratios in real time.

The study will be extended to other turbines on site (Frame 5 and Frame 7) to validate the generalization of observed trends and include transient conditions (start-up, load change).

Finally, exploring advanced wet dilution or water/steam injection techniques to attenuate thermal peaks in high-temperature regimes.

In addition, this dissertation offers a solid and practical methodological basis for understanding, monitoring, and environmental control of NO_x emissions in Frame 6 industrial gas turbines. It provides a robust scientific basis for future work and relevant support for publications on ecological engineering and combustion processes.