

# NON-THERMAL PLASMA TO REDUCE ENGINE EXHAUST GASOLINE GASES

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# **ABSTRACT**

#### M. Sc. Thesis

# NON-THERMAL PLASMA TO REDUCE ENGINE EXHAUST GASOLINE GASES

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Department of Physics

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The vehicle's engines have produced one of the most complex mixtures of environmental pollutants that raise causing concern for various environmental aspects owing to their retrograde effects on human health and air purity and quality where vehicle emissions control has become the most important topic of discussion due to its impact on our environment. The non-thermal plasma (NTP) technology will be considered to reduce gasoline engine emissions. It consists of an ionized gas, a gas in which sufficient energy is provided to free electrons from atoms or molecules and to allow the coexistence of species, ions, and electrons. The purpose of using non-thermal plasma is to selectively transfer the input electrical energy to the electrons, which would generate free radicals through collisions and promote desired chemical changes in the exhaust gas.

**Key Words**: Non-thermal plasma, NTP, Plasma, gasoline gases, Dielectric barrier

discharge, emissions.

Science Code: 20219

# ÖZET

#### Yüksek Lisans Tezi

# ATMOSFERİK BASINÇ PLAZMASI KULLANILARAK ÇEVREYE ZARARLI ATIK GAZLARININ FİLTRELENMESİ

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Araba motorları, insan sağlığı, hava saflığı ve kalitesi üzerindeki önemli etkileri nedeniyle çeşitli çevresel yönler için endişe uyandıran en karmaşık çevre kirletici etmenlerden birini oluşturmakta olup ve araç emisyon kontrolünün en önemli tartışma konusu haline gelmekte ve çevremiz üzerindeki etkileri tartışılmazdır. Bu çalışmada benzinli motor emisyonlarını azaltmak için termal olmayan plazma (NTP) teknolojisi dikkate alınacaktır. Plazma, atomlardan veya moleküllerden elektronları serbest bırakmak ve türlerin, iyonların, elektronların bir arada var olmasına izin vermek için yeterli enerjinin sağlandığı bir gaz olan iyonize bir gazdan oluşur. Termal olmayan plazma kullanmanın amacı, elektrik enerjisini, çarpışmalar yoluyla serbest radikaller oluşturacak ve egzoz gazında istenen kimyasal değişiklikleri teşvik edecek olan elektronlara seçici olarak aktarmaktır.

**Anahtar Kelimeler :** Termal olmayan plazma, NTP, Plazma, benzin gazları, Dielektrik bariyer deşarjı, emisyonlar.

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# SYMBOLS AND ABBREVIATIONS INDEX

# **SYMBOLS**

HC: hydrocarbon

CO: carbon monoxide

NO<sub>x</sub>: nitrogen oxides

O<sub>3</sub> : ozone

# **ABBREVIATIONS**

DBD : Dielectric barrier discharge

DC : Direct current

NTP : Non-thermal plasma

PM : Particulate matter

VOC : Volatile organic compounds

PPM : Parts per million

 $V_{pp}$ : Peak to peak voltage

# PART 1

#### INTRODUCTION

Although since the prehistory of mankind the transformation of nature has been a constant, it is known that the history of the severity of the impacts on the natural environment has been growing along with technological advances and discoveries. The Industrial Revolution with the emergence of modern economic modes of production marks a before and after in the footprint of environmental impacts on a planetary level. The Declaration of the United Nations Conference on the Human Environment, of 1972, held in Stockholm, proclaimed the defence and improvement of the environment for present and future generations as an urgent objective for humanity [1]. Air pollution is mainly related to intensive exploitation of natural facilities and the improvement of large industrial and urban concentrations, that can saturate the assimilating and regenerative capacity of the natural environment, giving rise to irreversible disturbances of the general ecological balance, whose Long-term consequences are not easily predictable.

The means of transport on which a person relies on in his daily life to travel contribute to significant pollution of the environment where the transportation is one of the most dangerous sources of air pollution in major cities, especially diesel cars because their exhaust contains toxic gases that are produced due to fuel combustion. It is considered the largest and most problematic, due to the components of the contaminants as well as because of the proximity of the resources of emissions to the contaminant. Hydrocarbons (HCs), nitrogen oxides (NOx), carbon oxides (CO), and particulate matter (PM) that can be inhaled (2.5 PM) that are pollutants emitted from the car engine which are harmful to the environment are major air pollutants [2]. They Contribute to adverse of deleterious environmental impacts such as the numerous health problems related to breathing, skin allergies and liver, damage to the nervous system and decreased lung function, also actively involved in numerous reactions, in

the troposphere and the stratosphere, contributing to the formation of photochemical smog and the greenhouse effect. They also play a role in acid sediment, since they conduce to the manufacture of radicals answerable for the conversion of sulfur oxides into sulfuric acid [3]. A similar situation occurs to nitrogen oxides and nitric acid, as well as the formation of peroxides that influence the acidic cloud formations and acid rain and the resulting acidification of aquatic systems, and degradation of general atmospheric visibility. This is the reason why emission standards have been imposed on car manufacturers; these increasingly strict standards require the use of exhaust gas after-treatment systems. In the case of gasoline vehicles, a single catalyst (three-way), very efficient, is used to remove CO, HC and NO<sub>x</sub>. Three-way catalysis appeared to meet increasingly severe discharge standards [4]. This technique, suitable for gasoline vehicles, allows the removal of NOx, CO and HC through a single catalyst, with an efficiency greater than 95%. The catalytic converter is a part of the exhaust system that transforms the harmful emissions generated by the engine into the non-hazardous compound, it is developed in 1974 by General Motors and made compulsory for car manufacturers in the 1990s, the catalytic converter is intended to reduce the toxicity of exhaust gases from vehicles with thermal engines. The role of the catalytic converter is to minimize the emissions of pollutants by transforming them into non-hazardous compounds [5]. As it's known, the majority of new gasoline vehicles now come standard with 3-way catalytic converters that cause a triple-action hence their name of three-way catalysts the action that performed is the transformation of carbon monoxide (CO) into carbon dioxide (CO2), a decrease of nitrogen oxides NOx to nitrogen (N2) and O2, and the HC (unburnt hydrocarbons) to carbon dioxide (CO2) and water (H2O) [6].

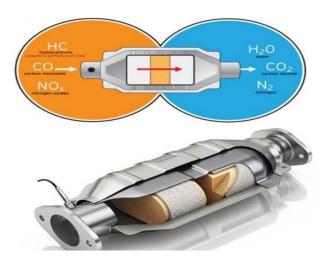


Figure 1.1. Three-way catalytic converters.

The catalytic converters consist of a stainless-steel chamber that contains a ceramic thermal insulator with a honeycomb structure. The exhaust gases pass through this honeycomb structure which increases the contact surface between the gases and the precious metals. A thin layer of precious metals lines this structure. Acting as a catalyst, it can cover an area of up to 4500 m2. Where the catalyst is a chemical element that accelerates a chemical reaction but is found intact at the end of this reaction. Three precious metals from the platinoid group are used: platinum, palladium and rhodium [7].

Catalytic converters cannot reduce emissions in the first few minutes during the warmup so the emissions cannot be catalyzed, as they need to reach a high temperature to operate Preheating of the catalytic converter is a possible solution to this problem [8].

The use of specialized devices for gasoline vehicles is an essential step to reduce this pollution that most capitals suffer from in the countries of the world. It can be cleaned through a catalytic process that converts into harmless ones, such as water and carbon dioxide as the main techniques used to solve air pollution. Plasma catalysis is a discipline of plasma processing that aims to produce highly materials with moderate conditions like semiconductors and nanostructures it combines with renewable electricity sources to produce many speciality chemicals such as ammonia by the decentralized method. Plasma catalysis is characterized by ultrafast reactions with a

minimal waste level production in comparison to other conventional wet chemistry techniques [9]. Plasma catalysis is increasing expanding interest for different gas conversion applications, such as converting CO2 into fuels and value-added chemicals, activating methane to hydrogen, higher hydrocarbons or oxygen, and synthesizing NH3 [10]. On the other side, plasma catalysis was exploited in air pollution control, such as the remediation of the volatile organic compound and removing particulate matter and NOx. The treatment of air by innovative processes that consume little energy remains a major challenge for improving our living conditions, especially in residential areas. A promising solution is to use the oxidizing power of a non-thermal plasma air at atmospheric pressure, associated with a catalyst. we must find the solution that implies a combination and compatibility of objectives related to economic development, health care and the quality of life of people, with the protection of our environment.

The plasma technology proposed here can solve the deficiencies mentioned above, since it is a continuous process, which does not require handling large amounts of dangerous chemical substances, in addition to requiring low energies for its supply. For example, to power the device that is used to treat car exhaust gases (less than 100W), with the energy provided from the battery it would be enough to start the removal process. This work presents a technological alternative for the treatment and control of atmospheric pollutants from mobile sources, in order to improve the environmental performance of means of transport; thus, achieving the reduction of harmful emissions into the atmosphere, that allows reducing emissions and therefore being able to reduce the environmental and health impact of polluting gases emitted by automobiles.

So, the non-thermal plasma (NTP) technology will be considered to reduce gasoline engine emissions. Plasma is the fourth state of matter. It consists of an ionized gas, a gas in which sufficient energy is provided to free electrons from atoms or molecules and to allow the coexistence of species, ions, and electrons. Plasma is divided into thermal or hot plasma and non-thermal or cold plasma. In the thermal category, the kinetic energy (temperature) of the charged particles and the kinetic energy (temperature) of the background gas is similar. In a non-thermal plasma, electrons have

higher kinetic energy than the energy corresponding to the random motion of gas molecules in the background. The purpose of using non-thermal plasma is to selectively transfer the input electrical energy to the electrons, which would generate free radicals through collisions and promote desired chemical changes in the exhaust gas.

# 1.1. PROBLEM STATEMENT

Emission of pollutants in gasoline engine exhaust gases: Internal combustion is one of the main sources of environmental pollution, which is why for several years the researchers have worked extensively to develop technologies to control these emissions. In general, nitrogen oxides (NOx) are emitted mainly by resources carrying and other industrial sources and contribute significantly to a diversity of environmental problems the level of ozone in the earth, these oxides in combination with hydrocarbons produce photochemical smog under the influence of light solar, the formation of acid rain and the resulting acidification of aquatic systems, and degradation of general atmospheric visibility. In the presence of air, NO is oxidized to NO2, with rapid conversion at high concentrations, and rapidly in presence of sunlight and hydrocarbons from unburned gasoline. It is toxic to the respiratory system causing lung infections and respiratory allergies, as it can spread through the alveolar cells and blood vessels of the lungs and damage their structure through exposure to oxidation. In this process, nitrogen oxides play an influential role in the photochemistry that occurs both in the stratosphere and in the troposphere (7). Acid rain usually forms in clouds, a place where nitrogen oxides react with water, oxygen, and other oxidizing substances. These compounds are converted to HNO 3, which then acidifies rain, snow or fog due to its high-water solubility. Nitrogen oxides also contribute to photochemical pollution because they promote ozone formation. We must find a way to eliminate or reduce the amount of NO x that is issued by the engine.

# 1.2. OBJECTIVES OF THIS WORK

The emission of pollutants contained in the exhaust gases of internal combustion engines constitute one of the main sources of environmental pollution. Where most of the polluting emissions come from vehicles that, originally, do not have anti-pollution control systems, which is aggravated by the scarce culture of maintenance that we have.

Among the polluting emissions produced by internal combustion engines, carbon monoxide (CO) in gasoline engines and solid particles in the form of ash and soot in diesel engines, resulting from excessively rich mixtures, stand out, by quantity and toxicity. and/or with excess fuel and air deficit. Other pollutants emitted in engine combustion are nitrogen oxides (NOx), resulting from high combustion temperatures, and unburned hydrocarbons (HC), resulting from incomplete combustion. Although the number of harmful emissions emitted by a single car may be negligible, the concentration of cars in large cities implies a significant risk; increasing levels of air pollution affect human health.

For this reason, intense work has been going on for several years to develop technologies to control these emissions. Very efficient catalysts have been developed in gasoline engines for the removal of carbon monoxide, hydrocarbons, and nitrogen oxides. Various technologies for treating nitrogen oxides and particulate matter for gasoline exhaust have been developed so far. The selective catalyst reduction (SCR) method was considered to reduce nitrogen oxides for car engines. In this method, ammonia is used as a catalyst. However, there are some disadvantages in the use of selective catalyst reduction catalysts, such as the possibility of ammonia leakage, catalyst poisoning, the need to discharge the catalyst under high-temperature conditions or the impact of sulfur, and the need to install urea remedy facilities. This work aims to focus on the enhancement of (NOx), ratio and CO in the exhaust gas. It works with the Al2O3 catalysts.

The application of plasma to treat exhaust gas emissions from automobiles is an interdisciplinary topic that has been fond of in mechanical, electrical, environmental,

chemistry and physics engineering. The primary objective of this study is to use a new and encouraging technology called cold plasma and use a catalyst to enhance the removal of harmful gases from gasoline exhaust, to enable the decrease of related ecological and health risks.

# 1.3. ORGANIZATION OF THE THESIS PROPOSAL

The rest of this thesis is organized as the following: related work and background are discussed in chapter 2. In chapter 3, presents Experimental and Discussion. Finally, the thesis conclusion and future works are presented in chapter 4.

# PART 2

#### LITERATURE REVIEW

This part discussed the most related work found in the literature for the problem which has been extensively studied in the literature. Extensive researches over the year have been done to obtain a low-fuel combustion engine, to increase efficiency and lower carbon emissions where Carbon monoxide (CO) and nitric oxides (NOx) are the most significant engine exhaust gases. Carbon monoxide and nitrogen oxides play an important role in the formation of ozone and smog in the lower atmosphere. Nitrogen oxides can cause acid rain. where the researchers paid great attention to this part by applying many experiments and systems to get the largest percentage of getting rid of these gases and to obtain the optimal percentages to get rid of these emissions and reduce the damage caused by these gases to the environment, the authors in [31] using a computational fluid dynamic model that based on a hybrid model combining plasma and a catalyst of DOC (diesel oxidation catalyst) with Pt/CeO2-Al2O3 and SCR (selective catalytic reaction) using V2O5/TiO2 where the plasma was used in the nonthermal exhaust to decrease pollutants when the catalyst was not hot enough. The system was consisting of a coaxial wire cylinder reactor. Reduction of NOx, NO2 and NO and radical based on the concentration of electric field intensity was achieved. The distribution of the transient temperature and CO in the catalyst channel, the backpressure of the catalyst, and the dispersion of NO throughout the catalytic converter concentration were investigated to determine the steady-state reduction efficiency of NO, CO, CH, and C3H6 to entry velocities and temperatures. At speed of 3 m/s, a temperature of 600 K, the highest electric field before the spark plug at 17 kV/cm, and 80 s cold start time of the engine, the reduction efficiencies of NO and C3H6 obtained about 9% and 99%, respectively in the steady-state, the reduction of CO, NO, and C3H6 in the catalyst is about 98%, 29%, 95%, respectively.

The authors in [32] studied non-thermal plasma mixed with activated Ag/Al2O3 catalyst using atmospheric pressure for NOx removal using hydrocarbon selective catalytic reaction at the result a strong increase in activity when compared with traditional thermal activation is observed with high conversions of both nitrogen oxides and hydrocarbons attained at 250°C. The silver catalyst is usually inactive. More important, In the lack of an external heat source, it was obtained significant activity at 25 °C. The low-temperature activity provides the basis for the application of non-thermal plasma to activate emission control catalysts during cold start terms which ruins an important problem for portable and fixed applications.

In [33], a plasma catalytic coupling process was used as an attempt to improve the conversion efficiency of nitrogen oxides over a wide temperature range (150-500 °C to 150-500 °C). Since the catalytic reduction of nitrogen oxides is effective at temperatures with high catalyst activity, the reduction of nitrogen oxides was carried out in the high-temperature region without the use of plasma. On the other hand, in the lower temperature region, plasma was formed in the catalyst layer to compensate for the reduced catalytic activity, thus increasing the NOx conversion efficiency, they aimed to further increase the NOx conversion using Ag/α. The effects of Al2O3 catalyst and a dielectric barrier discharge plasma, catalyst types, reaction temperature, reducing agent concentration (n-heptane) and energy density on NOx conversion efficiency were investigated. The results showed that the use of the plasma catalyst process at lower operating temperatures increased the removal of both NOx and naphthalene (simulating soot). Moreover, the soot mimic acts as a reducing agent to remove NOx, but with reduced NOx conversion. High NOx removal efficiency requires the addition of hydrocarbon fuel. The combined use of catalyst and plasma has solved the problem of poor removal of nitrogen oxides and soot at low operating temperatures or during temperature fluctuations in the 150-350 °C range. Specifically, highly efficient naphthalene removal was achieved with low-temperature adsorption on the catalyst followed by complete separation by the plasma catalyst at 350 °C. As a result of the comparative analysis of different catalysts, the catalytic NOx conversion efficiency in the high-temperature region was highest in the case of Ag - Zn /  $\gamma$  -Al2O3Ag - Zn / - Al2O3 catalyzed by more than 90%. In the low-temperature region, nitrogen oxides were hardly removed by selective hydrocarbon reduction, but when plasma was formed in the catalyst bed, the conversion of nitrogen oxides sharply increased to about 90%.

During the past period, many researchers have trusty their efforts to the removal of nitrogen oxides, and the most common method for achieving this has been a selective catalytic reduction. Where selective catalytic reduction such as Ag/Al2O3 is suitable for NOx removal due to low-cost Ag compared to other noble metals, that can be combined with catalytic particulate filters for simultaneous removal of NOx. It has been observed in many cases, one of which is automobile exhaust, that the temperature of the sources of NOx and soot emissions is lower than the temperature of activation of the catalyst. Therefore, the results showed either that the effectiveness of the catalyst is low at that temperature or that it is necessary to heat the system, which indicates a decrease in economic efficiency. Thus, the removal of nitrogen oxides and soot at low temperatures is a worthy research topic that continues to be of interest to enhance economic efficiency and facilitate practical application [34-36].

A series of studies was held to investigate the NOx efficiency of a constant diesel engine exhaust at no-load and 50% loaded terms, using an NTP catalyst or adsorbent process, The filtered exhaust before the treatment inclusive NO, NO2, CO, hydrocarbons, aldehydes and carbon dioxide. Using a two-stage plasma-activated alumina catalyst system, without adding any reduction, this process was shown an improvement in the NOx removal efficiency. The plasma reactor was operated at room temperature, while the catalyst reactor was operated at 300°C. The result scored approximately 57% of NOx removal using a two-stage system, in comparison with 20% and 22% using a separate catalyst or plasma treatment in order. The development in NOx removal efficiency was most evident when the plasma reactor was run at 150 °C. The NOx removal productivity using only the plasma treatment was approximately 5% while it increment to around 50% using the two-stage process. Plasma is believed to efficiently convert NOx to NO, given the exhaust-free state and also convert hydrocarbons to aldehydes, which react above 250°C over activated alumina, forming N2 resulting in increased NOx removal productivity [37,40].

The post-plasma selective catalytic reduction was carried out to the exhaust with six cylinders with 4.9L Isuzu diesel engine dynamometer system in particular at low

temperatures. In this approach, oxygenated hydrocarbons have been produced with the aid of using reforming the diesel via an air plasma chamber. The plasma exciting air and incredibly active oxygenated hydrocarbons were brought to a side stream of the exhaust of the Isuzu diesel engine before the SCR system. The plasma air including O3, a stronger oxidizing agent in comparison to O2, turned into believed to convert the NO to NO2 and partly oxidize hydrocarbons which then growth the NOx conversion in the SCR reactor, The experiments were conducted under a steady-state that simulated situations that supplied an actual vehicle certification test although the cold start and temporary running terms were excluded. Bilayer catalysts such as Ba/Y-Cu zeolite/Y-zeolite and Ba/Y-zeoliteY-Ag/Al2O3 were tested as SCR catalysts with Ba/Y-Cu zeolite/Y-zeolite catalysts, which show the best performance (about 60% average conversion mode of oxides). nitrogen). This became attributed to the higher oxidation activity of Cu catalysts as compared to the Ag catalysts because of prevention by heavy HCs that exist in the exhaust at temperatures below 300 °C. [41]

A combined plasma catalytic process was used in an attempt to increase the conversion efficiency of nitrogen oxides (NOx to NOx) over a wide temperature range (150-500 °C). Since NOx catalytic reduction is effective at temperatures with high catalyst activity, NOx reduction was performed in the high-temperature region without forming a plasma. The effects of catalyst types, reaction temperature, reducing agent concentration and energy density on the conversion efficiency of NOx to NOx were investigated. In the low-temperature region, NOx was hardly removed by hydrocarbon selective reduction, but when plasma was formed in the catalyst layer, the conversion of NOx sharply increased to about 90%. NOx conversion can be kept high at temperatures of 150-500°C by adding plasma according to the temperature change of the exhaust gas. As presented in this section, cold plasma has been found to have promising potential to remove NOx from exhaust gases. Various studies have been conducted to improve existing techniques and develop new methods to improve the performance of NTP. DBD reactor is more popular in emission reduction applications due to its easy integration into systems, efficiency and low operating cost.

# PART 3

#### THEORETICAL BACKGROUND

The papers introduced in the previous chapter showed that the results of this researches are very useful for the understanding whole problem. This section provides an overview of vehicle exhaust pollutants, Plasma Technology background in general.

# 3.1. THE VEHICLE EXHAUST POLLUTANTS

Vehicle pollutants cause prompt and long-term effects on the environment, as Vehicle exhaust emits a wide range of gases and solids, which causes global warming, acid rain, damage to the environment and human health, the following is the most important pollutants emitted from exhaust [11].

- Carbon monoxide (CO): It is a toxic gas that is colourless and odourless, and it is a pollutant that is mainly produced by the combustion of carbon fuels with a lack of oxygen. This contaminant binds to haemoglobin in the blood with a strength of 200-300 times compared to normal oxygenation and leads to difficulties in transporting oxygen to tissues. In the case of light concentration, it leads to a feeling of sleepiness, headaches and lack of alertness. And in the case of high concentration, it leads to death as a result of suffocation. Exposure over many years to low levels increases the prevalence of heart attacks.
- Fine particles that can be inhaled (2.5 PM): Today, the group of pollutants that are most dangerous to human health is considered among the total pollutants emitted from cars. particles of very small diameter (less than 2.5 microns) that penetrate without difficulty due to their precise diameter into the depths of the respiratory system and cause damage to it.
- The particles consist primarily of soot and the remains of unburned fuel, as well as other materials originating from the fuel, such as minerals and sulfur.

- Nitrogen oxides (NOx): It also contributes to acid rain, and irritates the human mucous membranes. It is a pollutant that results mainly from the oxidation of atmospheric nitrogen at high temperatures. Nitrogen oxides lead to an increase in lung sensitivity to diverse diseases of the respiratory tract and lead to an increase in the effects of these diseases on the patient.
- A mixture of hydrocarbon gases (HC): Unburned or partially burnt fuel, which is released mainly upon fuel loading and as a result of incomplete combustion. The large group of substances include toxic and carcinogenic substances, as well as active substances in the mechanism of ozone formation in the lower layers of the atmosphere.
- Ozone (O3) and oxidants: These are substances that are not emitted directly
  from car engines, but rather are formed as a late response to pollutants such as
  nitrogen oxides and hydrocarbons due to the influence of sunlight. This group
  of substances is considered the most dangerous to human health due to its
  strong oxidative activity

# 3.2. THE ATMOSPHERIC

To better understand the problem of air pollution, its origins, effects and dynamics of operation, it is necessary first to study the environment in which it is installed: the atmosphere is the first layer of gas surrounding our planet, with a thickness of approximately 10.000 kilometers. All climatic and atmospheric phenomena that affect the planet occur in it, as they regulate the entry and exit of earth energy, and thus its temperature, and it is the main means of heat transfer. It consists of a mixture of gases including nitrogen (N2), oxygen (O2), and carbon dioxide (CO2), in addition to other gases in minute quantities, such as argon, helium, neon and ozone. In the lower layers of the atmosphere, there is water vapour and dust impurities [12].

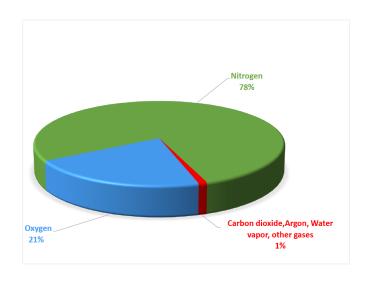


Figure 3.1. Atmosphere Gases.

The following table shows the composition by the volume of the atmosphere.

Table 3.1. Gases that make up the atmosphere.

Component	Chemical formula	Percentage
Nitrogen	N <sub>2</sub>	78.1%
Oxygen	O <sub>2</sub>	21.0%
Carbon Dioxide	CO <sub>2</sub>	0.0350%
Argon	Ar	0.9300%
Water vapor	H <sub>2</sub> o	0 - 4%
Neon	Ne	0.0018%
Helium	Не	0.0005%
Krypton	Kr	0.0001%
Hydrogen	H <sub>2</sub>	0.0001%
Ozone	O <sub>3</sub>	0.0001%
Xenon	Xe	0.0001%
Methane	CH <sub>4</sub>	0.0002%

The atmosphere, in turn, can be divided into different layers depending on the behaviour of the temperature to its height to the Earth's surface. The layers that constituting it are:

**Troposphere**: It is the closest to the Earth's surface, where clouds are formed and various atmospheric processes such as rains and fronts develop. Air temperature decreases with height. Most of the water vapour and CO<sub>2</sub> accumulate in this layer.

**Stratosphere**: In this layer, the temperature begins to increase with height, the phenomenon that is attributed to the presence of ozone  $(O_3)$ , since it is the gas that absorbs ultraviolet rays. Both of the formation and destruction of ozone are done by photochemical reactions.

**Mesosphere**: It is a layer in which the temperature decreases again with height due to the decrease in the ozone concentration.

**Thermosphere or Ionosphere**: In this layer, the temperature increases again with height. The presence of electrified particles gives rise to the presence of ionized layers that have the property of reflecting radio waves.

**Exosphere**: It constitutes the transition zone between our atmosphere and outer space, it contains most of the atmospheric ozone and absorbs much of the ultraviolet radiation.

#### 3.3. THE ATMOSPHERIC POLLUTION

Air pollution is not a new phenomenon, since the gases coming from the fire in the kitchen or the heater, and emissions that come from domestic waste, sewage and garbage, are a characteristic footprint of human activities. However, these pollution levels increased considerably after the industrial revolution.

As we have seen, the concern about air pollution goes back for many years. It is directly related to our modern lifestyles; how cities are built and planned, the inefficiency in the production of the products we consume and the services we require for our comfort, how we transport ourselves from a place to another and from the energy sources we use to heat and light our homes and jobs.

The increasing demand for energy has led to the indiscriminate burning of fossil fuels; as a consequence, gas emissions into the atmosphere have increased, putting human health and ecosystems at risk.

# 3.4. ORIGIN OF POLLUTANTS

Pollutants can be originated by natural processes and also by human activities, depending on the nature of the emitting source, pollutants can be classified to biogenic and anthropogenic. Biogenic sources correspond to the pollution events produced by natural phenomena. These include erosions, forest fires, volcanic eruptions, decomposition of vegetation, and dust storms.

Anthropogenic sources correspond to activities or interventions carried out by people, the main cause of combustion of materials used in industries, vehicles or in the home. This classification has in turn a subdivision into three groups: fixed sources, mobile sources and fugitive sources, The fixed sources correspond to those located in a particular, defined and immovable physical place. It considers that the emissions generated by the burning of fuels resulting from industrial and residential activities. Mobile sources correspond to those sources that can move; these are associated with gas emissions in exhaust pipes, brake and tire wear from different types of motorized transport, such as cars, trucks, buses and motorcycles. Fugitive sources include emissions that are not channelled through pipelines, chimneys or other systems to the outside, such as those from vehicular traffic on unpaved streets, construction and demolitions, among others.

Air pollution in urban areas can significantly worsen the quality of air breathed in indoor spaces, such as homes, offices, and indoors in general, especially when they are close to a source of contamination. Pollutants in the atmosphere consist of a wide variety of gases, vapours and particles, the presence and quantity of which affects people, plants, animals and materials. Depending on the origin of the pollutants, they can be classified into two large groups - primary and secondary - to better study on their origin, distribution and treatment or prevention.

**Primary pollutants:** They are those that come directly from sources of emissions, such as home heaters, industrial chimneys and automotive exhaust pipes.

**Secondary pollutants**: They are those that arise in the air as a result of chemical reactions that may occur between two or more primary pollutants, or between primary pollutants and elements of the atmosphere.

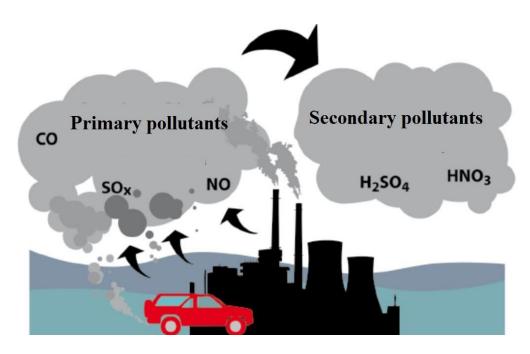


Figure 3.2. Primary and secondary pollution.

# 3.5. PLASMA TECHNOLOGY/ DEFINITION OF PLASMA

In 1879, the English physicist William Crookes discovered the fourth state of matter now called plasma. In 1929, Dr. Irwing Langmuir called the word plasma the ionized of a gas, which consists of electrically neutral molecules, fully or partially ionized atoms and electrons.

A plasma is an ionized gas obtained by the excitation of this gas via a supply of energy in thermal, radiative or electrical form. It is considered the fourth state of matter after solid states, liquids and gases [13]. This medium generally exhibits great reactivity. Indeed, the generated electrons collide with atoms and gas molecules and activate them. An ionization then occurs. Plasma contains many atoms, radicals, electrons,

excited molecules, ions, and it generates ultraviolet radiation as well as a transient electric field.

# 3.6. PLASMA TYPES

Various approaches can be used to determine or classify plasmas, one of them, considered the most important, is thermodynamics. There are two main types of plasma:

- Local thermodynamic equilibrium (LTE). They occur when the temperature of
  each of the species that make it up to coincide, except the radiation
  temperature. This is why they are also known as "thermal plasmas" or hot
  plasma that can be generated in plasma torches, electric arcs and experimental
  reactors at high temperatures.
- Plasmas out of local thermodynamic equilibrium. In this type of plasma, the ions (heavy particles) are kept practically at room temperature, while the free electrons are those that acquire high energies and temperatures. This is why they are also known as "cold plasmas" that called non-thermal plasma. These types of plasmas are commonly generated in dielectric barrier discharges (DBD), both at atmospheric pressure and reduced pressure, glow discharges and corona discharges.

The thermal plasmas present all the elements (electrons, ions, molecules) that approximately have the same energy and therefore the same temperature. In other words, the temperature of the electrons and the gas temperature are substantially equal. They are usually made under high pressure, and can be used in incineration, metallurgy, steel industry, cement industry and even in petrochemicals for the transformation of oil residues into intermediate products valuable. The second type is the non-thermal plasmas, also called non-equilibrium plasma. It is generated at atmospheric pressure and at room temperature where the different particles (electrons, ions, atoms, molecules) have very different average energies. The average energy of electrons is greater than that of heavy particles (atoms, molecules, radicals), while the gas temperature remains close to ambient temperature [14]. The majority of the discharge energy in non-thermal plasmas is expended in energetic electrons production

instead of heating the ions and neutrons. Thus, Energy is consumed in the plasma by the effect of electron dissociation and background gas ionization to produce radicals which in turn decompose toxic molecules. So, non-thermal plasma can eliminate toxic molecules near room temperature without wasting much energy in heating gas in the background.

The existence of ozone and nitrogen oxides in the effluents leaving non-thermal plasma air treatment systems constitutes the greatest drawback of this technology [15], which will require a post-treatment to eliminate these toxic by-products and more particularly ozone, of which the output concentration can exceed 100 ppm (v) (i.e. 0.2 g / m 3). In practice, ozone decomposes very rapidly at room temperature on a solid catalyst which may be based on activated carbon, zeolite or manganese oxide (MnO<sub>2</sub>). The presence of ozone is the major drawback of systems using non-thermal plasma to treat air by complete oxidation of the volatile organic compounds responsible for the pollution or the odour. In certain cases, this presence of ozone can prove to be an advantage because there are catalysts capable of decomposing ozone while allowing the use of this powerful oxidant to improve the elimination of residual pollutants after the plasma treatment. Non-thermal plasma appears promising due to its low-temperature characteristic, which may be suitable for certain processes because of its thermodynamics.

# 3.7. GENERATION OF A PLASMA (PLASMA REACTORS)

Plasma is generated and maintained through the supply of electrical energy. Between the different sources of electrical energy, we can find current devices direct (DC) or alternating current (AC) working at the mains frequency (~ 50 Hz), low frequency (<50 kHz), radio frequency (RF) (~ 13.56 kHz) and microwave (~ 2.45 GHz). On the other hand, there is a great variety of plasma types depending on the pressure range (10-1 ... 10 6 Pa), the type of gas and the boundary terms of the electrodes and walls that confine the plasma. Among the best known, we find homogeneous discharges, arcs, sparks, corona discharges and dielectric barrier, radiofrequency or microwave barriers so to generate plasma in the laboratory. A variety of methods, techniques and systems exist such as through electrical corona discharges, radio frequency discharges,

microwave discharges dielectric barrier discharges and electron beams, with a very important basic principle: providing a level of energy sufficient to remove one or more electrons from atoms and molecules of a gas. This supplied energy can have sources of heat (thermal ionization), electrical (electrostatic discharge), or light (photoionization).

An electric discharge, by definition, is the flow of an electric current between two electrodes. For this to happen, it is necessary to have a potential difference between both electrodes, as well as a conductive medium. In the case of electrodes separated by a gaseous medium, if the supplied energy manages to ionize some atoms of the gas between them, it causes the mobility of charges and therefore the conduction of electric current from one electrode to another.

Plasma chambers can be disunited into different classes with the type of power source (DC, pulsed DC, AC, RF), in which the electric discharge was used for this work. As in plasma production, there are different ways of causing electric discharges, applying a potential difference (voltage) or supplying a current flow (DC or AC). RF sources (radio frequency assigned for industrial use (13.56 MHz), or microwave sources (assigned frequency 2.45 GHz) can also be used.

- Electron beam: Electron beam irradiation is one of the non-thermal plasma formation methods. An electron beam (beam) is called a sharply focused stream of accelerated electrons. The flow of electrons emitted by the cathode is accelerated in a vacuum by the potential difference between the cathode and the anode, and then, is focused into a small spot (diameter from hundredths to several millimeters).
- Corona discharges: Corona treatment is obtained by creating a high-voltage and high-frequency electrical discharge, in a limited space (air gap) (1 or 2 mm), linear and uniform between an electrode subjected to high voltage (through a generator connected to a step-up transformer) and a counter electrode covered with insulating material connected to ground. The electric discharge causes ionization by impact. Some ions present in the air, accelerated by the applied electric field, hitting some neutral molecules and causing their

ionization. The new formed charged particles, in this way, ionize other molecules by impact through a snowball effect that causes the dielectric breakdown of the air.

Dielectric Barrier Discharge: The chamber in the present work is the Dielectric Barrier Discharge (DBD). It is used due to its efficiency in the degradation of toxic gases [16, 17 and 18]. Dielectric Barrier Discharge (DBD), or silent discharge, has been known for more than a century. The first reports were made by Siemens in 1857 [19], focusing on ozone generation which until a few years ago was the main application of DBD, which is why. It is also known as ozonation discharge where the discharge experiment device designed with many new features. Among them the electrode does not come into contact with the plasma, and it is located outside the discharge reactor. Hence the name of the DBD as "ozone discharge" for a long time. The DBD occur of two electrodes separated by one or more dielectric layers as illustrated in figure 3.3 [20]. Due to the presence of the dielectric material between both electrodes, this type of discharge requires alternating voltages for its operation, since it is an insulating material that does not allow direct current to pass through. Most of the materials used to form the dielectric barrier are glass, silica, polymers and ceramics, among others [21].

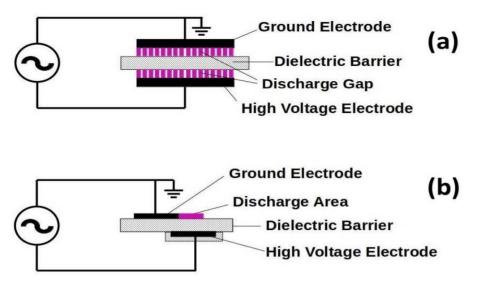


Figure 3.3. DBDs reactors [20].

The electric discharge formed in the closed space between the two electrodes is insulated by the dielectric material. Currently, DBDs at atmospheric pressure are commonly used in industrial applications such as ozone production, treatment of toxic gases, modification or sterilization of surfaces [22] [23]. This type of discharge has also been used to degrade compounds such as NO<sub>x</sub>, SO<sub>x</sub>, CO, CO<sub>2</sub>, mercury vapour and volatile organic compounds [24]. Cold plasma is generated when an electrical discharge is applied to the gas, which in this case is toxic gases. The discharge is formed between the electrodes, one of which is a metallic filament that is in the central part of the cylindrical reactor, and the other is found wrapping the outer wall (dielectric) of the reactor.

The formed discharges have the appearance of luminous filaments, which have a high density of electrons that collide with molecules and atoms causing their ionization. The generation of reactive species is considered the basis for the removal of pollutants by the ability of electrons to activate the worst gas molecules and rise them to new products without the need to heat the entire gas [25].

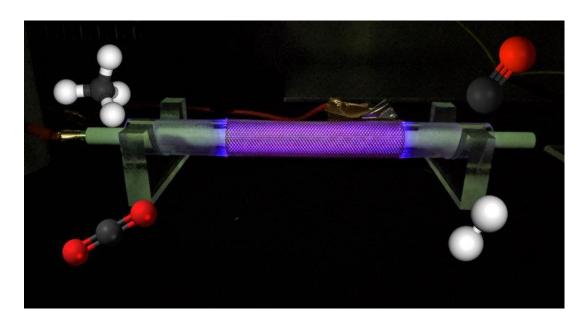


Figure 3.4. Plasma catalysis reactor [26].

The plasma catalysis reactor is shown in Figure 3.4.

# 3.8. GENERATION PLASMA APPLICATIONS

Plasma is generally known as the fourth state of matter. This grading finds its explanation by considering the first three states, in which passing from one to another only depends on the molecular energy that a system acquires. For a given compound, molecules in the gas state have more energy than in liquid and this, in turn, are more energetic than in solid. In this line, and without being a phase shift, yeeha gas receiving sufficient energy will pass to the plasma state, in which the gas has been fully or partially ionized. Stars, northern lights and lighting are a few examples about the best-known natural plasmas. Due to its high energy and reactivity, in the last decades, plasma applications have grown dizzyingly, both in basic research and at the industrial and technological level. Diverse applications, such as volatile organic compound (VOC) decomposition, NO<sub>x</sub> and SO<sub>x</sub> removal, ozone generation, surface processes, fuel reforming, hydrogen (H<sub>2</sub>) formation, and biomedical were use. The issue of plasma has become a very important and prominent topic in the research to find techniques for treating the environment.

Nuclear fusion: nuclear fusion is the process in which the nuclei of two atoms are fused to produce new, heavier nuclei, and thus, release very large energy. Among the conditions for plasma, the formation needs a very high temperature, which is about 10 million Kelvin. This high temperature is capable of transferring the substance to the plasma state. In electronic circuit industry, the low-temperature plasma is used. The electrical circuits that used in the manufacture of electronic devices contain tens of thousands, and in some cases, millions of transistors - semiconductors - very small, and this manufacturing process is done by the plasma that carves the circuits Electric on a silicon slide.

Preserving the cleanliness of the environment: it is one of the modern technologies in which developed countries work, as it converts toxic gases released by factories, such as sulfur monoxide, into non-toxic substances, using a device placed in the middle of the chimney which ionizes (converting elements into ions). These compounds are added to their basic elements by releasing a beam of high-energy electrons.

Some other applications: using plasma can sterilize medical instruments in hospitals and clinics, as it is the main light source for lighting in several types of lamps. It is also used in the treatment of liquefied gas and other waste. The Important industrial applications are the manufacture of hydrogen and ammonia; the products of great value today. It is used to increase the hydrophilicity of contact lenses, thus promoting eye health. Plasma is also used as a sterilizing tool; for construction spatial propellants or selectively modifying the properties of materials. For all, this and many other applications are not specified in the text for brevity. Plasma is currently fundamental and a very promising tool in a wide range of scientific and technological areas.

# 3.9. PLASMA CATALYSIS

Plasma catalysis is the combination of a catalyst (proper catalytic material) with a plasma to generate desirable products at the desired level and desirable efficiencies that cannot otherwise be reached by conventional catalytic methods [27]. The composition of non-thermal plasma and catalysis can be defined as an efficient and promising solution for converting renewable CO and H<sub>2</sub> into high-value chemicals at low temperatures and atmospheric pressures. Plasma stimulating processes can produce a synergistic effect. In the last decades, to overcome the weaknesses, plasma catalytic hybrid technology has received great attention as a promising technique for removing VOCs. VOCs encompass a large family of compounds. Some of them are of origin naturals, such as isoprene, pinene and limonene. Others, such as benzene and nitrobenzene, are of artificial origin. here are other examples that have been found in solvents such toluene, xylene, acetone, perchloroethylene as and tetrachlorethylene). The solvent is used most in the dry-cleaning industry. The integration of NTP and catalysts offers various advantages in conditions of energy efficiency, product selectivity, and carbon balance [28]. With many available research papers tackling the problem of removing VOCs by employing plasma catalytic hybrid technology, we reviewed the research according to the target pollutant. Zhu et al. (2018) employed the plasma-catalysis technology by using Ag/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, and scored about 93% conversion of toluene and energy efficiency of 0.07 g/kWh. They noticed that the using of an Ag / CeO<sub>2</sub> / Al<sub>2</sub>O<sub>3</sub> catalyst using plasma catalysis hybrid system enables high conversion of toluene into CO2 and H2O with a low concentration of ozone and nitrogen oxides [29]. S. Yao et al. (2020) proposed a plasma-catalysis technology (hybrid reactor) to improve the energy efficiency for toluene removal using plasma technologies. The result showed the increasing of the toluene conversion from 45.3% to 95.5%, as well as, energy efficiency can be improved from 53.5 g/kWh to 113.0 g/kWh by increasing the reaction temperature from 50 C to 250 C [30]. Song et al. (2019) conduct several experiments to separate the additives of diverse active species of plasma in toluene decomposition by a dielectric barrier discharge plasma with or without the CoMnOx/TiO<sub>2</sub> catalyst. The result shows that CoMnOx/TiO<sub>2</sub> catalyst, whether within or after the plasma zone, could efficiently decompose O<sub>3</sub> and, substantially, improve the utilization of the active kinds, thus increment the removal efficiency of toluene and the selectivity of COx [31].

## PART 4

### **METHODOLOGY**

Dielectric barrier discharge plasma is one of the most common methods for producing non-thermal plasma, which consists of a combination of high-energy electrons, free radicals, chemically active ions and exciting kinds, so it has the advantage of being susceptible to chemical reactions. This discharge has obtained an increasing interest in recent times for its applications in areas such as aerodynamics, surface treatments, ozone production and reduction of pollutants. The basic configuration consists of two electrodes, where at least one of them is covered by an insulating or dielectric material. For sufficient large voltage differences, electrical breakdown of the gaseous medium between the electrodes will occur, generating a current flow between the electrodes and the dielectric material. However, the charge cannot pass from one electrode to another, since the dielectric medium acts as a barrier (the mentioned medium does not undergo the breakdown). Charges accumulate on the surface of the insulator and generate an electric field that opposes that applied externally, attenuating the discharge. Therefore, it is a pulsed phenomenon, which must be generated using a variable voltage source. Depending on conditions, such as pressure, type of gas and electrode positioning, the discharge may be composed of streamers or have the characteristics of a glow transient discharge type. The experiment was conducted in a simulated environment.

The DBD reactor was chosen as the most appropriate configuration due to its simplicity and efficiency in exhaust handling. Barrier Dielectric Plasma (DBD) was recorded for the first time in 1857 by Werner von Siemens. In a DBD, the plasma is generated by applying an electrical discharge to a gas contained between two electrodes, of which at least one is electrically isolated from the gas by a dielectric material. This type of plasma, from an industrial point of view, has some advantages, such as the possibility of operating at atmospheric temperature and pressure; thereby,

reducing enormous costs. Due to the dielectric barrier present, a power source is required that allows the use of high-frequency alternating voltages to generate discharges.

### 4.1. EXPERIMENTAL SETUP

## 4.1.1. Design and Construction of DBD Reactors

For this study, a packed-bed DBD reactor is used Al2O3 as the catalyst is used. A cylindrical-coaxial geometry was used with two stainless steel electrodes and two dielectrics; the electrodes are separated by a space where the ionization of the plasma gas will take place. However, in the joint treatment of gases and higher flows, the efficiency is compromised since it is necessary to supply greater energy, which sometime is not achieved because of the fragility of the reactor. Another drawback of this material is the impossibility of installing them at the exhaust outlet of a car, as proposed in this work. The strong vibrations and rough use of the anti-pollution system can cause its breakdown. Therefore, a reactor with resistant materials is required, as well as, reducing energy consumption as much as possible. The DBD was connected to the power supply using internal and external electrodes, and the pulsed power technology was used for manufacturing plasma.

For the design and construction of the reactor, the following considerations were taken into account, according to the recommendations of various authors:

In any DBD arrangement, the geometry of the electrode is dictated by the dielectric configuration. For gas conversion applications, the cylindrical configuration is often preferential as it is more suitable for the uniform process of gas passing through the chamber volume and simple to apply; particularly, in automobile exhaust which is cylindrical in shape.

A DBD reactor can be constructed with one or both electrodes coated by a nonconductor material, then, it is referred to have a single or double barrier configuration. However, for gas conversion applications where the formation of

intermediate reagents is possible, a double barrier is the preferential configuration, since it chemically isolates the electrodes from the gases to be treated and from the reaction system that avoids the degradation and/or the interaction of electrodes with reactions.

In some research works, the choice is usually given to high dielectric strength and low distributing loss of materials, typically quartz or glass although the use of alumina has a lower dielectric strength.

In order to reach a solution that is efficient in removing NOx and CO2 from the emitted gases of cars, the experimental setup was prepared as shown in Figure 4.1.

The methodology of adequate ionization of the air is developed to generate plasma discharge in the degradation of pollutants and adapt the system of vehicles., the Kraft used to flow the exhaust gases to DBD reactors.

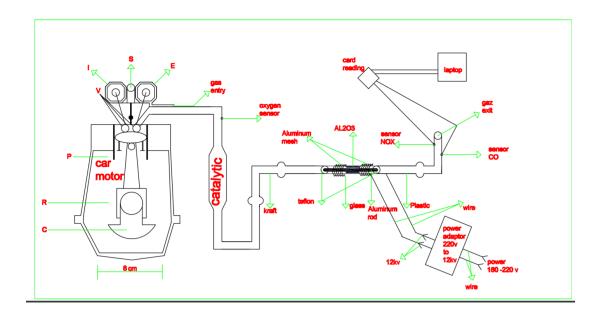


Figure 4.1. Experimental setup.

DBD reactor consists of an inner high-voltage electrode, an aluminium rod with an outer diameter of (34) mm. The dielectric barrier is made of a glass tube with an inner diameter of (43) mm. The DBD reactor used in the present work at atmospheric pressure conditions is shown in Figure 4.2.

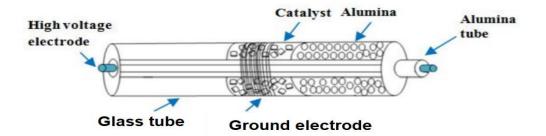


Figure 4.2. Dielectric barrier discharge plasma reactor.

The outer grounded electrode was a steel mesh-covered around the glass tube. The high voltage is transformed by an amplified signal generator, industrial test equipment power amplifier and transformer. Al2O3(alumina) was used as the catalyst, and the dielectric material was filled in between the glass tube and aluminium rod.

An alternating current (AC), high voltage in the range of 220 V to 12 kV, was applied to the discharge electrode to create plasma. An electrical transformer was used to raise the voltage, which is a piece of static electrical equipment converting electrical energy from the primary coils to magnetic energy in the heart of the magnetic transformer, and again to electrical energy on the side of the secondary transformer. The number of turns in the first coil must be less than the number of turns in the second coil. With the help of the adjustable power supply used in Figure 4.3, the gas sensors are operated. The Power Supply can provide voltage between 0-24V and current between 0-5A.



Figure 4.3. Adjustable power supply.

When exhaust gases pass through a high-voltage discharge (low-temperature plasma), they are bombarded with electrons, ions, atomic oxygen, ozone, hydroxyl groups,

excited molecules and atoms are formed. They are involved in plasma-chemical reactions with harmful impurities see Figure 4.4 the plasma when it is generated.

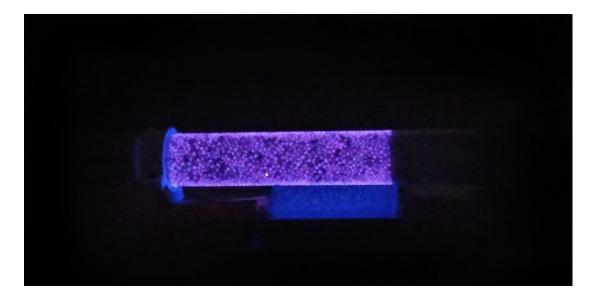


Figure 4.4. Dielectric barrier discharge plasma generation.

The catalyst material is usually made in the form of pellets, honeycomb monoliths, foam and coating of electrodes or reactor walls. Pellets of dielectric material - alumina the catalyst are in contact with the discharge, also, in contact with active, short-lived species such as excited atoms, molecules, radicals, photons and electrons. In this thesis, plasma-catalysis concerns on the single-stage process, where the catalysts are packed directly into the discharge distance of a coaxial DBD reactor. When the catalyst is placed directly in the plasma discharge, the chemical and physical features of the plasma and catalyst can be changed. The gas discharge promotes catalysis while the catalysts enhance the nonequilibrium of plasmas. A plasma-modulated catalyst would cause a significant modification of chemisorption and desorption, and thus in the activity and selectivity of the catalyst. This plasma action on a catalyst was used to prepare an effective catalyst for conventional catalysts. Al<sub>2</sub>O<sub>3</sub> is known as a good oxidation catalyst, due to the mobility of its vacancies and the ability to change its oxidation state easily.

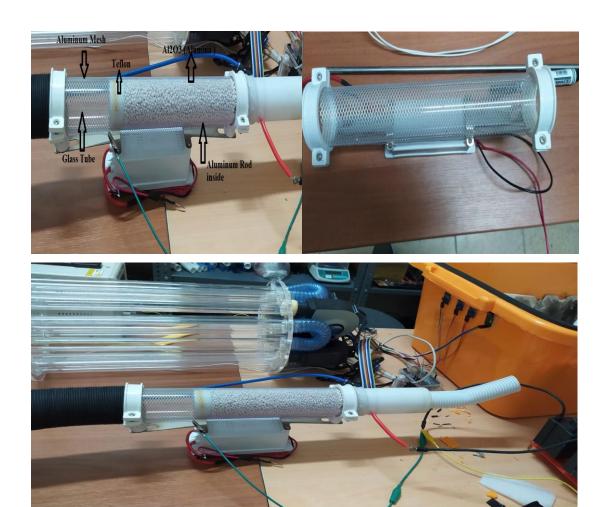


Figure 4.5. Dielectric barrier discharge plasma reactor (Implementation).

An aluminum mesh electrode was used on the outside to prevent the DBD reactor from overheating. Thanks to this, the observation of DBD was carried out.



Figure 4.6. Digital oscilloscope.

Figure 4.6 shows a dual-channel digital oscilloscope in the 40MHz band Owon HDS242 model used to measure the voltage and frequency values at the output of the power supply used to power the DBD reactor. The oscilloscope can collect 250 mega samples of data per second.



Figure 4.7. High voltage probe.

Figure 4.7 shows the 1000X attenuator probe used to measure the voltage and frequency values of the high voltage output power supply.



Figure 4.8. Data acquisition card.

Figure 4.8 shows the data acquisition card used to collect the data from the gas sensors and transfer them to the computer. Arduino Uno model card was used as the board. The interface of the card with the computer is provided by USB.

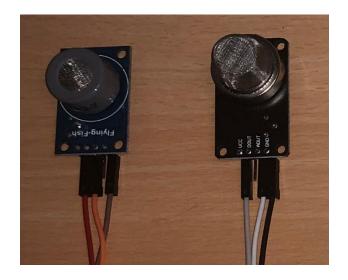


Figure 4.9. CO and  $NO_x$  gas sensors.

Gas sensors that measure MQ7 model CO and MQ135 model NOx gases in ppm are shown in Figure 4.9. CO sensor can measure between 0-10000 ppm and NOx sensor can measure between 0-1000 ppm.

The reactor temperature was measured using a Seek XR model IOS compatible thermal camera as in Figure 4.10. Portable thermal camera can measure between  $-40C^0$  to  $+330C^0$ . In addition, the camera has a resolution of 206x156 pixels.



Figure 4.10. Thermal camera.

We used a power supply to increase the voltage from 220 volts to 12 kilovolts as shown in Figure 4.11. It has power overcurrent and overheating protection. In addition, the voltage and frequency values of the power supply can be controlled.



Figure 4.11. High voltage power supply.



Figure 4.12. Power meter.

The power meter used to measure the power consumed by the high voltage power supply from the input network is shown in Figure 4.12.

### 4.2. EVALUATION RESULTS AND DISCUSSIONS

This section proceeds to describe, in details, the experimental conditions used in this thesis, as well as the presentation of the results obtained by applying the DBD before studying the effect of plasma on exhaust and the gaseous emissions that have been measured. The experiments, that have been done can be classified into two types: blank test (without [plasma catalysts), and tests with catalysts under plasma-. In order to analyze the efficiency of NO<sub>x</sub>, CO<sub>2</sub> removal from vehicle exhaust gases, experiments were conducted. The effect of NTP on CO<sub>2</sub>, NO<sub>2</sub> concentration is the decomposition of CO<sub>2</sub> molecules after applying plasma. This happened due to the electron impact reactions, which can reduce the CO<sub>2</sub> concentration. Moreover, different active oxygen kinds can be related to CO<sub>2</sub> concentration decrease.

We connected a kraft between the exhaust and the DBD, then sensors were placed after the DBD to measure the percentage of gases CO and NO<sub>x</sub> coming out before and after the operation of the DBD as in Figure 4.13.



Figure 4.13. The whole experience.

In Figure 4.14 the temperature of the DBD reactor in active and passive states was measured using a thermal camera. In Figure 4.14, the temperature of the reactor was measured as  $35C^0$  while the plasma was passive. While the plasma is active, the reactor temperature is at  $47C^0$ .

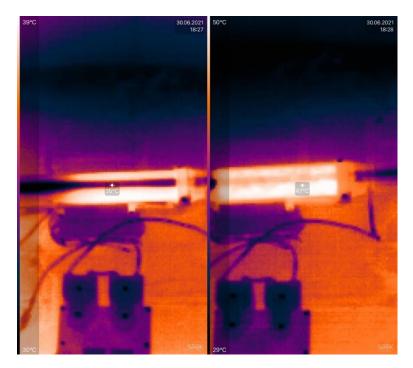


Figure 4.14. Thermal images of reactor temperature.

Figure 4.15 shows the measurement of carbon dioxide and nitrogen oxide concentrations using the Labview program at the moments when the plasma is active and passive.



Figure 4.15. Concentrations of carbon dioxide and nitrogen oxides.



Figure 4.16. Power measurement while plasma is active.

In Figure 4.16 shows how to measure power while the plasma is active. It is seen that the power consumption is approximately 107.3W on the power meter screen.

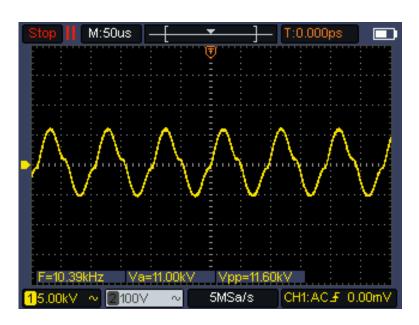


Figure 4.17. Oscilloscope screenshot in plasma active state.

Figure 4.17 shows the screenshot taken from the oscilloscope using a high voltage probe during plasma formation. The oscilloscope screenshot shows a sinusoidal signal with a frequency of approximately 10kHz and a value of 12kV Vpp.

Table 4.1. Power supply parameters used in the plasma catalyst process and values collected by sensors.

Parameters	DBD OFF (Control)	DBD	DBD	DBD	DBD	DBD
		ON	ON	ON	ON	ON
		(1)	(2)	(3)	(4)	(5)
CO (ppm)	4.55	3.4	3.3	3.4	3.2	3.2
NO <sub>x</sub> (ppm)	2	0.8	0.9	0.9	0.8	0.9
Voltage (kV)	0	12	12	12	12	12
Frequency	0	10	10	10	10	10
(kHz)						
Power (W)	0	107.3	107.3	107.3	107.3	107.3

When we look at the results in the table, we can say that there are significant decreases in CO and NOx values. Data were collected every 5 minutes. That is, the relevant ppm data was recorded in the table after saturation was completed.

It was not included in the study because its HC (hydrocarbon) values were low. For this reason, the focus was on CO and NOx gases, which are high in the exhaust gas. The use of the plasma catalyst system in conjunction with the vehicle catalytic converter system has contributed to a significant reduction in air pollution.

In future studies, we can say that power consumption will decrease by changing the electrode designs in the reactor. Because the design of the electrots will enable the DBD to be formed easily. Thanks to the change in the electrodes, the voltage and current values required for the formation of DBD can be further reduced.

Thus, it can be made a more portable and useful system. Higher reductions in gas emissions can be achieved by switching to different materials as catalyst material. For example, it is known that Pd/Al2O3 mixed catalyst materials have high effects on emission reductions.

### PART 5

### **SUMMARY**

Due to the increase in greenhouse gas concentration as a result of human production activities, the overall surface temperature of the earth has increased by 1°C since preindustrial time, bringing with it various changes in natural cycles, climate patterns and adverse effects. This could seriously endanger the life of all species on the planet. Experts predict a challenging future with CO2 emissions, still rising from humans, with events worse than what the planet is currently experiencing. The main pollutants emitted from gasoline engines are carbon monoxide and nitrogen oxides. DBD plasma reactors are of great importance for environmental and energy applications, such as CO2 and NOx conversion, but suffer from limited conversion and particular energy efficiency. The introduction of filler materials to improve reactor performance has been a common research topic. Reducing the reactor discharge gap to less than one millimeter can also improve the performance of the plasma. In this study, we combined both effects on the conversion and efficiency of CO decomposition and used a packaged-based DBD plasma reactor. The plasma catalytic reaction and the heat obtained from the plasma had a synergistic effect. NO2 adsorbed on alumina was efficiently separated by a simple packed-bed dielectric barrier discharge reactor with a special electrode, which can overcome the problems of regeneration and desorption of NOx, and deeply adsorbed NO2 residues without a solution, thereby enabling catalyst treatment at atmospheric pressure at low temperatures. As a result of our thesis, it has been possible to achieve significant reductions in harmful CO and NOx values released into the air by adding a plasma catalysis converter, in addition to the catalytic converter used in gasoline vehicles. Thanks to the portability of the system; it can be integrated into vehicles. Since the elements used in the reactor are passive, they can be used for a long time. This supports sustainability. In addition, the use of the system can be expanded because it is safe and easy to use.

When we examine the experimental data, we can say that the values of CO and NOx gases in ppm have decreased, and if we consider that this is valid for all cars, it will provide a great advantage for the environment. It is anticipated that this module we have developed will provide significant improvements by using it as a supplement with existing systems. The overall surface temperature of the earth has been raised by 1°C since the pre-industrial time due to greenhouse gas concentration increment as a consequence of the human productive activities, bringing with it several changes in natural cycles, the climate pattern and collateral effects that could place the life of all the species on the planet in severe danger. Experts predict a tough future, with events even worse than those the planet is going through now, caused by the CO2 human emissions, which are still increasing. The main pollutants emanating from gasoline engines are carbon monoxide and nitrogen oxides. DBD plasma reactors are of great importance for environmental and energy applications, such as CO2 conversion, NOx, but suffer from limited conversion and especially energy efficiency. The introduction of catalyst materials has been a common topic of research in order to increment reactor performance. Reducing the reactor discharge space to less than one millimeter can improve the performance of the plasma as well. In this work, we combined both effects and used the packet-based DBD plasma reactor on the conversion and efficiency of CO dissociation. Plasma catalytic reaction and heat reproduced from plasma made synergetic effect. NO2 adsorbed on activated carbon dissociated efficiently by a simple packed-bed DBD reactor with a special electrode that could overcome the problems of the regeneration and desorption of NO<sub>x</sub> and the problems of ruins of deeply adsorbed NO<sub>2</sub> without a solution and catalyst at atmospheric pressure and relatively low temperatures.

### REFERENCES

- 1. Gentimir, A., "Environmental Protection as Fundamental Right Guaranteed to The European Level", *Present Environment & Sustainable Development*, 14(2). (2020).
- 2. Agarwal, A. K., Singh, A. P., Gupta, T., Agarwal, R. A., Sharma, N., Pandey, S. K., and Ateeq, B., "Toxicity of exhaust particulates and gaseous emissions from gasohol (ethanol blended gasoline)-fuelled sparkignition engines", *Environmental Science: Processes & Impacts*, 22(7), 1540-1553. (2020).
- 3. Manisalidis, I., Stavropoulou, E., Stavropoulos, A., and Bezirtzoglou, E., "Environmental and health impacts of air pollution: a review", *Frontiers in Public Health*, 8, 14. (2020).
- 4. Selleri, T., Melas, A. D., Joshi, A., Manara, D., Perujo, A., and Suarez-Bertoa, R., "An Overview of Lean Exhaust deNOx Aftertreatment Technologies and NOx Emission Regulations in the European Union", *Catalysts*, *11*(3), 404. (2021).
- 5. Senthil Kumar, J., Ramesh Bapu, B. R., Sivasaravanan, S., Prabhu, M., Muthu Kumar, S., and Abubacker, M. A., "Experimental studies on emission reduction in a DI diesel engine by using a nano catalyst coated catalytic converter", *International Journal of Ambient Energy*, 1-7. (2019).
- 6. Naveenkumar, R., Kumar, S. R., PushyanthKumar, G., and Kumaran, S. S., "NOx, CO & HC control by adopting activated charcoal enriched filter in catalytic converter of diesel engine", *Materials Today: Proceedings*, 22, 2283-2290. (2020).
- 7. Kritsanaviparkporn, E., Baena-Moreno, F. M., and Reina, T. R., "Catalytic Converters for Vehicle Exhaust: Fundamental Aspects and Technology Overview for Newcomers to the Field", *Chemistry*, *3*(2), 630-646. (2021).
- 8. Tu, R., Xu, J., Wang, A., Zhai, Z., and Hatzopoulou, M., "Effects of ambient temperature and cold starts on excess NOx emissions in a gasoline direct injection vehicle", *Science of The Total Environment*, 760, 143402. (2021).
- 9. Bogaerts, A., Tu, X., Whitehead, J. C., Centi, G., Lefferts, L., Guaitella, O., ... and Carreon, M., "The 2020 plasma catalysis roadmap", *Journal of Physics D: Applied Physics*, 53(44), 443001. (2020).

- 10. Li, D., Rohani, V., Fabry, F., Ramaswamy, A. P., Sennour, M., and Fulcheri, L. "Direct conversion of CO2 and CH4 into liquid chemicals by plasma-catalysis", *Applied Catalysis B: Environmental*, 261, 118228. (2020).
- 11. Manisalidis, I., Stavropoulou, E., Stavropoulos, A., and Bezirtzoglou, E. "Environmental and health impacts of air pollution: a review", *Frontiers in Public Health*, 8, 14. (2020).
- 12. Bertrand, P., and Legendre, L. Earth, "Our Living Planet: The Earth System and Its Co-evolution With Organisms", Springer Nature. (2021).
- 13. Snoeckx, R.; Bogaerts, A., "Plasma technology—a novel solution for CO2 conversion?", *Chem. Soc.* Rev., 46, 5805–5863 (2017).
- 14. Liao, X.; Liu, D.; Xiang, Q.; Ahn, J.; Chen, S.; Ye, X.; Ding, T., "Inactivation mechanisms of non-thermal plasma on microbes: a review", *Food Control*, 75, 83–91 (2017).
- 15. V. R. Chirumamilla, W. F. L. M. Hoeben, F. J. C. M. Beckers T. Huiskamp, E. J. M. Van Heesch, and A. J. M. Pemen, "Experimental investigation on the effect of a microsecond pulse and a nanosecond pulse on NO removal using a pulsed DBD with catalytic materials", *Plasma Chem. Plasma Process.*, vol. 36, no. 2, pp. 487–510 (2016).
- 16. Zhang, H., Zhang, Q., Miao, C., & Huang, Q., "Degradation of 2, 4-dichlorophenol in aqueous solution by dielectric barrier discharge: effects of plasma-working gases, degradation pathways and toxicity assessment", *Chemosphere*, 204, 351-358 (2018).
- 17. Saleem, F., Khoja, A. H., Umer, J., Ahmad, F., Abbas, S. Z., Zhang, K., and Harvey, A., "Removal of benzene as a tar model compound from a gas mixture using non-thermal plasma dielectric barrier discharge reactor", *Journal of the Energy Institute*, *96*, 97-105 (2021).
- 18. Zhao, J., Zhang, A., Héroux, P., Sun, Z., and Liu, Y, "Remediation of diesel fuel polluted soil using dielectric barrier discharge plasma", *Chemical Engineering Journal*, 417, 128143 (2021).
- 19. Siemens, W. "Ueber die elektrostatische induction und die verzögerung des stroms in flaschendrähten", *Annalen der Physik*, 178, 66–122 (1857).
- 20. Piferi, C., Barni, R., Roman, H. E., & Riccardi, C., "Current Filaments in Asymmetric Surface Dielectric Barrier Discharge", *Applied Sciences*, 11(5), 2079 (2021).
- 21. Kim, J., Kim, S. J., Lee, Y. N., Kim, I. T., and Cho, G., "Discharge characteristics and plasma erosion of various dielectric materials in the dielectric barrier discharges", *Applied Sciences*, 8(8), 1294 (2018).

- 22. Ollegott, K., Wirth, P., Oberste-Beulmann, C., Awakowicz, P., and Muhler, M., "Fundamental Properties and Applications of Dielectric Barrier Discharges in Plasma-Catalytic Processes at Atmospheric Pressure", *Chemie Ingenieur Technik*, 92(10), 1542-1558 (2020).
- 23. Sharma, S. K., and Sharma, A., "Sterilization of microorganisms contaminated surfaces and its treatment with dielectric barrier discharge plasma", *Transactions of the Indian National Academy of Engineering*, 5(2), 321-326 (2020).
- 24. Damyar, N., Khavanin, A., Jafari, A. J., Mahabadi, H. A., Mirzaei, R., Ghomi, H., and Mousavi, S. M., "Removal of sulfur dioxide from air using a packed-bed DBD plasma reactor (PBR) and in-plasma catalysis (IPC) hybrid system", *Environmental Science and Pollution Research*, 1-16 (2021).
- 25. Bogaerts, A., and Centi, G., "Plasma technology for CO2 conversion: a personal perspective on prospects and gaps", *Frontiers in Energy Research*, 8, 111 (2020).
- 26. Internet: "Catalytic Conversion", https://www.plasmaleap.com/catalytic-conversion (2021).
- 27. Whitehead, J. C., "Plasma-catalysis: Is it just a question of scale?" *Frontiers of Chemical Science and Engineering*, 1-10. (2019).
- 28. Lu, W.J., Abbas, Y.W., Mustafa, M.F., Pan, C. and Wang, H.T., "A review on application of dielectric barrier discharge plasma technology on the abatement of volatile organic compounds", *Front. Environ. Sci. Eng.* 13: 30 (2019).
- 29. Zhu, B., Yan, Y., Li, M., Li, X. S., Liu, J. L., and Zhu, Y. M., "Low temperature removal of toluene over Ag/CeO2/Al2O3 nanocatalyst in an atmospheric plasma catalytic system", *Plasma Processes and Polymers*, 15(8), 1700215 (2018).
- 30. Yao, S., Chen, Z., Xie, H., Yuan, Y., Zhou, R., Xu, B., ... and Tang, X., "Highly efficient decomposition of toluene using a high-temperature plasma-catalysis reactor", *Chemosphere*, 247, 125863. (2020).
- 31. Song, H., Peng, Y., Liu, S., Bai, S., Hong, X., & Li, J., "The Roles of Various Plasma Active Species in Toluene Degradation by Non-thermal Plasma and Plasma Catalysis", *Plasma Chemistry and Plasma Processing*, 39(6), 1469-1482 (2019).
- 32. Oskooei, A. B., Koohsorkhi, J., and Mehrpooya, M., "Simulation of plasma-assisted catalytic reduction of NOx, CO, and HC from diesel engine exhaust with COMSOL", *Chemical Engineering Science*, 197, 135-149 (2019).

- 33. Stere, C. E., Adress, W., Burch, R., Chansai, S., Goguet, A., Graham, W. G., ... and Hardacre, C., "Ambient Temperature Hydrocarbon Selective Catalytic Reduction of NOx Using Atmospheric Pressure Nonthermal Plasma Activation of a Ag/Al2O3 Catalyst", *Acs Catalysis*, *4*(2), 666-673 (2014).
- 34. Nguyen, V. T., Nguyen, D. B., Heo, I., and Mok, Y. S., "Plasma-assisted selective catalytic reduction for low-temperature removal of NOx and soot simulant", *Catalysts*, *9*(10), 853 (2019).
- 35. Andreoli, S., Deorsola, F. A., Galletti, C., and Pirone, R., "Nanostructured MnOx catalysts for low-temperature NOx SCR", *Chemical Engineering Journal*, 278, 174-182 (2015).
- 36. France, L. J., Yang, Q., Li, W., Chen, Z., Guang, J., Guo, D., ... and Li, X., "Ceria modified FeMnOx—Enhanced performance and sulphur resistance for low-temperature SCR of NOx", *Applied Catalysis B: Environmental*, 206, 203-215 (2017).
- 37. Sitshebo, S., Tsolakis, A., Theinnoi, K., Rodríguez-Fernández, J., and Leung, P., "Improving the low temperature NOx reduction activity over a Ag-Al2O3 catalyst", *Chemical Engineering Journal*, *158*(3), 402-410 (2010).
- 38. Rajanikanth, B. S., Srinivasan, A. D., and Ravi, V., "Discharge plasma treatment for NO/sub x/reduction from diesel engine exhaust: a laboratory investigation", *IEEE Transactions on Dielectrics and Electrical Insulation*, *12*(1), 72-80 (2005).
- 39. Rajanikanth, BS, and Srinivasan, A. D., "Pulsed plasma promoted adsorption/catalysis for NOx removal from stationary diesel engine exhaust", *IEEE Transactions on Dielectrics and Electrical Insulation*, 14 (2), 302-311. (2007).
- 40. Rajanikanth, B. S., Srinivasan, A. D., and Ravi, V., "Discharge plasma treatment for NO/sub x/reduction from diesel engine exhaust: a laboratory investigation", *IEEE Transactions on Dielectrics and Electrical Insulation*, 12(1), 72-80 (2005).
- 41. Rajanikanth, B. S., Subhankar, D., and Srinivasan, A. D., "Unfiltered diesel engine exhaust treatment by discharge plasma: Effect of soot oxidation", *Plasma Science and Technology*, 6(5), 2475 (2004).
- 42. Cho, B. K., Lee, J. H., Crellin, C. C., Olson, K. L., Hilden, D. L., Kim, M. K., ... and Nam, I.S., "Selective catalytic reduction of NOx by diesel fuel: Plasma-assisted HC/SCR system", *Catalysis Today*, *191* (1), 20-24 (2012).

# **RESUME**

Abdallah Dwaikat was born in Irbid in 1992; He completed his primary and secondary education in the same city. Graduated from high school Shafiq Irshaidat. He started his education at Tafila Technical University, Faculty of Science, Department of Physics in 2010 and graduated in 2015. He started working as a school teacher in 2015 in Al Saad Ben Abe Wakaas high school for Boys. After working for a while at Al Saad Ben Abe Wakaas high school for Boys High School in 2015, she worked as a science teacher in UNRWA. He has completed his master's program, which he started at the Department of Physics in 2019, at Karabuk University, Institute of Science, Department of Physics. He started working at the Ministry of Education as a Physics and science course teacher in 2021 and is still working in the same place.