



**PRODUCTION OF CATALYSTS FOR THE VALORIZATION OF PLASTIC
WASTE, AND FOR THE WET PEROXIDE OXIDATION OF PARACETAMOL**

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Abstract

The efficient treatment of waste plastics and pharmaceutical pollutants is of conspicuous environmental, social and economic benefits. Therefore, here it is approached the application of catalysts that can be efficient in mitigating both environmental problems. In this work, four different catalysts were prepared. Three of them were synthesized by co-precipitation of Ni, Al and Fe nitrates with different mass ratios (5%Ni:95%Al, 20%Ni:80%Al and 10%Ni10%Fe80%Al). The fourth catalyst was prepared by wet impregnation of nickel on alumina. Then fresh catalysts were characterized by Fourier Transformed Infrared Spectroscopy and X-ray diffraction to observe crystalline phases. Carbon structures were prepared from low-density polyethylene, used as representative compound of plastic solid waste by Chemical Vapor Deposition over 20% Ni/Al catalyst in a tubular furnace. Scanning Electron Microscopy analyses were performed, identifying the carbon nanostructures with size variation (1 μm to 4 μm). For paracetamol (PCM) removal Catalytic Wet Peroxide Oxidation was assessed with 20%Ni:80%Al, 10%Fe:10%Ni:80% and commercial Al_2O_3 catalysts. The conversion of paracetamol, hydrogen peroxide and Total Organic Carbon (TOC) were monitored by High-Performance Liquid Chromatography, UV-Vis spectrophotometer and TOC analyzer, respectively. The iron-containing catalyst showed the highest catalytic activity in the CWPO of PCM satisfactory conversions (complete removal of PCM after 4 h of reaction time under the following operating conditions: $C_{cat} = 2.5 \text{ g/L}$, $C_{PCM,0} = 100 \text{ mg/L}$, $pH_0 = 3.5$, and $C_{H_2O_2} = 472.4 \text{ mg/L}$).

Keywords: Environmental applications; Plastics Solid Waste; Upcycling; Paracetamol; Carbon Nanotubes; Catalytic Wet Peroxide Oxidation.

Resumo

Um tratamento eficiente de resíduos plásticos e poluentes farmacêuticos traz benefícios ambientais, sociais e econômicos notáveis. Portanto, neste trabalho é proposta a aplicação de catalisadores que possam ser eficientes na mitigação de ambos os problemas ambientais. Neste trabalho preparou-se quatro tipos diferentes de catalisadores. Três deles foram sintetizados por co-precipitação dos nitratos de Ni, Al e Fe, como diferentes proporções de massa (5%Ni:95%Al, 20%Ni:80%Al and 10%Ni10%Fe80%Al). O quarto catalisador foi preparado por impregnação úmida de níquel em alumina. Em seguida, os catalisadores frescos foram caracterizados por Espectroscopia no Infravermelho Transformado por Fourier e difração de raios X, para observar as fases cristalinas. As estruturas de carbono foram preparadas a partir, do polietileno de baixa densidade, usado como composto representativo de resíduos sólidos de plástico, e pelo método de Deposição Química por Vapor realizada em um forno tubular e aplicação do catalisador de 20% Ni/Al. Realizou-se análises de microscopia eletrônica de varredura, para identificar as nanoestruturas de carbono com variação de tamanho (1 μm a 4 μm). Para a remoção do paracetamol (PCM), o método utilizado foi a Oxidação Úmida Catalítica com Peróxido de Hidrogênio, realizado com os catalisadores 20%Ni:80%Al, 10%Fe:10%Ni:80% e alumina comercial. A conversão do paracetamol, peróxido de hidrogênio e carbono orgânico total, foram monitoradas por cromatografia líquida de alta eficiência, espectrofotômetro UV-VIS, e TOC respectivamente. O catalisador contendo ferro mostrou a maior atividade catalítica no processo de CWPO, obtendo conversões satisfatórias de PCM (remoção completa do paracetamol após 4 horas, nas seguintes condições de operação: $C_{cat} = 2.5 \text{ g/L}$, $C_{PCM,0} = 100 \text{ mg/L}$, $pH_0 = 3.5$, and $C_{H_2O_2} = 472.4 \text{ mg/L}$).

Palavras-chave: Aplicações Ambientais; Resíduos Sólidos – Plástico; Reutilização; Paracetamol; Nano tubos de Carbono; Oxidação Catalítica do Peroxido Úmido .

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LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Processes
CNTs	Carbon Nanotubes
CVD	Chemical Vapor Deposition
CWPO	Catalytic Wet Peroxide Oxidation
DWCNT	Double-Walled CNTs
EBSD	Electron Backscatters Diffraction
EU	European Union
FTIR	Fourier Transformed Infrared Spectroscopy
GHG	Greenhouse Gas
HPLC	High-Performance Liquid Chromatography
IC	Inorganic Carbon
MWCNT	Multi-Walled CNTs
NSAID	Nonsteroidal Anti-Inflammatory Drug
PA	Polyamides
PCM	Paracetamol
PE-LD	Polyethylene - Low Density
PE-HD	Polyethylene - High Density
PET	Polyethylene Terephthalate
PMMA	Polymethyl Methacrylate
PP	Polypropylene
PS	Polystyrene
PS-E	Expanded Polystyrene
PSWs	Plastic Solid Wastes
PUR	Polyurethane
PVC	Polyvinyl-Chloride
SD	Sustainable Development
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SWCNTs	Single-Walled CNT
TC	Total Carbon
TEM	Transmission Electron Microscopy

TOC

Total Organic Carbon

UV

Ultraviolet

WWTP

Wastewater Treatment Plants

XRD

X-Ray Diffraction

1 INTRODUCTION

In a world facing global challenges such as a fast-growing population, food security, and climate change, the world needs to choose and rely on the most efficient solutions in order to guarantee a sustainable development (SD)^{1,2}. Over the past few years, SD has emerged as the latest development catchphrase. A wide range of non-governmental as well as governmental organizations has embraced it as the new paradigm of development³.

Thinking about sustainable development Europe has initiated the transition from a linear towards a circular and resource-efficient society and the unique characteristics of plastics allow them to make a great contribution toward this social transformation^{1,2}.

Plastics have become key materials in strategic sectors such as packaging, building & construction, transportation, renewable energy, medical devices or even sports, to mention but a few, owing to their versatility and their high resource efficiency. However, most plastics are mass-produced and low-priced; hence they are readily discarded after use. In fact, some of them (for packaging purposes) have only one use. Waste management is needed to minimize the plastic solid wastes (PSWs) and to reduce their environmental impacts. In this sense, waste reduction, recycling (mechanical, chemical, and thermal) as well as landfilling are considered as common solutions^{4,5}.

Nevertheless, the way plastics are currently produced, used and discarded fails to reach the benefits of a circular economy and harms the environment². Thus, there is an urgent requirement to tackle environmental problems from the consumption of plastics. The society needs to push for the most sustainable option of waste management, fostering recycling, using energy recovery as a complementary option and restricting the landfill deposit of any recoverable plastic waste^{6,7}.

Last decade, an increasing interest in the valorization of PSWs into nanostructure carbon-based materials, especially carbon nanotubes (CNTs), has been observed. For this purpose, it is necessary the development of a suitable versatile catalyst that allows the growth of CNTs from diverse plastics, e.g. polypropylene, polyethylene. CNTs are very stable materials having considerable chemical inertness due to the strong covalent bonds of the carbon atoms on the nanotube surface. Many potential applications have been proposed for carbon nanotubes, including catalysis, conductive and high-strength composites, energy

storage and energy conversion devices, sensors, field emission displays, and radiation sources, hydrogen storage media, and nanometer-sized semiconductor devices, probes, and interconnects^{8,9}.

Still thinking in a more sustainable world, pollution by various pharmaceuticals has become an environmental problem because of the increasing production and utilization of these products¹⁰. The risk of contamination and environmental pollution caused by drugs lies in the fact that they have high biological activity and ability to affect the metabolism of the living beings, even in small concentrations in the soil or in the water¹¹. In addition, the prolonged contact of drugs and pathogenic forms of bacteria in the environment significantly increases their resistance to drugs, reducing the efficiency of antibacterial agents used in the treating of infectious diseases¹².

Among pharmaceutical compounds that can cause pollution of water, one that deserves attention is paracetamol (acetaminophen, 4-acetylamino-phenol), that has recently been discovered as a potential pollutant of contaminated waters¹³⁻²⁰. Paracetamol is an analgesic and antipyretic drug that is largely accumulated in the aquatic environment due to its inefficient removal by conventional sewage treatment plants, also representing an important material for the industry of manufacture of azo dyes and photographic chemicals²¹. The concern about the environmental impact of its biodegradation products has been raised, because of its hepatotoxicity and the possibility of those products to be toxic or hazardous in trace amounts¹⁴.

Between the possible treatments that can be used to degrade the paracetamol from wastewaters are the advanced oxidation processes (AOPs). Advanced oxidation processes are defined as those which involve the generation of hydroxyl radicals in sufficient quantity to affect water purification²². In 1987, when the concept of AOP was presented by William H. et. al., it was mentioned that the AOPs were treatments carried out with mild conditions, however, the treatments have been explored in more severe temperature and pressure in order to ensure bigger conversions nowadays. These treatments are very interesting, due to its efficiency for the degradation of soluble organic contaminants in water²³.

Catalytic wet peroxide oxidation (CWPO) is an AOP recognized as a low-cost technology by the fact that it operates with mild conditions (from ambient temperature to 140 °C and typically at atmospheric pressure until 10 bar)²⁴. In the CWPO process, hydrogen

peroxide (H_2O_2) acts as an oxidant and a catalyst is used to decompose the H_2O_2 molecules into hydroxyl and hydroperoxyl radicals ($\text{HO}\cdot$ and $\text{HOO}\cdot$). Hydroxyl radicals are highly oxidizing species, being able to efficiently degrade the organic pollutants present in water. The use of H_2O_2 as a source of hydroxyl radicals is environmentally-friendly because it is well-known that its total decomposition products are oxygen and water. That makes the CWPO-based water treatment further attractive from a sustainable point of view^{18,19}.

This dissertation work deals with the preparation of catalyst materials to be used in the CWPO process for the removal of paracetamol from aqueous solution and in the thermochemical treatment of plastics for the production of carbon structures.

2 STATE OF THE ART

2.1 POLYMER AND PLASTICS

The sciences have been trying to simulate nature in designing smart synthetic materials. Materials that respond to stimuli induced by pH, ionic strength, light, electric or magnetic field, chemical, and biochemical boost, shape changes, tuning of adhesion and wettability, or electrical responses. In this way, some science research efforts are focused on the synthesis and characterization of polymers²⁶.

Plastics is the term commonly used to describe a wide range of synthetic or semi-synthetic materials that are used in a huge and growing range of applications. Plastics are not just one material, but instead are a whole family of hundreds of different materials, designed to meet the needs of every single application in the most efficient way possible^{1,2}.

Plastics are synthetic polymers that have existed for just over a century. However, the first set was synthesized by the residue of phenol-formaldehyde resin (called Bakelite at the time) made by Leo Baekeland in his garage in Yonkers, New York, in 1907²⁷.

The word *Polymer* originates from the Greek *poly* (many) and *meros* (parts). The polymers derive their exceptional properties from an unusual molecular architecture that is unique to polymeric materials, consisting of long-chain macromolecules and derived from reactions among smaller units called monomers. The conversion of the monomer to the polymer involves a rearrangement of electrons. The monomer employed in the preparation of a polymer is referred to as the structural unit^{28,29}.

Polymers can be classified in many different ways. The most obvious classification is based on the origin of the polymer, i.e., natural vs. synthetic. Other classifications are based on the polymer structure, polymerization mechanism, preparative techniques, or thermal behavior. There are a large number of synthetic, for example, fibers, elastomers, plastics, adhesives, etc. Each itself has subgroups. Therefore, the plastic Polymer can be subdivided into thermoplastic and thermosets^{28,29}.

2.1.1 Thermoplastic

The most commonly used thermoplastic was developed after the 1930s. Among the firsts to be synthesized, there is the so-called vinyl plastic which is derived from ethylene²⁷.

Thermoplastics have the ability to soften and flow when subjected to an increase in temperature and pressure, and can be shaped into definite shapes. This amendment is a reversible physical transformation. Thus, it is possible to subject them to new applications of temperature and pressure, which will cause the softening effect to occur again. Therefore, thermoplastics are fusible and soluble²⁹.

Among the most common and most commercially available thermoplastics, we have:

- Polyethylene Terephthalate (PET): Bottles for water, soft drinks, cleaners;
- Polypropylene (PP): Food packaging, hinged caps, microwave-proof container, automotive parts, bank notes;
- Polystyrene (PS): Eyeglasses frames, plastic cups, egg trays;
- Polyethylene - low density and high density (PE-LD/HD): Reusable bags, trays, and containers, agricultural film;
- Expanded polystyrene (PS-E): Packaging, building insulation;
- Polyvinyl-chloride (PVC): Window frames, profiles, floor and wall coverings, pipes, cable insulation, garden hoses, inflatable pools;
- Polymethyl methacrylate (PMMA);
- Polyamides (PA).

2.1.2 Thermosets

Plastics called thermosets are a family of plastics that undergo a chemical change when heated, creating a three-dimensional network. After they are heated and formed these plastics cannot be re-melted and reformed^{1,2}.

The most common and most commercially available thermoplastics are:

- Polyurethane (PUR): Building insulation, pillows, and mattresses, insulating foams for fridges;

- Epoxy resins: Adhesives, sports equipment, electrical and automotive components;
- Silicone: Prostheses, hand cream, handicraft, and kitchen products;
- Phenolic resins: Billiard balls, laboratory benches, coatings, and stickers.

2.1.3 Plastics Demand in Europe

Plastics become ideal for a wide range of industrial, agricultural, as well as the generation of products that support and facilitate the day to day, because of their versatility. Currently in Europe, the most used plastics are: PS 6.7%, followed by PET 7.4%, PUR 7.5%, PVC 10%, PE-HD 12.3%, PE-LD 17.5%, PP 19.3% and finally other types of plastics with 19.3%^{1,2}.

The Europe plastic converters demand 51.2 million tonnes of plastic waste for the year 2016. The largest producers are Germany, Italy, France, Spain, the United Kingdom, and Poland, only these six countries are already responsible for generating three million tonnes of plastics waste. Portugal is the 12th country that generates the most plastic waste in the European Union. It is possible to observe the contribution of each country for the years of 2016 and 2017 in the following Figure 1^{1,2}.

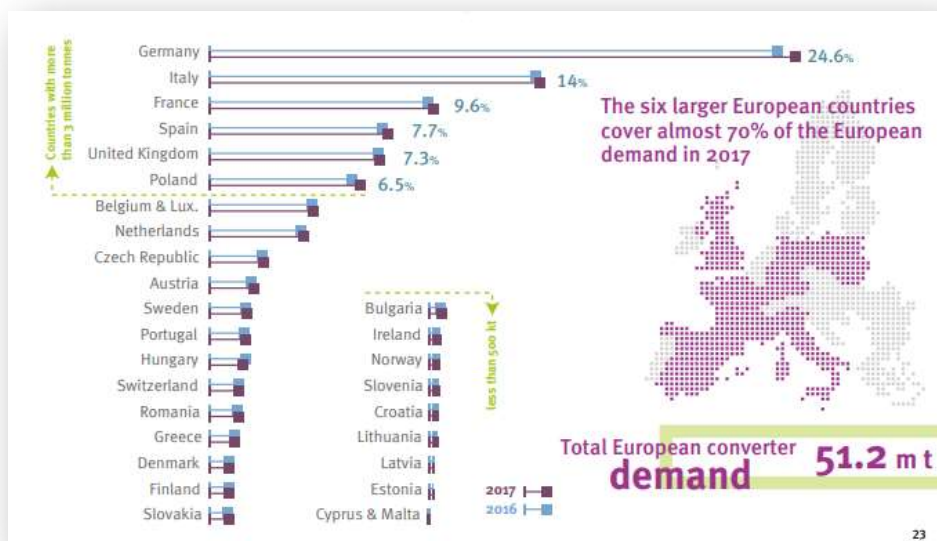


Figure 1: EU plastics demand by country¹.

It is estimated that in 2016 the global production of plastic reached the mark of 208 million tons where Europe is responsible for producing 19% of that amount, losing only for China with 29%. It is possible to observe the distribution of world production in the graphic, following in Figure 2^{1,2,30}.

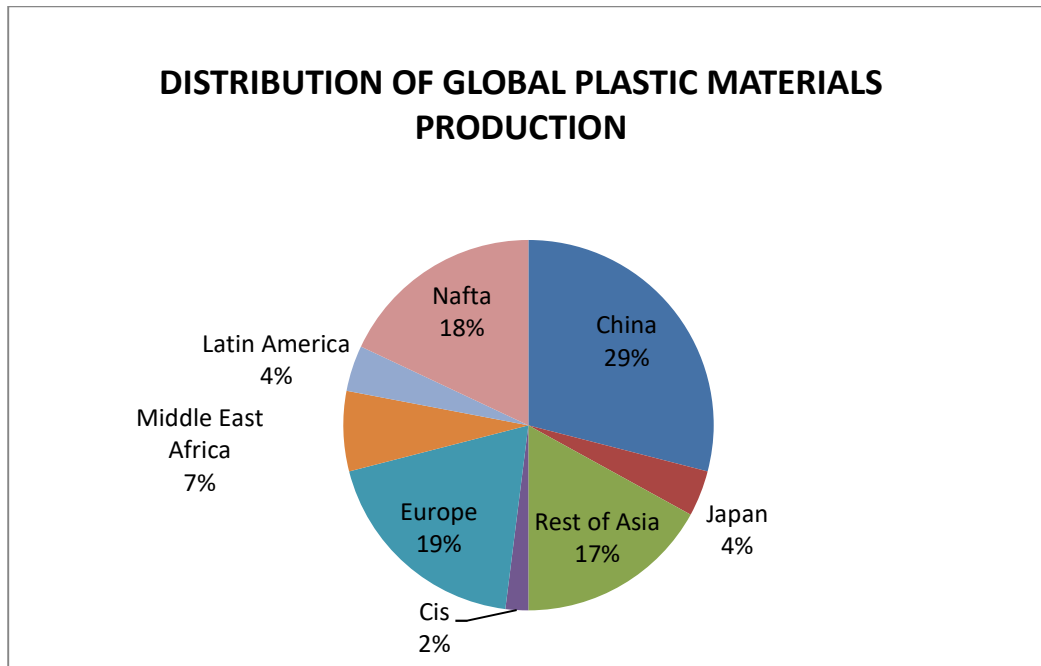


Figure 2: Global distribution in the production of plastic materials^{1,2}.

In this way, this large Market for plastics is destined to a wide range of applications. Where the production of packaging represents 39.9% of the amount, followed by civil construction with 19.7%, automotive industry 10%, electronic products 6.2%, clothing, leisure and sports products 4.2% and agriculture 3.3%. Other productions such as home appliances, mechanical appliances, furniture, and even medicine represent 16.7% of the manufacture of plastics products^{1,2}.

It is estimated that the plastics industry generates Jobs for more than 1,5 million people, with 60 thousand active companies, moving a balance of trade of 15 billion euros and contributing with 30 billion euros in European public finances in the year 2016^{1,2}.

Therefore, it is possible to observe that besides important for economy plastics are also necessary for the welfare and technological advances.

2.1.4 Options for the treatment of plastic solid waste

Just as performance during use is a key feature, the durability of Polymer materials due to their lifespan, maintenance and replacement also become essential. In this way, the deterioration of these materials depends on the duration and the extent of the interaction with the environment^{31,32}.

The low degradability of Polymer causes these materials to remain for years in the environment, increasing the problems of pollution of water and soil, causing concern about the destination of plastics. Increasingly, raw materials such as crude oil are scarce for plastics synthesis and recycling of plastic waste is becoming more important.

Therefore, plastic materials should not be used linearly, but in a circular way. A circular economy reduces the environmental impacts associated with the production, manufacture, and use of plastics. The longevity of this material will be greater as well as the more profitable energy efficiency, and will cause the CO₂ emission to be reduced. It is possible to identify the life cycle of plastic in the following Figure 3.



Figure 3: Full life cycle².

At the end of their life, plastics are still very valuable resources that can be transformed into new raw materials or into energy. Also, within this life cycle, the priority of the treatment of plastic waste is established. This can be analyzed in Figure 4.

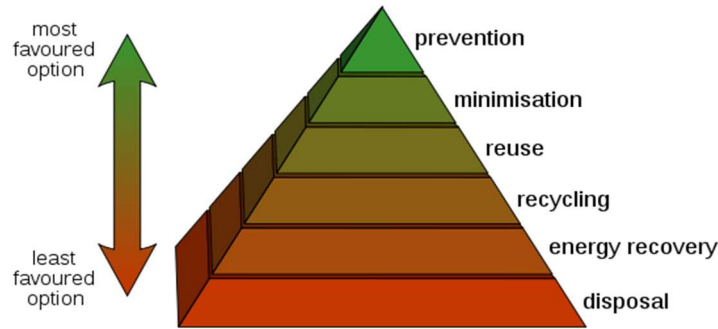


Figure 4: Waste hierarchy¹.

At the top of the pyramid of solid waste management, prevention and minimization, when it is not possible to follow these options, the waste used should primarily be recycled, contributing to the circular economy, or disposed of in a landfill, in the last case^{33,34}.

The reuse of plastic is preferable to recycling because it uses less energy and fewer resources. Thus, the reuse of plastics has several advantages, such as (i) conservation of fossil fuels, since the production of plastic uses 4-8% of global oil production; (ii) energy reduction and solid urban waste generation; (iii) reduction of carbon dioxide (CO₂), oxides of nitrogen (NO_x) and emissions of sulfur dioxide (SO₂)⁴.

2.1.4.1 Mechanical recycling

Due to their versatility, the polymers can be used in numerous applications to produce wide-ranging products. Thus, plastics have made a significant contribution to various fields of human activity such as agriculture, medical, transportation, piping, electrical and heat insulation, packaging, manufacturing of household and electronic goods, furniture and other items of daily or specific use³¹.

Mechanical recycling comprises the reintroduction of used thermoplastics in the extrusion cycle in order to remold these materials into new useful products. The mechanical recycling of the PSW (plastic solid waste) can only be carried out in single polymer plastic,

for example, PP, PS, PE, etc. The more contaminated the waste, the more difficult it will be to recycle it mechanically^{4,35}.

The efficiency of this process depends on the separation of the plastics from the rest of the municipal solid waste components. The first step is to collect this residue, which may be previously separated, or not²⁷.

After the plastic has been delivered to the recycling plant, the separation, washing and preparation steps of the waste plastics are essential to produce high quality, clear, clean and homogeneous final products¹².

Classification and identification should be carried out in a short time, so as not to cause damage to the recycler's finances, this can be done manually or automated. In the separation of plastic bottles, there are automated techniques, which separate the bottles by size and shape. Another form of classification is density classification. However, this method of classification is not always effective, because most plastics have very close densities^{4,36}.

After proper separation of the materials, the next step to be followed is grinding, the single polymer plastics which have been sorted according to their grade are ground together. Thereafter, the washing and drying process is performed. Agglutination is the step where the product is collected to be stored and sold after the addition of pigments and additives, or sent for further processing. In the extrusion, the plastic is extruded into filaments and then pelletized to produce a single polymer plastic^{4,36}. The processes of mechanical recycling can be observed in Figure 5.

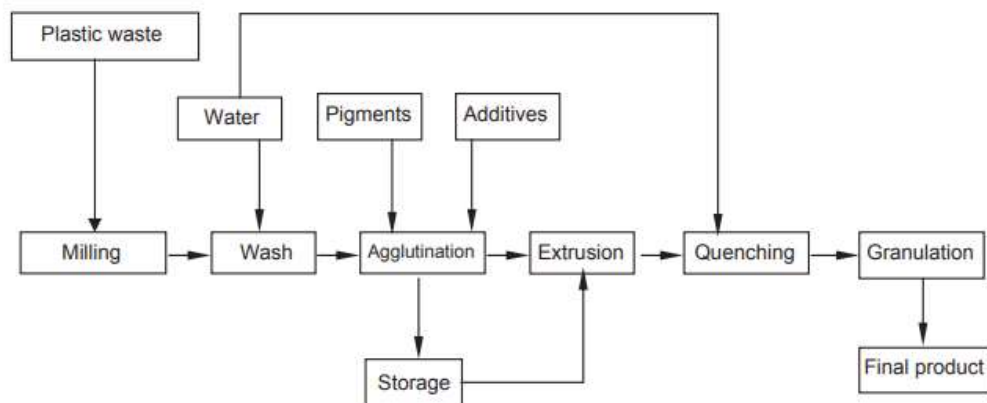


Figure 5: Stages of mechanical recycling³⁶.

Mechanical recycling is interesting because it allows the plastic to be used as a raw material in other plastic products. A series of products found in our day to day comes from the process of mechanical recycling such as grocery bags, pipes, gutters, profiles of windows and doors and shutters, etc^{4,36}.

2.1.4.2 Energy recycling

Energy recovery implies burning waste to produce energy in the form of heat, steam, and electricity. This is a very sensible way of waste treatment only when material recovery processes fail due to economic constraints. Plastic materials possess a very high calorific value^{4,37}.

The energy recycling processes can be identified as co-incineration by the direct combustion process of a single stage of waste, fluidized bed and two-stage incineration, rotary combustion and cement kiln or municipal waste combustion^{4,37}.

A benefit associated with this process is the large reduction in the volume of waste (up to 90%) which reduces the necessity of landfilling^{4,38}.

However, a number of environmental concerns are associated with energy recovery PSW, mainly emission of certain air pollutants such as CO₂, NO_x, and SO_x. Thus, waste incinerators have been required to install sophisticated exhaust gas cleaning equipment. Depending on the regulations of the country concerned, this gas cleaning equipment can be large and expensive^{4,38}.

2.1.4.3 Chemical recycling

Chemical recycling enables the production of raw materials through post-consumer materials³⁹.

In the traditional chemical industry process, raw materials account for 60% to 90% of production costs, and with chemical recycling products are mainly hydrocarbons, which can be used as fuels for energy generation, or as raw materials, the market can adhere to an environmental solution, with an economic investment^{39,40}.

Carbon is the main constituent of plastics, therefore, the plastics, becomes an excellent source of carbon for future uses. And the thermochemical treatment of them, an excellent way to obtain these carbons³⁹.

Chemical recycling is a process that converts plastic, for example, into smaller molecules, usually liquids or gases. The term chemical is used, due to the fact that an alteration is bound to occur to the chemical structure of the polymer⁴.

The technology behind its success is the depolymerization processes that can result in a very profitable and sustainable industrial scheme, providing a high product yield and minimum waste. Under the category of chemical recycling advanced process appear e.g. pyrolysis, gasification, liquid–gas hydrogenation, viscosity breaking, steam or catalytic cracking and the use of PSW as a reducing agent in blast furnaces^{4,39}.

2.1.4.4 Thermolysis

Thermolysis is the treatment of PSW in the presence of heat under controlled temperatures without catalysts. Thermolysis processes can be divided into advanced thermochemical or pyrolysis (thermal cracking in an inert atmosphere), gasification, and hydrogenation (hydrocracking)⁴.

The gasification of plastic is carried out by heating the material combined with air/O₂. This forms a CO + H₂ (syngas), which can go into refinery processes and help to make methanol, ammonia, and oxo-alcohols. The process given above needs a pumpable liquid feedstock that is obtained by liquefaction; the gasification takes place in oxygen at 1200–1500 °C, 20–80 bar, where a residence time of a few seconds gives a 98–99% conversion into gases plus a slag³⁷.

Hydrocracking is one of the oldest hydrocarbon conversion processes. Catalytic hydrocracking plays a key role in petroleum processing, providing high-value transportation fuels and upgrading low-quality feedstocks to make them suitable for further processing⁴¹.

It is elucidated that the pyrolysis process is capable of treating many solid hydrocarbon residues while producing a clean fuel gas with a high calorific value. Besides that, provides a number of advantages, such as environmental, operational and financial benefits. Environmentally, pyrolysis provides an alternative solution to landfilling and

reduces greenhouse gas (GHG) and CO₂ emissions. Operational advantages could be described by the utilization of residual output of char used as a fuel or as a feedstock for other petrochemical processes. Financially, pyrolysis produces a high calorific value fuel that could be easily marketed and used in gas engines to produce electricity and heat⁴.

2.1.5 Advanced solutions in the management of waste plastic

The fact that carbon is the major constituent of plastics, the waste plastics can, therefore, provide a carbon source for carbon-based value-added products³⁹.

Carbon is one of the most important elements. Different shapes of elemental carbon have played important roles in humanity. Charcoal and soot have been known and utilized for various purposes since ca. 5000 BC, but as recently as 35 years ago only graphite and diamond were listed as carbon allotropes⁴². Materials such as light hydrocarbons, carbon black and activated carbon, carbon fibers, fullerenes, carbon nanotubes, and graphene can be obtained from the waste plastic³⁹.

This study will focus on the efforts, made in recent years, to explore ways of recycling plastic wastes into carbon nanotubes (CNTs).

Carbon nanotubes (CNTs) are nanomaterials that have attracted great research interest because of their unique properties and promising applications. CNTs possess extremely high tensile strengths, high moduli, large aspect ratios, low densities, good chemical and environmental stability, and high thermal and electrical conductivities^{39,42}.

Because of these features, the CNTs have numerous potential applications, which include, but are not limited to, composites, electrodes, electronics, photovoltaic, biological devices³⁹.

CNTs can be classified multi-walled with a central tubule of nanometer diameter surrounded by graphitic layers separated. By contrast, single-walled CNTs (SWCNTs) are a cylindrical tube formed by wrapping a single-layer graphene sheet. According to the wall number of a CNT, it can be classified as an SWCNT, double-walled CNT (DWCNT), triple-walled CNT (TWCNT), or multi-walled CNT (MWCNT)⁴⁰.

Therefore, CNTs are formed under appropriate conditions at the presence of carbonaceous feedstock, heat and, typically, catalysts. There are four major different methods for the production of CNTs: arc discharge, laser ablation, chemical vapor deposition (CVD), and combustion (flame) synthesis³⁹.

The concept of synthesizing CNTs using solid polymers was first reported by Iijima since 1991⁴. However, when studying this type of conversion, it is necessary to analyze the types of plastics to be used, conversion processes, growth conditions, catalysts and quantities and qualities of the resulting CNTs⁴³.

In this way, as for the use of polymers, it is possible to observe in Table 1 the main commercial polymers (plastics), used for CNTS production experiments, as well as their percentage carbon content.

Table 1: Carbon Contents in Major Commercial Polymers³⁹.

Polymer	Carbon content (in wt %)
Polyethylene (PE)	85.6
Polypropylene (PP)	85.6
Polystyrene (PS)	92.2
Polyethylene terephthalate (PET/PETE)	62.6
Polyacrylonitrile (PAN)	67.9

In turn, the conversion of these polymers can be classified into two categories. One-pot conversion where the synthesis of CNTs occurs upon the in-situ formation of carbon feedstocks from the solid plastic waste. And, stepwise conversion where the synthesis of CNTs occurs after the formation of carbon feedstocks from the solid plastic waste³⁹.

One-pot synthesis of carbon nanotubes typically starts with solid polymers which are mixed with catalysts. A heat resource is then applied to catalytically decompose (pyrolysis) the plastics. The decomposed products, either in liquid or gaseous phases, serve as carbon sources for the growth of CNTs on the catalysts³⁹.

The stepwise conversion process features sequential reactions, typically starting with the thermal decomposition of plastics. As a second step, the resulting gaseous products (hydrocarbons) are then channeled downstream where they react with catalysts to form CNTs⁴⁴.

Based on the types of reactors that are used for the synthesis of the nanoproducts we have: quartz tube, autoclave, the crucible, fix bed (tube furnace, muffle furnace), moving bed, and, fluidized bed⁴⁵.

Whatever the CNT preparation method is applied, the CNTs are always produced with a number of impurities whose type and amount depend on the technique used. These impurities interfere with most of the desired properties of CNTs and cause a serious impediment in detailed characterization and applications⁴⁶.

However, currently, the common method widely accepted in the synthesis of CNTs is the Chemical Vapor Deposition (CVD) method due to its simplicity and low cost. The main advantages of CVD are easy to control of the reaction course and high purity of the obtained material^{46,47}.

There are two types of a furnace for this modality, one is a horizontal configuration, and the second is a vertical configuration. In the synthesis of CNTs by CVD, the catalyst is deposited on the substrate and then the nucleation of catalyst is carried via chemical etching. After the reactor/furnace is heated to the sufficient reaction temperature between 600–1200 °C, is made to react in a reaction chamber over the surface of metal catalysts for a given time period (usually 15–60 min). The general nanotube growth mechanism in the CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal and the saturation of carbon atoms in the metal nanoparticle^{47,48}.

The catalyst is the key factor for CNT growth. Catalyst is frequently defined as materials which accelerate the chemical reaction without themselves undergoing change^{42,49}.

Catalytic degradation of plastic waste is more advantageous than simple thermal degradation as the latter requires comparatively high temperature and produce low-quality reaction products. Catalytic degradation takes place at a considerably lower temperature and produce hydrocarbons, and eliminating further up-gradation steps⁵⁰.

Transition metals, especially Fe, Co, and Ni are active for CNT synthesis. These active elements are usually loaded onto catalyst support by co-precipitation or other loading methods widely used in petroleum and chemical processes⁴².

As temperatures rise, catalyst particles liquefy, are saturated with carbon, and nanotubes grow via extrusion⁴².

2.1.6 Current panorama of plastic waste management and treatment in the European Union

Today, in the move towards reaching zero settlement and sustainability, the priority objectives from UE to be achieved by 2020 are in execution⁵¹. Examples are:

1. Protect, conserve and strengthen the Union's natural capital;
2. To make the Union a low-carbon economy, the use of resources, green and competitive;
3. Protect citizens of the Union against environmental pressures and health risks and well-being;
4. Maximize the benefits of Union environmental legislation by improving its application;
5. Improve the knowledge base on the environment and broaden the rationale for the policies;
6. Ensure investments for the environment and climate policy and to consider the environmental costs of any activities of society;
7. Better integrate environmental concerns into other policy areas and ensure consistency in creating a new policy;
8. Make the Union's cities more sustainable;
9. Help the Union to address the international environment and climate change more efficiently.

As most plastics are mass-produced and low-priced, they are readily discarded after use. Waste management is needed to minimize the plastic wastes and to reduce their environmental impacts, and typically, waste reduction, recycling (mechanical, chemical, and thermal) as well as landfilling are considered common solutions³⁹.

In fact, to carry out the remit of the basic law, all plastics will ultimately be required to be recycled. However, as regards recyclability, most commodity plastics are relatively stable making monomer recovery poor⁵.

Therefore, to understand the life cycle of plastics products it is important to understand that not all plastics products are the same and not all have the same service life. Some plastic products have a shelf life of less than one year, some others of more than 15 years and some have a lifespan of 50 years or even more¹.

Thus, from production to waste, different plastic products have different life cycles and this is why the volume of collected waste cannot match, in a single year, the volume of production or consumption^{1,2}.

Currently, in the European Union, about 27.1 million tonnes of plastics are collected after consumption, to be destined to landfills, recycling, and energy recycling Figure 6^{1,2}.

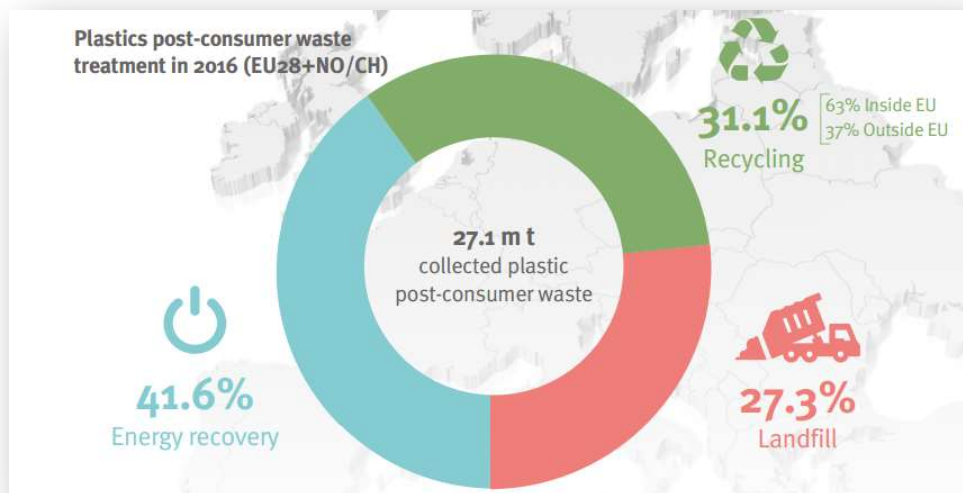


Figure 6: Plastics post-consumer waste treatment in 2016 in European Union².

However, in ten years, plastic waste recycling has increased by almost 80%. From 2006 to 2016 the volume of collecting plastic waste to recycling increased by 79%, energy recovery increased by 61% and landfill decreased by 43%^{1,2}.

On the other hand, the landfill disposal goal has become real. Nine European countries achieved a recovery rate of more than 95% of post-consumer plastic waste Figure

7, where can opt for recycling treatments (green part) and energy resources (blue part). These countries also have a landfill ban. Six of these countries are also among the countries with the highest recycling rates (over 30%)³⁰.

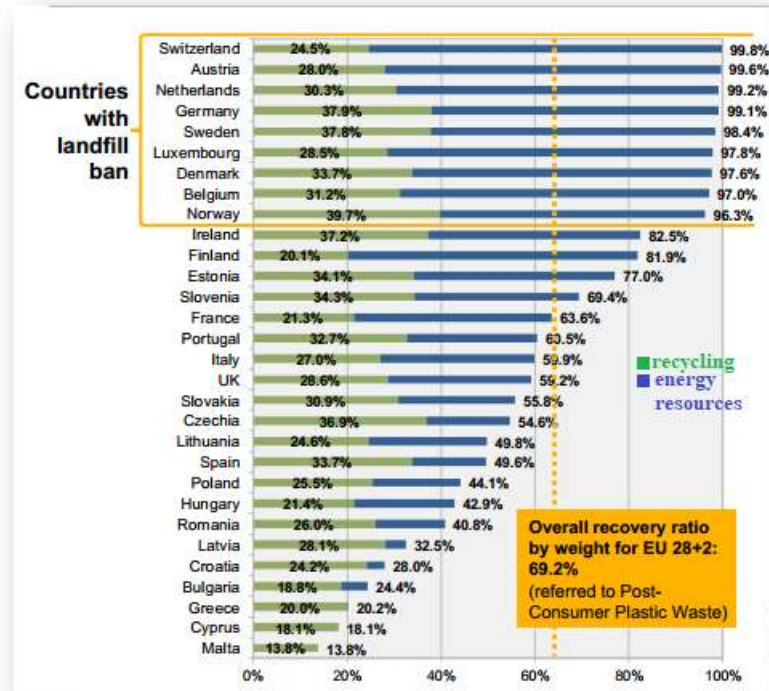


Figure 7: Recovery of Plastics Waste 2014: Green parts of the column = Recycling; Blue parts of the column = energy resources ³⁰.

In addition to future goals, the European Union proposes to establish even more rigorous and clear laws in relation to solid waste management. An example of this is the Action Plan for the Circular Economy⁶.

Circular Economy is a strategic concept based on the prevention, reduction, reuse, recovery, and recycling of materials and energy. Replacing the concept of end-of-life of the linear economy with new circular flows of reuse, restoration, and renovation, in an integrated process^{6,52}.

As part of its ongoing effort to transform Europe's economy into a more sustainable economy and to program the ambitious Circular Economy Action Plan, in January 2018 the European Commission adopted a new set of measures. The EU Strategy for Plastics in the

Circular Economy across Europe, thus focusing on concomitance with the general plan for Circular Economy, but with a particular plastics strategy only⁵².

In this way the Circular Economy for plastics has as strategies the following topics:

- Making recycling profitable for business: new packaging rules will be developed to improve the recyclability of used plastics in the market and increase demand for recycled plastic⁵²;
- Rejecting plastic waste: European legislation has already led to a significant reduction in the use of plastic bags in several Member States. The new plans will now turn to other plastics and single-use fishing gear, supporting national awareness campaigns and determining the scope of new rules at EU level⁵²;
- Stop throwing trash at sea: New rules on port reception facilities will deal with marine litter, with measures to ensure that waste generated on ships or collected at sea is not left behind but returned to land and properly managed there. Measures to reduce administrative burdens for ports, ships, and competent authorities are also included⁵²;
- Boosting investment and innovation: The Commission will provide guidance to national authorities and European companies on how to minimize plastic waste at the source. Support for innovation will be expanded with an additional € 100 million financing the development of smarter and recyclable plastic materials, making recycling processes more efficient and tracking and removing hazardous substances and contaminants from recycled plastics⁵²;
- Boosting change around the world: As the European Union does its own work from home, we will also work with partners from around the world to develop global solutions and develop international standards. We will also continue to support others, as made with the cleansing of the Ganges River in India⁵².

On the other hand, when the waste is not captured and treated correctly, the incorrect destination of the waste causes several impacts, environmental problems, economic and human health.

2.1.7 Environmental impacts - incorrect generation and destination of plastic waste

After the Industrial Revolution in the eighteenth century, which began in England, the generation of products gained a new frame, leaving behind the slow and handmade production to produce accelerated and mechanized. The seventeenth century was also marked by the great technological advance, revolutionizing the way of producing as well as the form of consumption⁵³.

Another important factor for the analysis of consumption and accelerated production is population growth. In the year 1950, the world population was approximately 2.5 billion people. However, by the year 2000, there were more than 6 billion human beings on the planet⁵⁴.

In this way, the factors mentioned above have caused a change that has altered the global economy, the generation and consumption of products as well as the physical and environmental aspects, triggering in a variety of impacts to the environment.

One example is the form of consumption and the production of fossil fuels or a secondary source derived from them. Since then, we have drilled millions of barrels of oil per day, tapping into natural gas reserves and mining increasingly large quantities of coal. In this sense, it is known that plastics are synthetic polymeric organic materials that mostly have the petroleum raw material⁵⁵.

Oil is an important source of energy, this product is mainly used in the form of automotive fuels, such as gasoline and diesel, as well as in the operation of thermoelectric power plants, for example. In addition, it is an important raw material used in the manufacture of plastics, paints, synthetic rubbers among other products⁵⁵.

To supply this market, many countries have invested in the extraction of this material. The United States, which is the world's largest power, leads the ranking of oil consumption, followed by China and Japan. On the other hand, regarding Russia's oil production followed by Saudi Arabia, and the United States command this scenario. It is possible to analyze the twenty countries that most consume and produce according to Figure 8^{55,56}.



Figure 8: Top 20 countries that most consume/produce Oil⁵⁶.

Associated with this consumption and production, we have the environmental and social impacts linked to the extraction, transportation, refining and various forms of oil consumption⁵⁵.

The first operation for oil exploration is the drilling; followed by the extraction, which is termed upstream process. Midstream is the process of distributing and transporting products from the refinery to the place of consumption. Downstream refers to the stage at which raw materials are transformed into end products. In addition to being costly processes, they are severely aggressive to the environment⁵⁵.

Therefore, it is possible to observe that all phases of the oil cycle have effects on our health and the environment. For example, drilling and extraction are risky operations for workers, exposing them to chemicals such as cadmium, arsenic, cyanide, and lead. Spills can contaminate marine life and fishing, as well as cause explosions and fires. Inadequate drilling leads to contamination of surrounding communities, affecting mammals birds and humans⁵⁵.

In the refinery operation, the combustion process results in atmospheric pollution, causing atypical phenomena such as acid rain. Polluting chemical products can be toxic and when emitted without proper control, they end up affecting air and soil⁵⁵.

While accidents with large oil tankers attract more attention, the cumulative effect of chronic spills and leaks on car or pipeline transport causes greater environmental damage and damage to wild communities⁵⁵.

Therefore, it is notable that the whole process of obtaining petroleum generates environmental impacts, and with the production and use of the derived products, it is not different⁵⁵.

One of the most controversial oil by-products is fuels, which are responsible for changing greenhouse gas levels, warming the Earth's surface and the depths of the oceans, changing the Earth's ice sheets and accelerating the hydrological cycle, as well as modifying the global climate patterns⁵⁵.

However, the production of plastic wastes that are mostly derived from petroleum does not differ in generating environmental impacts of other products affecting all elements of Earth.

2.1.7.1 Environmental impacts associated with plastic waste

Plastic pollution in the natural environment has attracted much attention from both researchers and the general public. Pollution from plastics has generated many damages, related to human health, fauna, and flora.

In the oceans, for example, the threat to marine life comes in various forms, one particular form of human impact constitutes a major threat to marine life: is the pollution by plastic debris. For over two millennia humanity indiscriminately discarded their waste around the edges of the oceans as well as lakes and rivers. In fact, there used generally accepted that due to its geographical extent, the oceans had an infinite capacity to assimilate evictions of all types of waste^{27,57}.

The sources and forms of contamination of the aquatic environments are numerous, the wastes deposited incorrectly in the streets, are taken, loaded or discharged intentionally in the waterways. Improper or illegal disposal of industrial or public waste is very recurrent⁵⁸.

Waste dumping in oceans is as common as land dumping, commercial fishing, recreational boats, cruise ships, or offshore oil platforms contribute greatly to pollution of water bodies⁵⁸.

In this way, marine life deals with factors where about 80% of the annual contribution comes from land-based sources and the main contributor is plastic waste. Concurring with materials such as paper, wood, metals, glass, sanitary waste and hospital plastics are highlighted being found in greater quantity, it is possible to observe this condition in the following Figure 9^{58,59}:

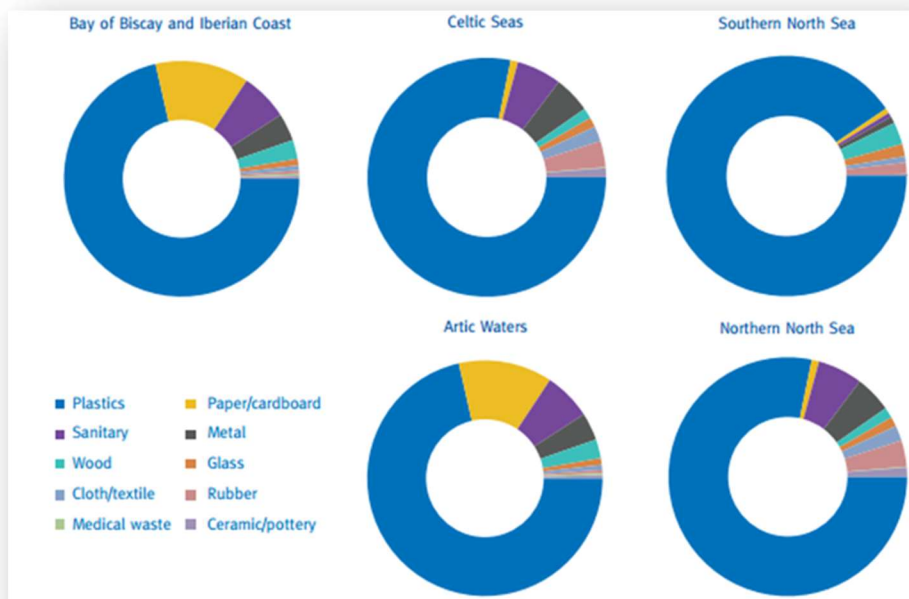


Figure 9: Marine composition of pollution by plastic material¹.

Another worrying factor is that an average of 70 kg of plastic is found every square kilometer at the bottom of the sea. Only 1% of marine plastics are found floating or near the surface of the ocean^{1,58}.

In contrast, the amount of plastic waste dumped on the beach is five times greater, about 2.000 kg of plastic waste per km². This residue comes from the incorrect allocation of the beach visitors, or also washed by the flow of sea currents between the beach and the sea^{1,58}.

Other threats to marine life, are primarily due to ingestion of plastic detritus and entanglement in packaging bands, synthetic ropes, and lines, or drift nets⁵⁷. Ingestion seldom leads to immediate mortality in organisms; however, effects have long-term consequences, including blockage of the intestinal tract, inhibition of gastric enzyme secretion, reduced

feeding stimuli, and decreased steroid hormone levels, delays in ovulation and failure to reproduce⁶⁰. The potential pathways of plastic debris transportation and its biological interactions are exemplified in the following Figure 10.

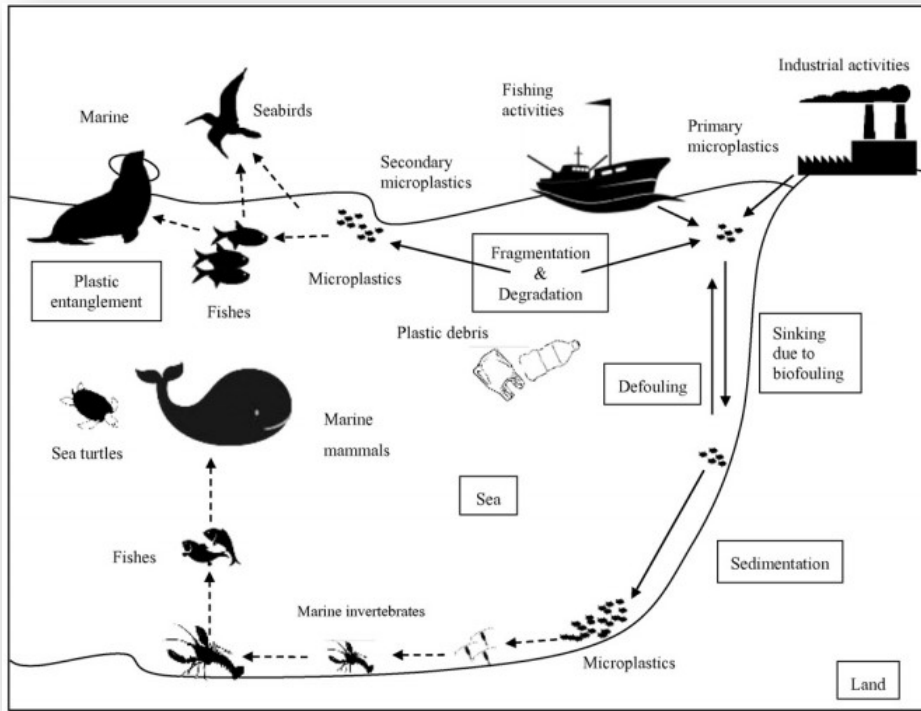


Figure 10: Routes of marine plastic pollution⁶⁰.

The incorrect allocation of this amount of plastic waste interferes with the quality of water, the diversity of marine life and the proper functioning of the hydrological cycle. Examples of impacts from marine debris are innumerable, and may negatively impact humans, wildlife, habitats, and the economic health of communities^{58,60}.

With regard to impacts is for humans, visitors to a beach may be harmed by broken glass, medical waste, fishing line, and discarded syringes; swimmers, divers, and may curl or cut themselves in submerged or floating debris. The presence of viral load items may pose a risk of contamination by *E. coli*, or other harmful bacteria, and even viruses can be found in these waters. Consumption or contact with water polluted with these contaminants and pathogens may result in infectious hepatitis, diarrhea, bacillary dysentery, rashes, and even typhoid and cholera⁵⁸.

In this sense, plastic pollution may also cause aesthetic and economic impacts. Debris makes coastal zones, lakes, rivers, or water parks unattractive and potentially dangerous, necessitating the release of government funds for the recovery and maintenance of aquatic life. On the other hand, marine debris can discourage people from fishing, boating, swimming and visiting the coastal area, weakening the local tourist economy⁵⁸.

2.2 CONTAMINATED WATERS

Water resources occupy a special place among other natural resources. It is essential for life, and although abundant on Earth, it consists mainly of aquatic resources that are not directly usable by humans, such as the saltwater of the oceans and seas (97.2% of the total mass of water) and glaciers (2.15%). Only about 0.65% of the total mass of water can be used directly by humans. However, by the year 2025, it is estimated that 5 billion people, out of a total population of about 8 billion, will be living in countries with water stress (using more than 20% of their available resources)^{61,62}.

One of the major threats to water quality is chemical pollution from heavy metals, solvents, dyes, pesticides, etc. Chemicals enter the aquatic medium in several different ways, either dumped directly, such as industrial effluents, or from wastewater treatment plants (WWTP) that do not fulfill their obligations⁶³.

In the past, the focus was on detecting the severe, direct effects of individual pollutants and the short-term negative impact on ecosystems. Furthermore, larger and larger quantities of persistent substances are being found at long distances from their sources of discharge⁶³.

In this way, a new significant class of water pollutants has emerged, the pharmaceuticals and personal care products. Its widespread use has promoted its entry into natural resources. As an example, the recent analysis made in effluents has shown the presence of significant amounts of pharmaceutical drugs, not only in effluents arising from pharmaceutical industries, but also in surface and ground waters, and even in drinking waters⁶⁴.

Has been an increasing concern about the occurrence of pharmaceutical products in the aquatic environment. As they are resistant to biological processes, as well as to physicochemical treatments such as coagulation-flocculation or adsorption on activated carbon⁶⁵.

Pharmaceuticals are a large and diverse group of compounds designed to prevent, cure and treat disease and improve health. Thousands of tons of pharmaceuticals are used yearly with different purposes such as the prevention, diagnosis, cure, and mitigation of diseases or just to improve the state of health not only in humans but also in animals. Their usage and consumption are increasing consistently due to the discoveries of new drugs, the expanding population and the inverting age structure in the general population, as well as due to the expiration of patents with resulting availability of less expensive generics⁶⁶⁻⁶⁸.

The presence of pharmaceuticals, even at trace concentrations, affects the quality of water and constitutes a risk of toxicity for ecosystems and living organisms. Effects such as the development of antibiotic-resistant microbes in the aquatic environment, fish reproduction changes due to the presence of estrogenic compounds, also the behavior and migratory. This also constitutes a public health problem since pharmaceuticals have been even found in drinking water supplies^{64,69,70}.

Compared with conventional pollutants, as phenolic compounds and chlorinated derivatives, many pharmaceuticals possess water solubility, and most of them distribute and migrate in the environment by the aqueous phase transfer and food chain diffusion. Particularly, paracetamol (acetaminophen drug) is frequently detected in rivers, lakes, and groundwaters. For this reason, a lot of effort from the scientific community exists in order to search new wastewater treatment technologies that can completely degrade the paracetamol present in water⁷¹.

Paracetamol (N-acetyl-para-aminophenol or para-acetyl-amino-phenol, also known as acetaminophen) is a nonsteroidal anti-inflammatory drug (NSAID) and is one of the top 200 prescriptions overall the world, which is commonly used in order to relief the tension headache, muscular aches, general pain, and rheumatic pain⁷². Was synthesized in 1878 by Morse and first used clinically by von Mering in 1887⁷³.

2.3 ADVANCED OXIDATION PROCESSES FOR POLLUTED WATER TREATMENT

Several technologies are available to remove industrial organic wastes, such as biological, thermal and chemical treatments. Conventional biological processes represent an environmentally friendly way of treatment with reasonable costs; however, they are not adequate to treat non-biodegradable wastewaters and, usually, require a long residence time for micro-organisms to degrade the pollutants⁷⁴. On the other hand, there are still issues to be raised such as the fact that heat treatments have many drawbacks, such as the considerable emission of other hazardous compounds. Chemical treatments, which include flocculation, precipitation, activated carbon adsorption, air removal or reverse osmosis, are not solving the need for post-treatment treatment. Particularly, when it comes to the treatment of phenols⁷⁵.

Alternative pollutants destructive technologies are advanced oxidation processes (AOPs)⁷⁴. AOPs are characterized by a common chemical feature: the capability of exploiting the high reactivity of HO• radicals in driving oxidation processes that are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants. Contaminants are oxidized through four different reagents: ozone, hydrogen peroxide, oxygen, and air or their combination⁷⁴.

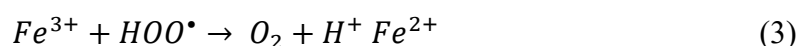
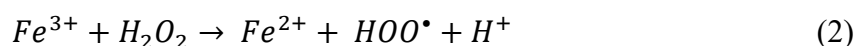
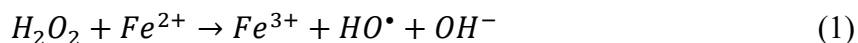
To choose the most appropriate technology, some aspects, such as the concentration and nature of the pollutants and the volume of wastewater, should be considered. In this way, it is possible to choose between: methods based on ultrasound, plasma and electrohydraulic discharge, along with processes based on hydrogen peroxide (H₂O₂ + UV, Fenton, photo-Fenton and Fenton-like processes), photolysis, photocatalysis and processes based in ozone (O₃, O₃ + UV and O₃ catalyst)⁷⁴.

2.3.1 Fenton

The Fenton process was discovered more than one hundred years ago by Henry J. Fenton. The scientist reported in his article that hydrogen peroxide could be activated by iron salts in order to oxidize tartaric acid. Despite that, the process was only used for the first time for the removal of organic pollutants in the 1960s¹⁶. The interest of researchers around

the world for this classic reactive system began around 1990 when some articles reported results obtained with the use of the Fenton process in the treatment of wastewater, and the interest in this field of study continues nowadays since the number of investigations on this application is still rising considerably ^{76,77}.

The mechanism of the Fenton process is based on the generation of hydroxyl radicals from the decomposition of hydrogen peroxide in the presence of ferrous iron (Fe²⁺) at acid conditions, yielding Fe³⁺ with the formation of hydroxide ions (OH⁻) and hydroxyl radicals HO• (Eq. 1). In the sequence of the reaction cycle, the ferric ion generated by oxidation in the first reaction reacts with hydrogen peroxide-producing hydroperoxyl radicals and regenerating the catalyst, as described in Eq. 2. The hydroperoxyl also reacts with the ferric ion, regenerating more the catalyst (Eq. 3)^{19,77,78}.



Basically, the Fenton process possesses several important advantages for water/wastewater treatment: (i) A simple and flexible operation permitting easy implementation in existing plants; (ii) Easy-to-handle and relatively inexpensive chemicals; (iii) No need for energy input^{61,79}.

Nevertheless, the following drawbacks have been also noted: (i) Rather high cost and risks due to the storage and transportation of H₂O₂^{61,80}; (ii) Need of important amounts of chemicals for acidifying effluents at pH 2–4 before decontamination and/or for neutralizing treated solutions before disposal; (iii) Accumulation of iron sludge that must be removed at the end of the treatment.

In the last few years, the scientific community has shown an effort in order to develop heterogeneous catalysts that could avoid the formation of iron sludge, which would complicate the discharge of the effluent resultant from the Fenton treatment, once the amount of iron sludge would not be appropriate for reutilization ^{74,81}. The goal of the treatment of wastewaters by using Fenton oxidation is to accomplish the almost complete degradation of the organic pollutants trying to avoid the formation of undesirable compounds that would complicate even more the discharge of the wastewaters. The oxidation of the organic

pollutants produces intermediate species, which can be oxidized to CO₂, H₂O and inorganic salts⁸².

2.3.2 Catalytic wet peroxide oxidation

Wet peroxide oxidation processes have emerged as a viable alternative for the wastewater treatments of medium-high total organic carbon concentration⁷⁴.

In CWPO, H₂O₂ is employed as an oxidant and a catalyst is used to promote the decomposition of H₂O₂ to hydroxyl radicals, vital species to the successful implementation of CWPO. As explained before, hydroxyl radicals are highly oxidizing species, able to degrade most of the organic pollutants, and the H₂O₂ used to produce these radicals is well established as an environmentally friendly agent since its total decomposition products are oxygen and water^{83,84}. Hydrogen peroxide does not form any harmful by-products, and it is a non-toxic and ecological reactant⁷⁴.

The typical heterogeneous catalysts employed in CWPO processes consists of an active phase, some transition metal like Fe, supported on a material with high porosity and surface area⁸⁵. The use of supported catalysis allows the increasing of the surface area that provides the metal species. Some possible materials that can be employed as catalyst supports are alumina, silica, activated carbons, and clays. Even though the advantages of CWPO, its application to wastewater treatments has been restricted, since most of the catalysts have shown moderate activity but low stability, with metal leaching occurring into solution^{86,87}.

A fundamental study field of the CWPO process is the catalyst support typically used. Some of the materials that appear in the literature as catalyst supports include zeolites, silica, alumina and clays^{82,83,88,89}.

Between the problems that usually appear in CWPO, the metal leaching of the metallic phase to the reaction medium is that one been more studied^{90,91}. This led to the study of different methods to synthesize metal-free materials, capable to catalyze the decomposition of H₂O₂⁹². A class of materials that has attached attention from the scientific community are metal-free catalysts, for example activated carbons, which were found to be active catalysts for the CWPO of organic pollutants without any supported phase⁸⁵.

The development of metal-free catalysts for the CWPO process is of great interest because these materials are able to prevent iron leaching, deactivation and the use of high-cost metals. The possibility to synthesize a metal-free catalyst for CWPO of organic pollutants represent an advantage in comparison with the Fenton process, once that the use of these materials does not result in the formation of iron sludge, as occurs in Fenton⁹⁰. In the studies regarding the use of metal-free catalysts in CWPO is related that the pollutant oxidation is, in general, moderate or low activities, being obtained for the removal of organic compounds even when using doses of H₂O₂ higher than the stoichiometric⁹³⁻⁹⁵.

2.4 OBJECTIVES

This study will focus on the development of catalysts based on nickel, iron and (or) aluminum in the form of nanoparticles in order to value PSWs in carbon nanotubes (CNTs) and to treat water by the CWPO method contaminated with paracetamol. The preparation of the suitable catalysts is very important as it will be possible to classify some characteristics of the catalysts and to evaluate whether the preparation of the materials was successful.

3 MATERIALS AND METHODS

3.1 REACTANTS

The reactants used in this work are described below, according to the application for which they were used.

Production of catalysts:

- Nickel (II) nitrate hexahydrate: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99% of purity) provided by Merck;
- Nickel (II) chloride hexahydrate: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (95% of purity) provided by Fisher Chemical;
- Aluminum nitrate nonahydrate: $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98% of purity) provided by VWR;
- Iron (III) nitrate nonahydrate: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98% of purity) provided by Sigma-Aldrich;
- Aluminum oxide: Al_2O_3 provided by BASF;
- Ammonium hydroxide: $\text{NH}_4(\text{OH})$ provided by Panreac;
- Distilled water.

CWPO:

- Paracetamol (98%). Alfa Aesar; Formula: $\text{C}_8\text{H}_9\text{NO}_2$;
- Hydrogen peroxide (30% w/v). Fisher Chemical; Formula: H_2O_2 ;
- Titanium (IV) oxysulfate (99.99%). Aldrich; Formula: TiOSO_4 ;
- Sulfuric acid (98%). Labkem; Formula: H_2SO_4 ;
- Sodium sulfite anhydrous (98%). Panreac; Formula: Na_2SO_3 ;
- Ultrapure water;
- Distilled water.

Production of CNTs:

- PE-LD (Molecular Weight Distribution 35000 g/mol, $\text{H}-(\text{CH}_2-\text{CH}_2)_n-\text{H}$), provided by Sigma-Aldrich, MERCK;

3.2 CATALYST PREPARATION

Catalyst based on Ni, Fe and Al co-oxides were prepared by different methodologies: (1) wetness impregnation of Al_2O_3 in powder form with a Ni precursor and (2) co-precipitation of Ni, Fe and Al nitrates with NH_4OH .

3.2.1 Ni/ Al_2O_3 by wetness impregnation

The catalyst was prepared by the method of wetness impregnation of Al_2O_3 with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ^{96,97}. The following ratio was determined by 5% NiO over 2 g of Al_2O_3 . First, alumina, which was supplied in pellets form, was crashed, milled and grinded to obtain powder Al_2O_3 in the following range of size: 53-106 μm .

In a round bottom flask was added 2.0 g of Al_2O_3 , 2 mL of the solution containing 1.67 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 mL of distilled water was collected, and 8 mL of distilled water. The flask was then coupled to the rotary evaporator and kept under constant stirring at 80 °C for 2 h until liquid part being evaporated. Then, the resultant material was calcined for 3 h at 800 °C. Figure 11 shows the round bottom flask with the sample coupled in the rotary evaporator.

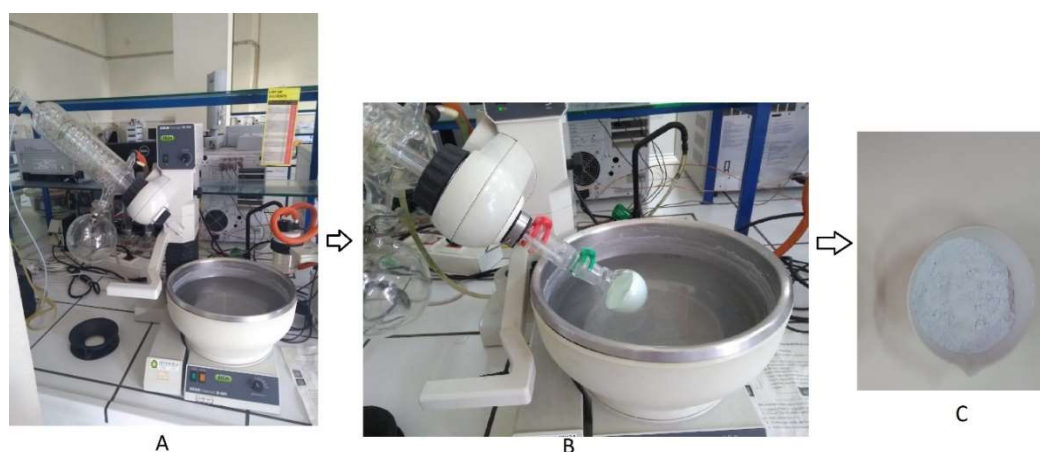


Figure 11: Wetness impregnation. A) rotary evaporator. B) the round bottom flask with the sample coupled in the rotary evaporator. C) final appearance of the catalyst.

3.2.2 Ni-Al Co-Oxide

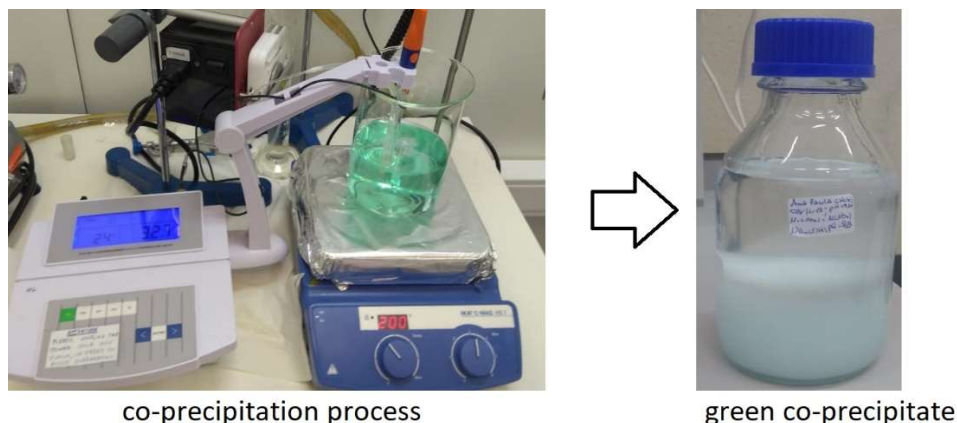
Ni-Al co-oxide catalysts were synthesized by co-precipitation route using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors, this process is adapting the process described by Chunfei Wu *et al*^{98,99}.

Two concentrations of Nickel (II) nitrate (5% and 20%) were stipulated for this procedure, and the concentration aluminum nitrate was maintained. The first step followed was the calculation of precursors for 5% Ni/Al catalyst (in addendum).

First, the following ratio was determined 5% of NiO over 2 g of Al_2O_3 and, 20% of NiO over 2g of Al_2O_3 . The second step was dilution and preparation of the solutions, the required amount of each reagent was weighed: 5% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.983 g), 20% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.91 g) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (37.56 g). The reactants were then diluted in 250 mL of distilled water. Subsequently, the volumetric flask containing the 5% dilution of nickel (II) nitrate was mixed with the dilution of aluminum nitrate in a 500 mL flask. Likewise, the volumetric flask containing the 20% dilution of nickel (II) nitrate was mixed with the dilution of aluminum nitrate in a 500 mL flask. Getting two solutions.

For the co-precipitation process, ammonium hydroxide ($\text{NH}_4(\text{OH})$) (1 M) was used, prepared by means 15.41 ml of NH_3 (25%) diluted in 100 ml of distilled water.

The precipitator [$\text{NH}_4(\text{OH})$] was added dropwise to the first aqueous solution containing 5% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to the final pH (about 8) under strong stirring during the precipitation process. The pH around 8 was obtained, with the addition of approximately 170 mL of $\text{NH}_4(\text{OH})$. For the second co-precipitation process of the 20% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, the same procedure was followed, but the volume of ammonium hydroxide reached 190 ml. The solution rested overnight, showing the decanting of a green precipitate. The co-precipitation procedure and the result can be seen in Figure 12.

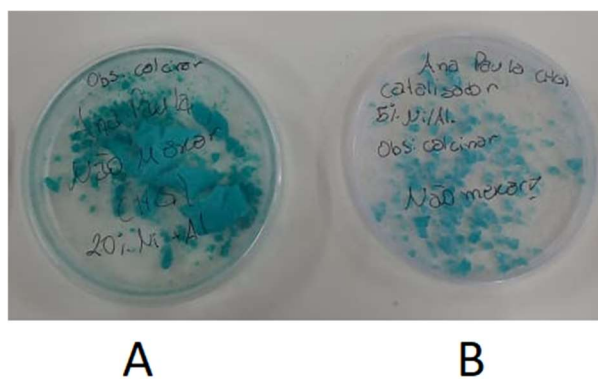


co-precipitation process

green co-precipitate

Figure 12: Co-precipitation process.

After 18 hours, the solutions were centrifuged for 10 minutes to remove the green co-precipitate, to dry completely, they were placed in the oven at 60 °C for 12 hours. It is possible to observe the result of the dry co-precipitate of 20% and 5% in the image indicated as A and B respectively, shown in Figure 13.



A

B

Figure 13: samples after centrifugation and drying.

In the final processing of the catalyst, the samples were manually ground in the crucible and brought to a calcining furnace for 3 hours at 800 °C, the final aspect of the catalyst being 5% and 20% before and after the calcination shown in the image below, respectively, and can be seen in Figure 14.

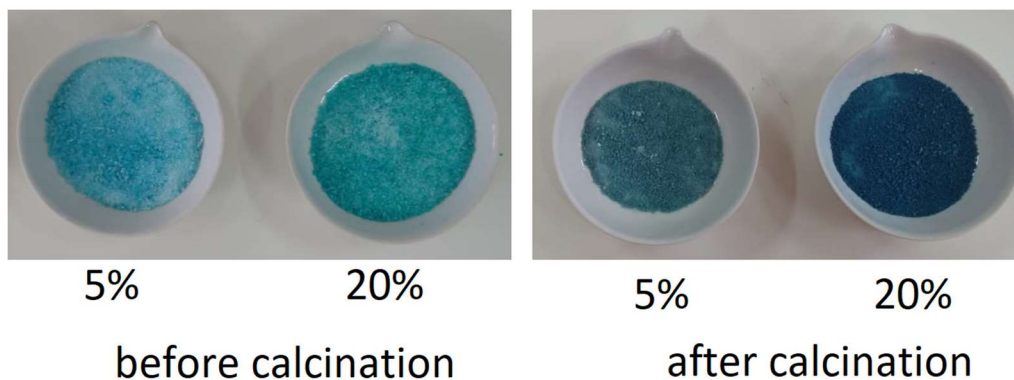


Figure 14: Catalyst after grinding and calcination

Following the same co-precipitation method, a catalyst with, 20% of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 20% of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and Al_2O_3 was also prepared.

3.3 CHARACTERIZATION OF FRESH CATALYSTS

3.3.1 Fourier transformed infrared spectroscopy (FTIR)

Analysis of infrared spectra can tell you what molecules are present in a sample; this is why infrared spectroscopy is useful¹⁰⁰. The FTIR spectra of the 4 different samples were recorded on a Perkin Elmer FT-IR spectrophotometer UATR Two infrared spectrophotometer, with a resolution of 4 cm^{-1} . The range of wavenumber used in the analysis was from 450 to 4000 cm^{-1} . All the measurements were done from the solid samples at room temperature. This analysis was performed at the Analytical Chemistry Laboratory of the Bragança Polytechnic Institute (IPB).

3.3.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive analytical method to analyze material properties like phase composition, structure, texture and many more of powder samples, solid sample or even liquid samples¹⁰¹. The measurements of powder X-ray diffraction (XRD) were performed in a PANalytical X'Pert PRO equipped with a X'Celerator detector and secondary monochromator ($\text{Cu K}\alpha \lambda = 0.154\text{ nm}$; data recorded at a 0.017° step size).

3.4 CNTs CHARACTERIZATION

3.4.1 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructural characteristics of solid objects. The primary reason for the SEM usefulness is the high resolutions that can be obtained when bulk objects are examined: values of the order of 10 nm. Another important feature of SEM imagen is the tree-dimensional appearance of the specimen, which is a direct result of the large depth of focus¹⁰². The samples were collected in powder to be analyzed, in the scales of 400, 4, and 1 μm .

3.5 SYNTHESIS OF THE CARBON NANOTUBES

The reactor used in this procedure was the vertical/horizontal tubular furnace supplied by TERMOLAB, the company ensures that the ovens were designed and built according to technical standardization and legal provisions at the level of machine safety (Machinery Directive 98/37 / CE). The oven has the characteristics described in Table 2.

Table 2: Characteristics of the vertical/horizontal tubular furnace.

Designation	Value	Unit
<u>DIMENSIONS</u>		
Internal tube diameter	50	mm
Length of the hot zone	500	mm
<u>GENERAL</u>		
Electric potential	230	V
Frequency	50	Hz
Power	4.5	kW
Maximum temperature	1200	$^{\circ}\text{C}$
Cooling water flow	1 to 2	L/min

The tubular oven can be mounted vertically and horizontally. In this case, the vertical position was chosen because it best fits the laboratory, Figure 15.

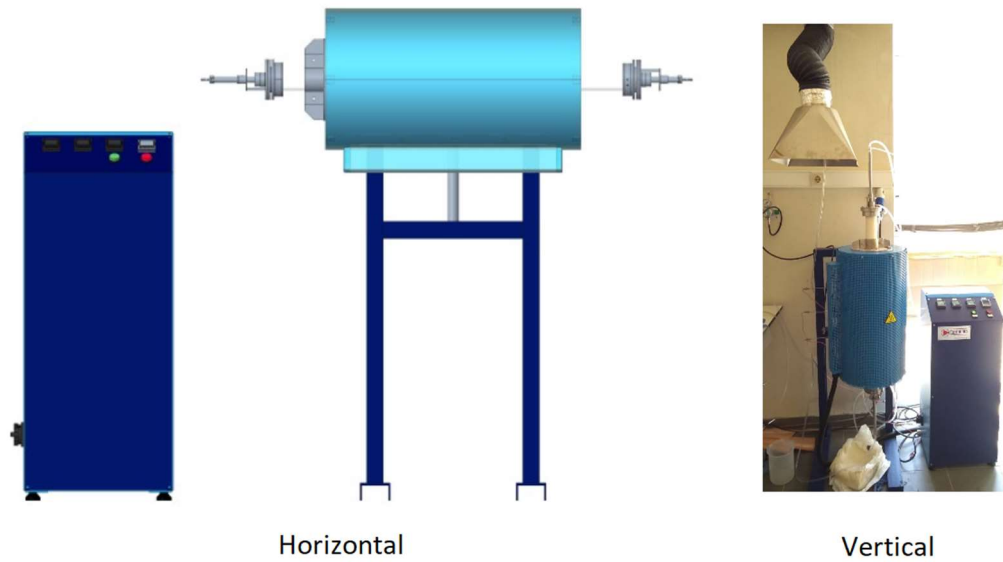


Figure 15: Equipment overview.

The equipment requires a connection to a single-phase 16 Amp electric power. For tubes and flange installation, the instructions were followed (Figure 31, in addendum):

After assembling the tubular furnace, it was necessary to program the Programmable Controllers. EPC3000 controllers are a range of programmable single loop process controllers that are certified for cybersecurity communications robustness. The display of the EPC3000 controllers can be seen in the following Figure 16.

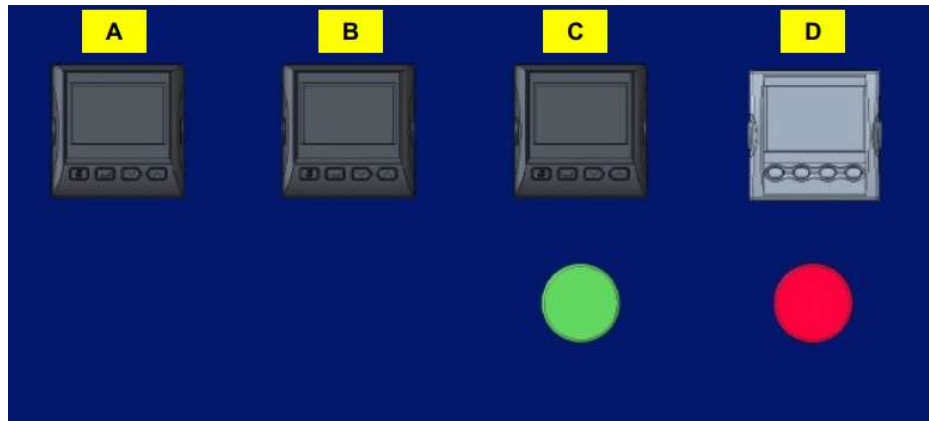


Figure 16: Control panel.

The green button is for the initiation of the system, the red button is designed for the power of the reactor. The controller identified as A is a slave controller, it shows upper zone temperature information, controller B is the master controller, it has central zone temperature, the controller identified with C is a slave controller, it reports the temperature of the zone bottom, D is the temperature indicator of the sample.

EPC3000 Controllers have 5 levels of operation. Level 1 has no password; the control is active and only the home list is accessible. Level 2, the control is active and an extended home list is accessible, the password is required. Level 3, the control is active and the complete operator parameter set is shown and modifiable, the password is required. Configuration level is used to set up the whole controller. In addition, the QuickStart Mode is provided to allow users to configure the product in the minimum number of operations. It is only available at power up after the instrument is cold started or by holding the Page key during power-up. In this experiment, it was established that the controllers work independently, establishing three different temperatures, $T_1 = x_1$ °C, $T_2 = X_2$ °C, and $T_3 = 1000$ °C, for this, level 3 was required. The following Figure 17 shows the steps to trigger the level 3.

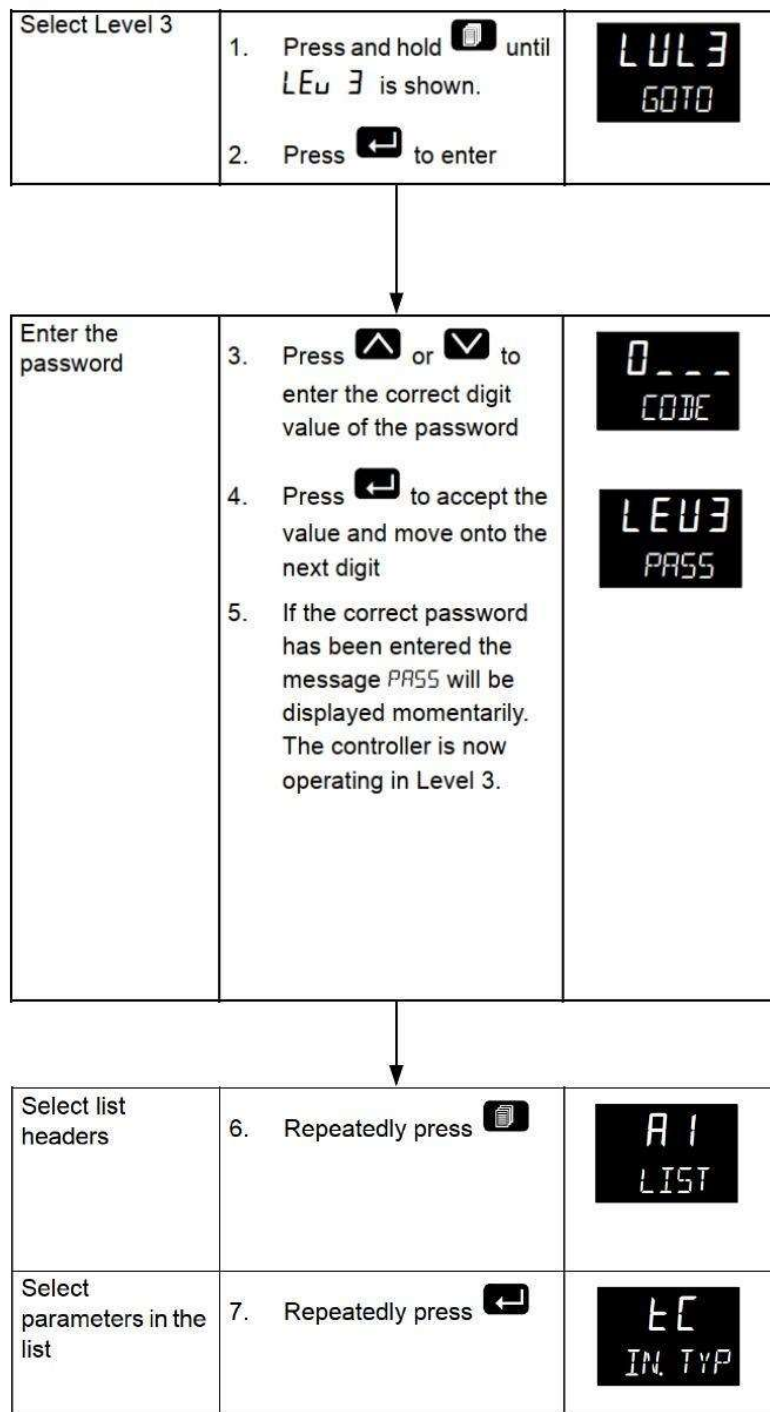


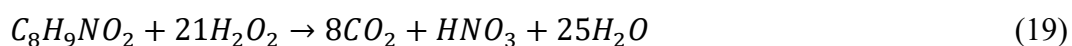
Figure 17: Level 3 access steps.

After finalizing all programming and correct assembly of the tubular furnace, 10 g of polymer and 2 g of catalyst (20% Ni/Al) were placed in a crucible, the vitreous carbon crucibles were placed in the tubular furnace in an inert atmosphere created by the circulation

of nitrogen. The crucible containing the catalyst and the polymer will remain in the tubular furnace for 3 hours at a temperature of $T_1= 505\text{ }^\circ\text{C}$, $T_2= 705\text{ }^\circ\text{C}$, and $T_3= 1000\text{ }^\circ\text{C}$.

3.6 CWPO OF PARACETAMOL

Batch oxidation runs were performed under the stoichiometric amount of hydrogen peroxide for mineralization of paracetamol, according to the following chemical equation.



Considering that 100 mL of the paracetamol solution, the amount of hydrogen peroxide necessary to proceed with the experiment was found to be equal to 158 μL of a 30%w/v peroxide solution provided by Sigma Aldrich. The oxidation reactions were carried out in a 250 mL well stirred (600 rpm) round flask reactor, equipped with a condenser and a temperature measurement thermocouple. The reactor was loaded with 100 mL of 100 ppm of paracetamol solution to simulate hospital wastewater effluents, previously acidified until pH 3.5 by means of H_2SO_4 . The system was heated by immersion in an oil bath monitored by a temperature controller until $80\text{ }^\circ\text{C}$, which was the temperature used in the oxidation runs. When the temperature stabilized, the stoichiometric amount of hydrogen peroxide was added to the reaction system. After the complete mixing of the reactants, the amount of catalyst necessary to reach 0.25 g/L was added into the reactor. This moment was then considered as the beginning of the CWPO run ($t_0 = 0\text{ min}$).

The samples for analysis were periodically withdrawn at selected times: 5, 15, 30, 60, 120, 240, 360, 480 and 1440 min. At each time, 3 samples of 1 mL were collected and stored in different eppendorfs, previously prepared according to the analysis that it would be done (H_2O_2 concentration, paracetamol concentration, and Total Organic Carbon). Each sample was centrifugated in order to separate the catalyst from the liquid aliquot. After the last sample was withdrawn, the catalyst was separated by filtration, liquid media stored and catalyst washed with distilled water and dried in an air oven at $60\text{ }^\circ\text{C}$ overnight. In Figure 18 it is possible to see the system used in the CWPO runs.



Figure 18: System used in the CWPO experiments.

4 RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF FRESH CATALYST

4.1.1 Fourier Transformed Infra-Red (FTIR)

Fourier Transform Infrared Spectroscopy (FT-IR) was used to investigate functional groups of the synthesized catalysts in the range of 400 cm^{-1} until 4000 cm^{-1} wavenumber. The FTIR spectra obtained by the analysis of the different catalysts prepared by co-oxide of 5% Ni/Al and 20% Ni/Al are shown in Figure 19.

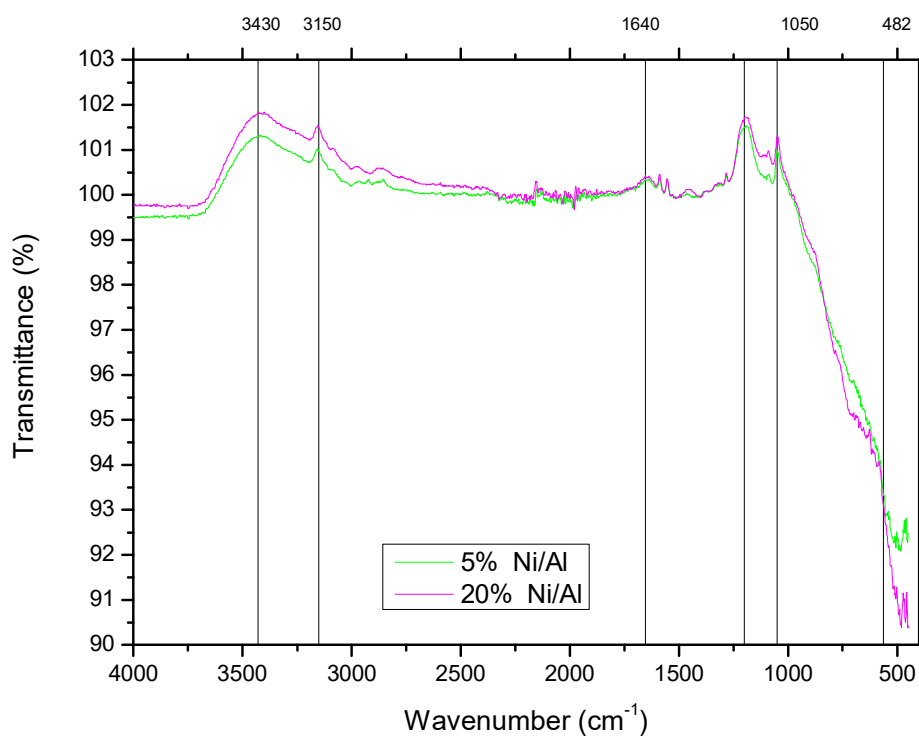


Figure 19: FT-IR spectra of the co-oxide method of 5% Ni/Al and 20% Ni/Al.

In Figure 19 relate to the catalysts of co-oxide, it is possible to observe the first band appearing at 3430 cm^{-1} and another in the second one at 3150 cm^{-1} , both for the 5% Ni/Al and 20% Ni/Al samples. The broad peak centered at about 3500 cm^{-1} corresponds to the vibration bands of hydroxyl ($-\text{OH}$) groups hydrogen bonded to water molecules. The H_2O bending vibration can be observed at 1640 cm^{-1} . The appearance of these vibrations is probably due to the absorption of water in all samples after calcination. The band at 1200

cm^{-1} shows the presence of the nitrate ion in each sample. The mode of carbonate vibration can be seen in the band of 1050 cm^{-1} . The sharp but small bands at 562 cm^{-1} are translational modes of oxygen in AlO_6 octahedra. However, these same small bands may represent the presence of Ni-O at 482 cm^{-1} bands^{103,104,105}.

The FTIR spectra obtained by the analysis of the different catalysts prepared by wetness impregnation of 5% Ni/ Al_2O_3 and alumina are shown in Figure 20.

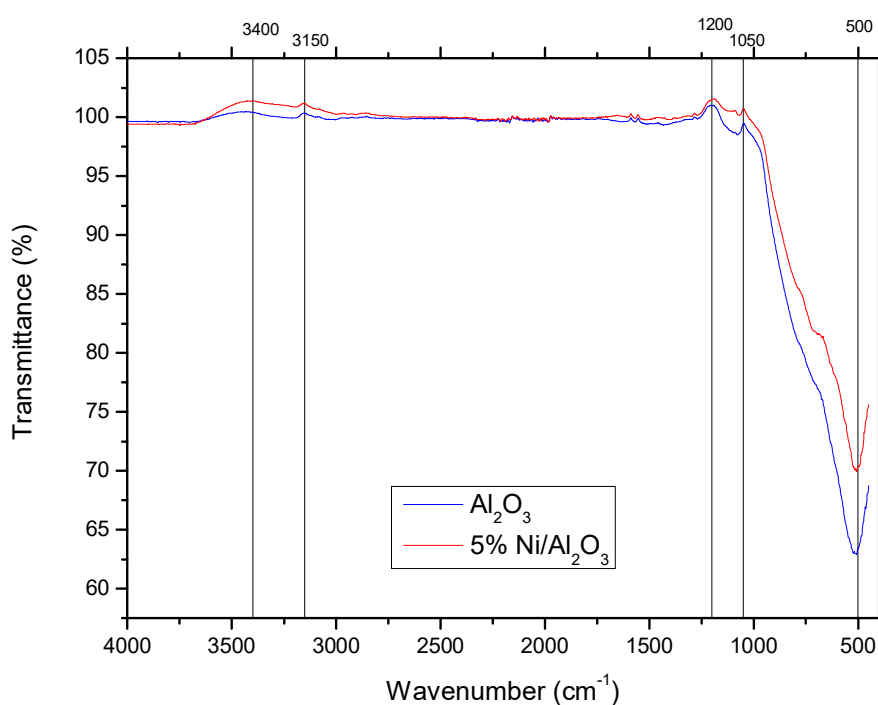


Figure 20: FTIR spectra of Al_2O_3 and wetness impregnation of 5% Ni/ Al_2O_3 .

Again, it is possible to realize in Figure 20 the first band appearing in a range of 3400 cm^{-1} at 3150 cm^{-1} for both samples, this band is due to the $-\text{OH}$ band stretch for absorbed water¹⁰⁶. The IR spectra in two cases, exhibit metal-oxygen stretching frequencies in the range 500 cm^{-1} at 900 cm^{-1} associated with the vibration of Ni-O, Al-O and Ni-O-Al bonds¹⁰⁷. The similarity between the two spectra shows the low interference of Ni over Al_2O_3 .

4.1.2 X-Ray Diffraction (XRD)

In order to determine crystalline phases composition of 5%Ni/Al and 20% Ni/Al the samples were subjected to X-ray diffraction analysis (XRD). It was identified the presence of Ni, Al, NiO, and NiAl₂O₄, Figure 21 gathers the XRD diagrams of the analyzed samples.

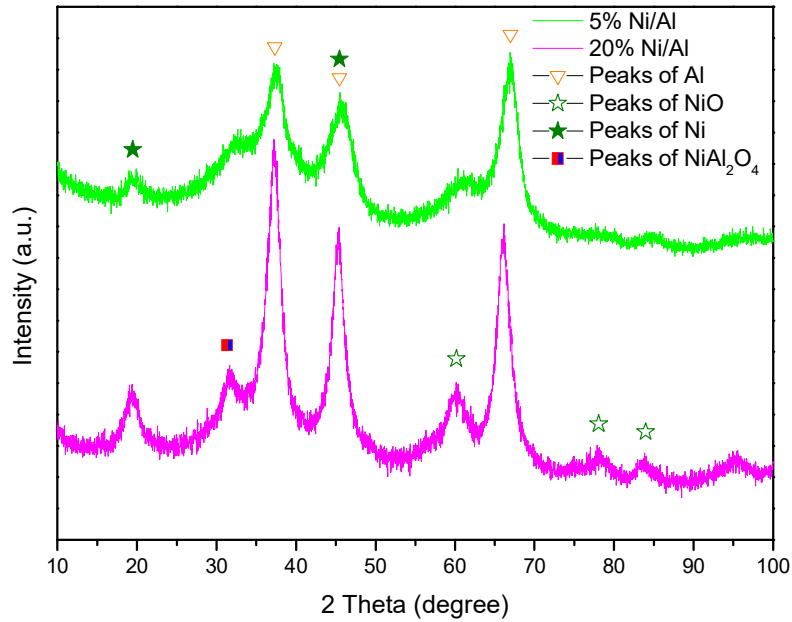


Figure 21: XRD results for 5% Ni/Al and 20% Ni/Al.

The easily identified peaks centered at 37°, 45.5°, and 67°, confirmed the presence of aluminum. The presence of Ni in the cubic form is seen at peaks of 19°, and 45.5°. The cubic NiO was detected in the XRD results, at peaks of 59.6°, 77.8°, and 84°. Finally, the NiAl₂O₄ was detected at the peak of 31.5° more expressively in the sample of 20% Ni/Al. Nickel aluminate, (NiAl₂O₄) is a transition metal spinel, which falls under the category of normal spinel with aluminum in octahedral sites and nickel in tetrahedral sites. NiAl₂O₄ acts as catalytic support, which can provide a stabilizing effect while maintaining a high degree of chemical inertia. In general, high surface area materials will have the small particle size^{108, 109}. Another element that should be highlighted is the presence of cubic NiO. Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide, most attracting features of NiO are: excellent durability and electrochemical stability; low material cost; promising ion storage material in terms of cyclic stability; large span optical density; and the possibility

of manufacturing by variety of techniques¹¹⁰. As matter of fact, it is possible to distinguish that all peaks found in the spectrum are more intense for the 20% Ni/Al sample.

The samples of 5 %Ni/Al₂O₃ were also submitted to X-ray diffraction analysis, and the results are shown in the following Figure 22.

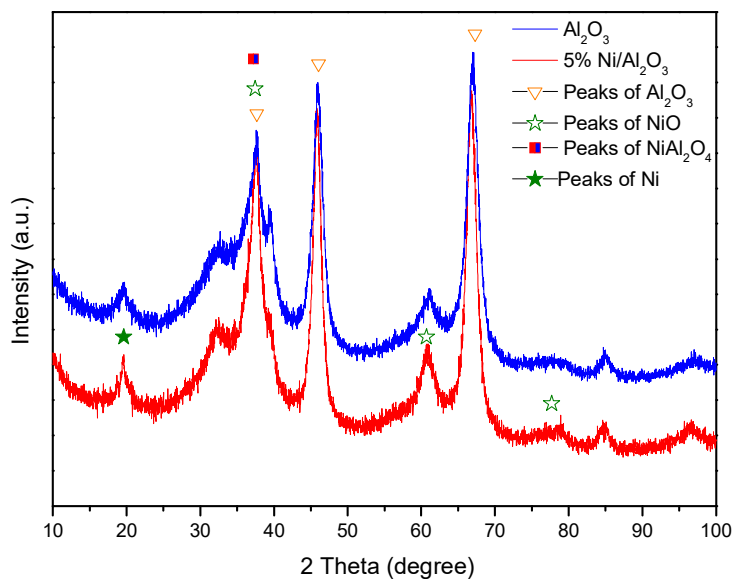


Figure 22: XRD results for Al₂O₃ and wetness impregnation of 5% Ni/Al₂O₃.

In this catalyst, Al₂O₃ phases and nickel crystalline phases were detected. The overlap of Al₂O₃ and nickel oxide form the composite layer of NiO - Al₂O₃ which is an amorphous phase. The smaller amount of Ni interacts with alumina and form nickel aluminate (NiAl₂O₄) composite layer which is an amorphous phase or a crystalline phase with crystallite sizes smaller than the detection limit of XRD.

XRD scans show some diffraction peaks at 37.5°, 46°, and 67°, which were attributed to the cubic structure of Al₂O₃. The cubic NiO peaks were observed within 37.5°, 61°, and 79°. The Peak observed in 37.5° attributing to NiAl₂O₄ peak, this peak in the sample of 5% Ni/Al₂O₃ is displaced, this is associated with the calcination temperature.

4.1.3 Catalyst production yield

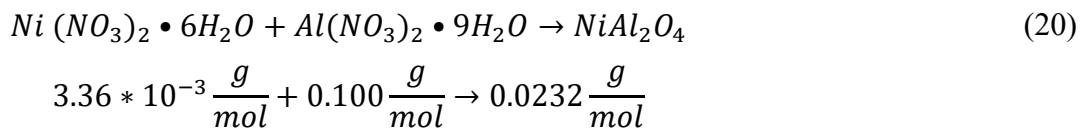
After interpreting XRD, it was possible to detect the presence of Nickel Aluminate in both spectra, and from the identification of this element, we intend to quantify the yield of catalyst production.

For the 5% Ni/Al catalyst production, the values identified in the following Table 3 were applied.

Table 3: Catalyst production data of 5% Ni/Al.

The catalyst of 5% Ni/Al			
Component	Molar Mass (g/mol)	Weight used (g)	Mole (mol)
Ni(NO ₃) ₂ •6H ₂ O	290.8	0.98	3.36•10 ⁻³
Al(NO ₃) ₃ •9H ₂ O	375.1	37.71	0.100
Nickel Aluminate	Molar Mass (g/mol)	Catalyst Production (g)	Mole (mol)
NiAl ₂ O ₄	176.6	4.1	0.0232

Thus, to calculate the production yield of this catalyst, the first step is analyzing the balanced chemical reaction, and find out if there is any limiting reagent in this reaction. Exemplified in the following equation (20).



Now check for any limiting reagent failures that would cause it to stop immediately, even if the other reagent is present so that a Cross-multiplication applies to the two elements that appear in the reaction. The calculation for nickel is described in equation (21).

$$3.36 * 10^{-3} \text{ g/mol of Ni} \quad (21)$$

$$\rightarrow 0.0232 \text{ g of NiAl}_2\text{O}_4$$

$$1.68 * 10^{-3} \text{ g/mol of Ni} \rightarrow x$$

$$x = 0.0116 \text{ g of NiAl}_2\text{O}_4$$

For aluminum reagent, the same calculation was followed, equation (22).

$$\begin{aligned}
 &0.100 \text{ g/mol of Al} && (22) \\
 &\rightarrow 0.0232 \text{ g of NiAl}_2\text{O}_4 \\
 &0.05 \text{ g/mol of Ni} \rightarrow x \\
 &x = 0.0116 \text{ g of NiAl}_2\text{O}_4
 \end{aligned}$$

From the equations above, it is noted that in this reaction there is no occurrence of limiting reagent, with equality in the reaction, so we calculate the production yield. Using again cross-multiplication.

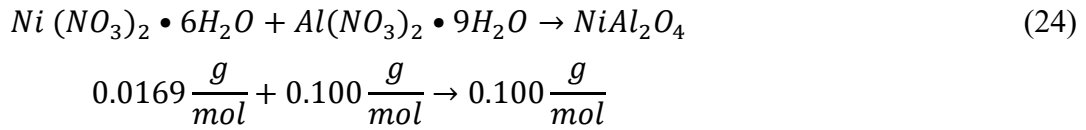
$$\begin{aligned}
 &0.1033 \text{ (theoretical yield)} \rightarrow 100\% && (23) \\
 &0.0232 \text{ (real yield)} \rightarrow x \\
 &x = 22.4\%
 \end{aligned}$$

Therefore, the real yield for the catalyst containing 5% nickel over aluminum was 22.4%. From now on, the same calculations will be followed to find the yield of the other catalysts. The next catalyst to be analyzed (20% Ni/Al) contains the same elements in its composition, differing only in the concentration of the above-mentioned catalyst. In this way, it will be possible to analyze whether the nickel concentration interferes with catalyst production. The data of the elements used in the production of this catalyst can be seen in Table 4.

Table 4: catalyst production data of 20% Ni/Al

The catalyst of 20% Ni/Al			
Element	Molar Mass (g/mol)	Weight used (g)	mol
Ni(NO ₃) ₂ •6H ₂ O	290.8	4.91	0.0169
Al(NO ₃) ₃ •9H ₂ O	375.1	37.5	0.100
Nickel Aluminate	Molar Mass (g/mol)	Catalyst Production (g)	mol
NiAl ₂ O ₄	176.6	5.22	0.0295

In order to calculate the production yield, the balance chemical of the reaction is analyzed. As described in equation (24).



Verification of occurrences of limiting reagents. Equation (25) for nickel reagent:

$$\begin{aligned} 0.0169 \text{ g/mol of Ni} &\rightarrow 0.0295 \text{ g of NiAl}_2\text{O}_4 & (25) \\ 8.45 * 10^{-3} \text{ g/mol of Ni} &\rightarrow x \\ x &= 0.01475 \text{ g of NiAl}_2\text{O}_4 \end{aligned}$$

Now we see, if in this case, aluminum may be a limiting reagent. Equation (26).

$$\begin{aligned} 0.100 \text{ g/mol of Al} &\rightarrow 0.0295 \text{ g of NiAl}_2\text{O}_4 & (26) \\ 0.05 \text{ g/mol of Ni} &\rightarrow x \\ x &= 0.01475 \text{ g of NiAl}_2\text{O}_4 \end{aligned}$$

As there is no occurrence of limiting reagents, the production yield is calculated:

$$\begin{aligned} 0.1169 \text{ (theoretical yield)} &\rightarrow 100\% & (27) \\ 0.0295 \text{ (real yield)} &\rightarrow x \\ x &= 25.2\% \end{aligned}$$

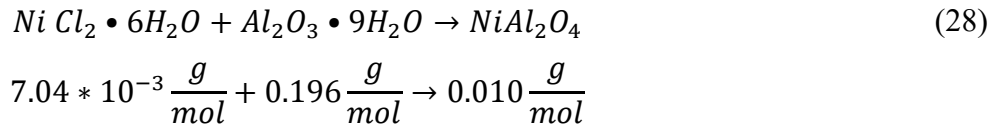
The catalyst of 20% Ni/Al had a real yield of 25.2%, compared with the 5% Ni/Al catalyst, the 20% Ni/Al catalyst presented a higher percentage yield than the first one of 2.8%, but this increase in the amount of production is not directly linked to the efficiency of the catalysis process.

The same calculations were used for the 5% Ni/Al₂O₃ catalyst, but the chemical elements used are others, so the amount of the elements is shown in Table 5 below, followed by the yield calculations.

Table 5: catalyst production data of wet impregnation of Ni/Al₂O₃.

Ni/Al₂O₃ Wet impregnation Catalyst			
Element	Molar Mass (g/mol)	Weight used (g)	mol
NiCl ₂ •6H ₂ O	237.9	1.67	7.04*10 ⁻³
Al ₂ O ₃	101.96	2	0.196
Nickel Aluminate	Molar Mass (g/mol)	Catalyst production (g)	Mol
NiAl ₂ O ₄	176.6	1.78	0.010

Balanced chemical reaction steps:



Verification of occurrences of limiting reagents. Equation (29) for nickel:

$$\begin{aligned} 7.04 * 10^{-3} g/mol \text{ of Ni} &\rightarrow 0.010 g \text{ of NiAl}_2O_4 & (29) \\ 3.52 * 10^{-3} g/mol \text{ of Ni} &\rightarrow x \\ x = 5 * 10^{-3} g \text{ of NiAl}_2O_4 \end{aligned}$$

And, equation (30), for alumina.

$$\begin{aligned} 0.196 g/mol \text{ of Al}_2O_3 &\rightarrow 0.010 g \text{ of NiAl}_2O_4 & (30) \\ 0.098 g/mol \text{ of Ni} &\rightarrow x \\ x = 5 * 10^{-3} g \text{ of NiAl}_2O_4 \end{aligned}$$

As there is no occurrence of limiting reagents, the production yield is calculated:

$$\begin{aligned} 0.2030 \text{ (theoretical yield)} &\rightarrow 100\% & (31) \\ 0.010 \text{ (real yield)} &\rightarrow x \\ x = 4.92\% \end{aligned}$$

The nickel and alumina catalyst presented the lowest yield in the production of 4.92%.

4.2 EXPERIMENTAL REACTION

4.2.1 CNTs production

As mentioned above, 10 g of polymer and 2 g of catalyst (20% Ni/Al) were placed in vitreous carbon crucibles and allocated in the reactor. The vitreous carbon crucibles containing polymer were allocated at the top of the reactor, and the vitreous carbon crucibles with catalyst at the bottom. In Figure 23 it can be seen both crucibles.



Figure 23: Crucibles containing polymer (low-density polyethylene) and catalyst (20% Ni/Al).

The experiment with the tubular furnace started at room temperature of 26 °C in all zones (TC1, TC2, and TC3). Controls were programmed to raise the temperature to 10 °C/min, and the experiment was then set to time zero. The following Table 6 exemplifies the temperatures collected over time.

Table 6: Phases in the temperature increase of the tubular furnace.

Phase 1 (20 min of the experiment)			
Zone	TC1	TC2	TC3
Temperature (°C)	77	109	200
Phase 2 (45 min of the experiment)			
Zone	TC1	TC2	TC3
Temperature (°C)	187	260	500
Phase 3 (1:00 hours of the experiment)			
Zone	TC1	TC2	TC3
Temperature (°C)	334	479	750
Phase 4 (1:50 hours of the experiment)			
Zone	TC1	TC2	TC3
Temperature (°C)	505	705	1000

After the TC3 zone reached 1000 °C, the vitreous carbon crucibles were kept at this temperature inside the reactor for one hour, after that time the reactor was turned off, and when the temperature inside the reactor returned to ambient, the crucibles were removed from the reactor. In Figure 24 (catalyst after) below is the vitreous carbon crucibles after being removed from the tubular oven.



Figure 24: Crucibles containing carbon structures by chemical vapor deposition.

In Figure 24 the crucible with catalyst before the procedure appears to be more empty, and the crucible with catalyst after the procedure appears to be slightly fuller and in black color. The crucible with catalyst after the procedure appears to be fuller due to the process of chemical vapor deposition (CVD), which is a synthesis process that the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit. Therefore, the carbon evaporates, depositing in the catalyst causing carbon structures to grow¹¹¹. In turn, black coloring may indicate the presence of carbon.

As stated above, the analysis used to detect the presence of carbon structures was scanning electron microscopy (SEM). Figure 25 shows the sample collected.

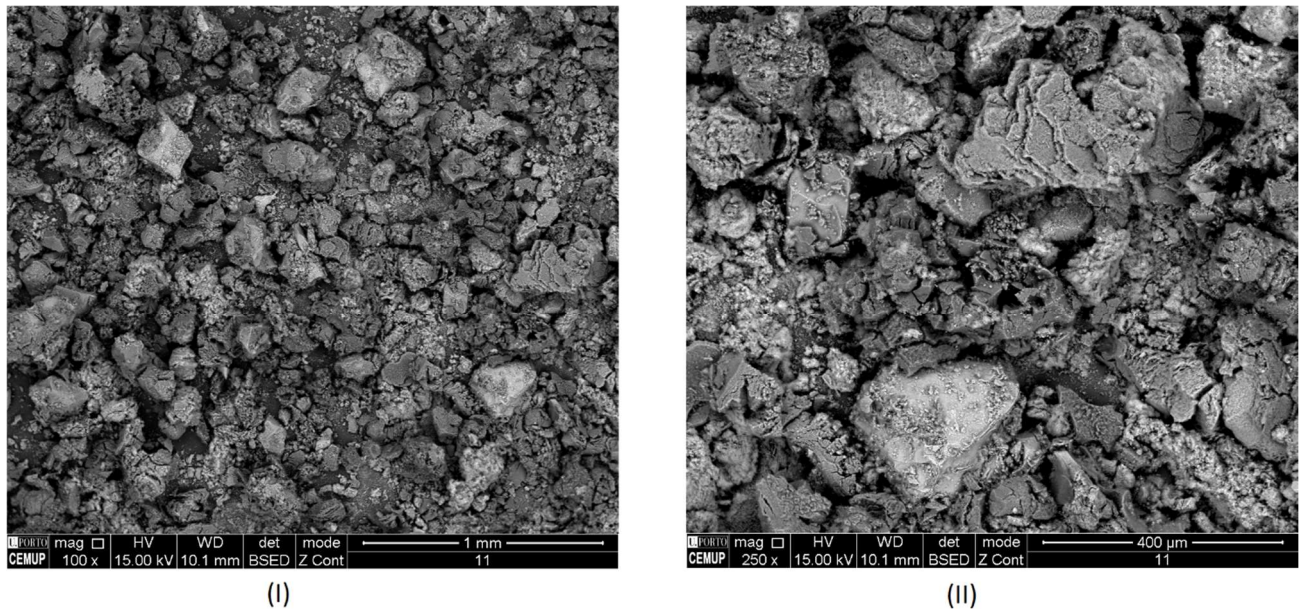


Figure 25: Analysis of carbon structures (SEM): (I) 1mm of size; (II) 400 μm of size.

The samples represented in Figure 25 (I), are in an approximation of 100 x, and scale of 1 mm, and the Figure 25 (II), 250 x of approximation and 400 μm of scale, but in these images it is not possible to identify the presence of carbon nanotubes, therefore, five readings of other points in greater approximations were performed. Within this sample, five points were chosen to be analyzed on enlargement, the chosen points are represented in Figure 26.

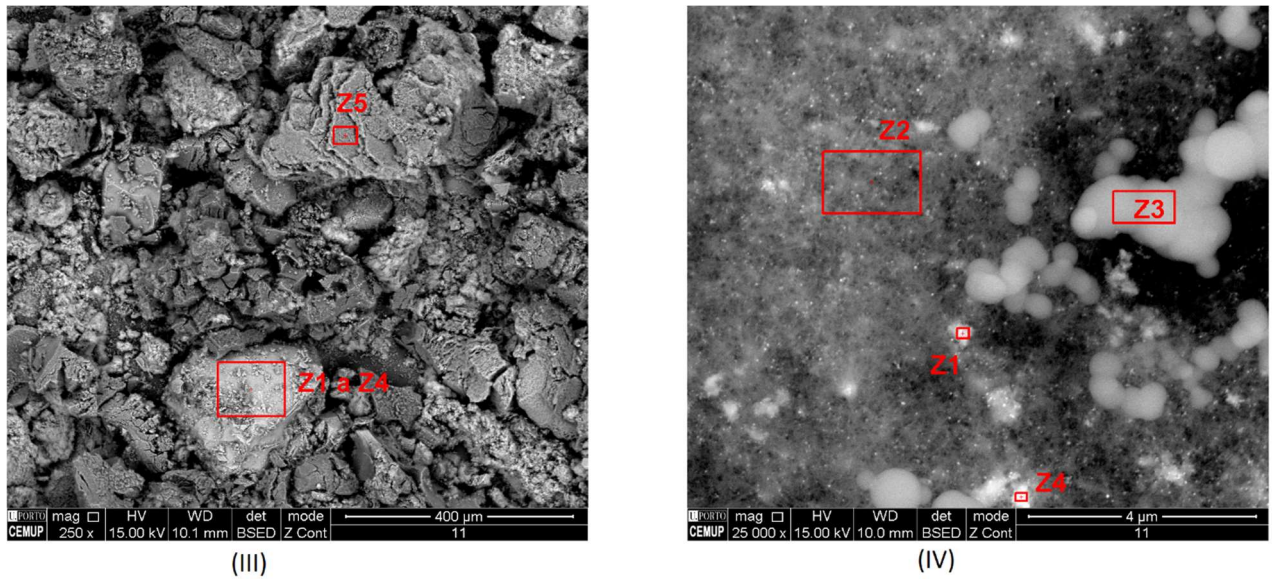


Figure 26: Points are chosen: (III) Z1 to Z4 and Z5 scale of 400 μm ; (IV) Z1, Z2, Z3 and Z4 scale of 4 μm .

In Figure 26, the Electron Backscatters Diffraction (EBSD) was used, this technique allows the crystallographic analysis of materials, i.e. the determination of the crystalline orientation punctually or in specific areas¹¹². In Figure 26 (III) it is interesting to note that the bright parts may represent the presence of metals. the study of the microstructure of metals it's called Metallography is used to reveal the microstructure of metals, which is affected by alloy composition and processing conditions; In most of the time, the distinction between microstructural constituents is hindered by the lack of contrast between them or between the matrix, The key to obtaining an accurate interpretation of a microstructure is a properly prepared specimen which is truly representative of the material being examined, so it is advisable to subject the sample to a chemical attack, whose function is to delineate the contours between phases and grains, increase contrast and enable their visualization and location under the microscope^{112, 113}. As shown in Figure 26 (IV) it is important to note that the little white dots representing the co-oxide Nickel and Alumina catalyst. In Figure 27 (V) it's possible to see the points Z1, Z2, Z3, and Z4, in another mode, the secondary electron (SE) these electric are low energy and form high-resolution images.

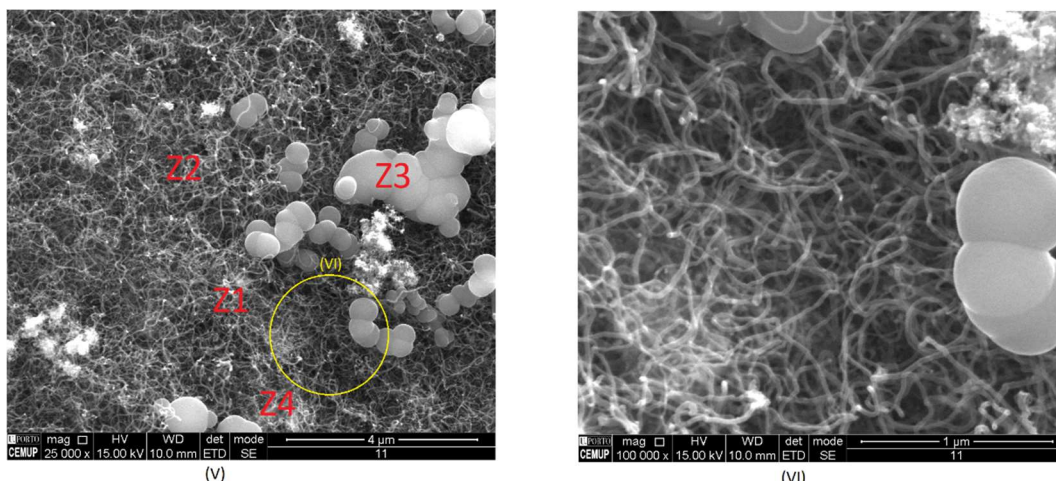


Figure 27: Mode SE: (V) Z1, Z2, Z3 and Z4 size of 4 μm ; (VI) Image, size of 1 μm .

About Figure 27 (V) it is possible to observe more clearly the thin and elongated structures that are the carbon nanotubes, and carbon spheres, which are the larger circular structures. As well as it is possible to identify the white dots, being them the catalyst of nickel and alumina, from which the carbon nanotubes grow, it is well known that catalyst particle size is a decisive parameter in growing CNTs, in the catalytic chemical vapor deposition (CVD) method, the diameter of grown CNTs is almost equal to that of the catalyst particles. However, for the determination of the diameters, as well as the identification of multiple or single walls (MWNTs, SWNTS), it is necessary to read the samples by TEM (Transmission Electron Microscopy), but in this investigation, only the SEM analysis was performed. Thus, it was identified by SEM that carbon nanotubes found in this experiment have a size ranging from 1 μm to 4 μm . The structures in Figure 27 (VI) have a scale of 1 μm , may give an illusion of the structure being hollow, which is important because it classifies this structure into nanotubes, but confirmation of this information is only possible with TEM analyzes¹⁴.

In turn, in Figure 28, we will see the amount of each element found, in this case, we found carbon, oxygen, nickel, and aluminum at each point for Z1, Z2, Z3, and Z4.

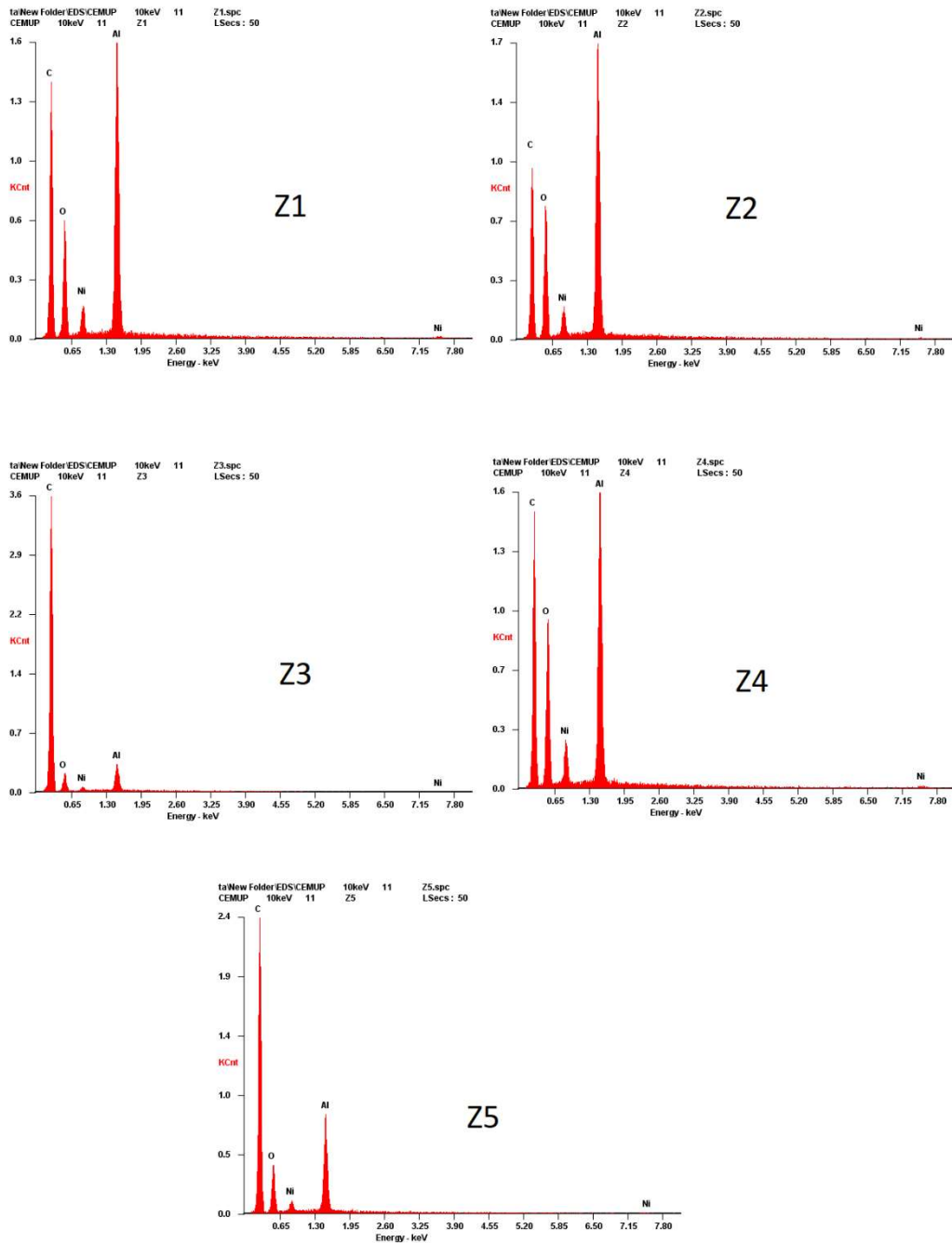


Figure 28: Spectra for element identification, carbon, oxygen, nickel, and aluminum: Z1; Z2; Z3; Z4; Z5.

Firstly, it is noted that four elements (C, O, Ni, and Al) were found in the four spectra (Z1, Z2, Z3, Z4, and Z5), but in different quantities for each one. The presence of oxygen is explained due to an unforeseen accident, as the reactor still running and hot had a decoupling from the bottom due to pressure, or human error, and this caused it to oxygenate, because as the experiment was performed in an inert atmosphere created by the circulation of nitrogen, the presence of oxygen was not expected. While the presence of carbon was found in higher

concentrations in the following order of points, Z3, Z5, Z4, Z1, and Z2. Hereby from Figure 27 it is known that the points Z3, Z5, Z4, and Z1 are carbon spheres, which explains the presence of a higher carbon concentration, however the sample Z1 is a collection of carbon nanotubes. By contrast, the presence of catalysts is found in smaller quantities in the Z3 sample, and relatively equal in the other points.

4.2.2 Catalytic Wet Peroxide Oxidation (CWPO)

Among all the catalysts produced (5% Ni/Al, 20% Ni/Al, 5% Ni/Al₂O₃ and, Fe + Ni/Al₂O₃), to perform the CWPO experiment, only three catalysts were chosen. Therefore, 20% Ni/Al catalyst was chosen for its higher concentration and better spectral results. The catalyst Fe + Ni/Al₂O₃ was chosen too because they have iron in their structure. And, alumina to determine if catalyst production is more effective than using the commercial product.

In doing so, after performing the CWPO experiment, the samples were analyzed for Paracetamol determination, by the High-Performance Liquid Chromatography (HPLC). In order to determine H₂O₂, we use the UV/VIS spectrometer apparatus. Thus, the results obtained from paracetamol and hydrogen peroxide concentration for the three catalysts are shown in Figure 29.

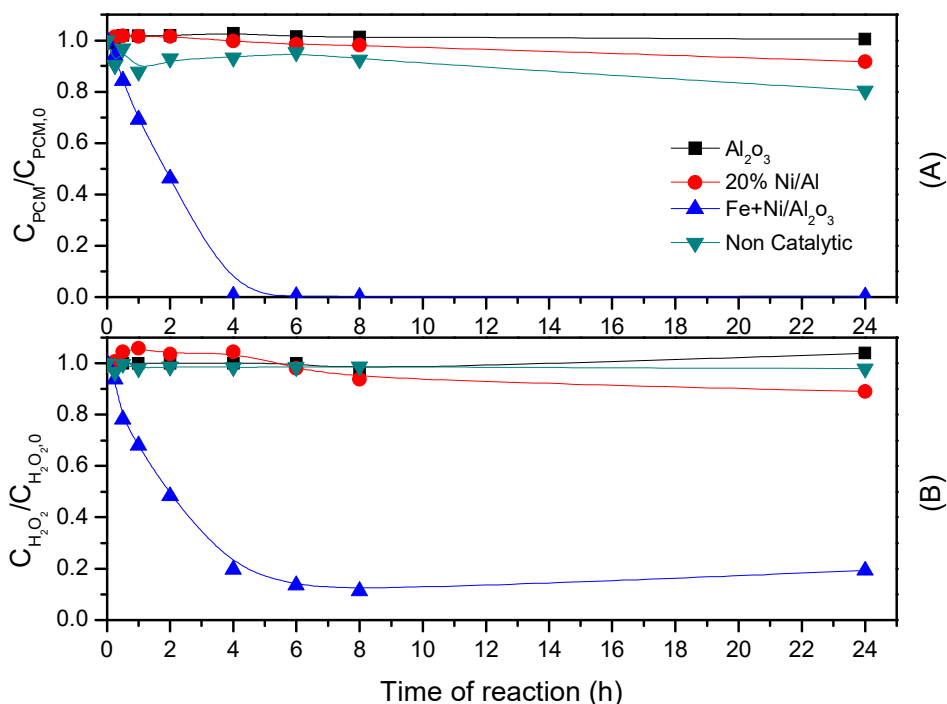


Figure 29: Normalized concentration of (A) PCM and of (B) H_2O_2 along reaction time.

Analyzing the concentration profile of paracetamol in Figure 29A, it is interesting to observe that the materials containing iron ($\text{Fe} + \text{Ni}/\text{Al}_2\text{O}_3$) showed catalytic activity, enabling the decomposition of H_2O_2 and allow to reach a conversion of hydrogen peroxide higher than 80% after 24 h. In addition, it is possible to conclude that the material with the best activity is the $\text{Fe} + \text{Ni}/\text{Al}_2\text{O}_3$, with the almost full conversion of paracetamol between 480 and 1440 min of reaction. While, the 20% Ni/Al catalyst showed an 11% conversion of hydrogen peroxide, which is low compared to the iron-containing sample. However, commercial alumina presented the most unsatisfactory conversion of only 2.3%, basically the same value as the reaction where no catalyst was applied.

Figure 29B supports the hypothesis that $\text{Fe} + \text{Ni}/\text{Al}_2\text{O}_3$ had the best activity, once that presented the faster conversion of H_2O_2 and paracetamol compared with the other materials. The best activity for the $\text{Fe} + \text{Ni}/\text{Al}_2\text{O}_3$ can be explained by the fact that between the catalyst, it's the only containing iron.

The iron-containing catalyst showed approximately zero conversion in time from 240 to 1440 min. In general, even at the low conversion of paracetamol in the application of the

catalyst of 20% Ni/Al, this catalyst still showed better results than using alumina or not applying catalysts.

Total organic carbon (TOC), were also performed with the samples withdrawn from the reaction media at different times. In general, carbon is present in two forms: inorganic and organic carbon (IC and OC, respectively) the TOC index measures both and subtracting inorganic carbon from total carbon produces TOC¹¹⁵. The result of the TOC measurement for the catalysts Al₂O₃, 20% Ni/Al, and Fe + Ni/ Al₂O₃ and the non-catalyst is shown in Figure 30.

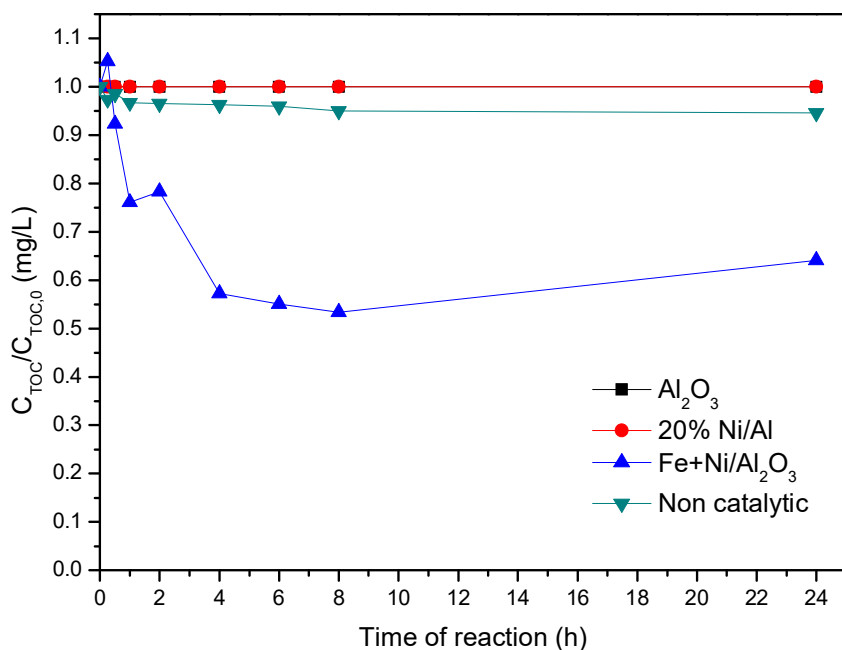


Figure 30: Normalized concentration of TOC for along time.

As can be observed that the ferrous material presented the higher conversions of TOC, which agrees with the results obtained so far for the paracetamol and H₂O₂ conversion. In fact, for all the three analyses the ascending order for the conversions is Fe + Ni/Al₂O₃, 20% Ni/Al, and alumina which gives more representativeness for the result, once that the tendency was obeyed for the correlated analysis. The catalyst with iron (Fe + Ni/ Al₂O₃) presented an appreciable conversion, in this case, with a conversion that reached an incredible 64% of mineralization. Comparing the results obtained by catalyst 20% Ni/Al the

result obtained wasn't much lower, 63% conversion. The use of commercial alumina is consistent with the other results and is not very useful compared to the non-catalyst results.

5 CONCLUSIONS AND FUTURE RESEARCH

5.1 CONCLUSION

As only one catalyst was analyzed for the production of carbon structures, it was not possible to compare its efficiency with other catalysts, but the result was satisfactory due to the production of carbon nanotubes and carbon spheres.

About the CWPO experiments, it was showed that the catalyst with iron is very efficient for paracetamol oxidation to carbon dioxide compared to the other catalysts produced, under soft conditions of temperature and pressure.

In general, it has been realized that even when a catalyst was not efficient in treating a specific environmental pollutant, it does not make it disposable. An example of this was the 20% Ni/Al catalyst, it did not produce sufficiently acceptable results in the CWPO process, which makes it not recommended for use on large scale, but their results for the production of CNTs were interesting enough to continue searching.

5.2 FUTURE RESEARCH

Four types of catalysts were produced by two different methods for the treatment of two distinct pollutants. It would be interesting if all the catalysts were tested in both pollutant mitigation methods (CWPO and CNTs production). And, due to the fact that iron-containing materials have better results in CWPO, an attractive way forward is to join efforts to produce an iron-based catalyst that is useful in the production of CNTs and treatment of acetaminophen.

In the case of CNTs, it is also important to test different polymers as well as a residual plastic test. With reference to the catalysts, the test of the different concentrations as the 5% Ni/Al and 20% Ni/Al catalysts had been proposed, and thus to analyze the interference of the amount of the transition metals. It is also suggested to perform the analysis by TEM, to have a better knowledge of the carbon structures produced.

In addition, a different model pollutant could be used in order to evaluate the versatility of materials and their catalytic activity in the CWPO of these compounds. Another

interesting analysis would be the use of the catalysts for the CWPO of real effluents, containing not only one pollutant but a set of pollutants. This would allow the evaluation of the catalysts in a different matrix, closer to reality.

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7 ADDENDUM

7.1 Ni/Al₂O₃ by wetness impregnation

The equation below exemplifies the calculation for the determination of 5% NiO:

$$\begin{aligned}\frac{x}{x+2} &= 5\% \rightarrow x = 0.05 * (x+2) & (4) \\ &\rightarrow x - 0.05x = 0.1 \\ &\rightarrow 0.95x = 0.1 \rightarrow x \\ &= 0.1\end{aligned}$$

Thus, to find the required moles, we divide the specified amount by the molar mass of NiO (74.69 g/mol), represented in the following equation.

$$NiO = \frac{0.1 \text{ g}}{74.69 \text{ g/mol}} = 1.33 * 10^{-3} \text{ mol} \quad (5)$$

However, the precursor used in this case was NiCl₂•6H₂O and this element has a molar mass of 237.9 g/mol and purity of 95 %. For this dilution correction and purity, calculations were required.

$$237.9 \frac{\text{g}}{\text{mol}} * 1.33 * 10^{-3} \text{ mol} = 0.318 \text{ g} \quad (6)$$

Purity Calculation:

$$\begin{aligned}0.318 \text{ g} - 95 \% & & (7) \\ x - 100\% & \\ x = 0.335 \text{ g} & \end{aligned}$$

Calculation of the required dilution:

$$\begin{aligned}0.335 \text{ g} - 2 \text{ mL} & & (8) \\ x - 10 \text{ mL} & \\ x = 1.677 \text{ g of } Ni(NO_3)_2 \cdot 6H_2O & \end{aligned}$$

The following equation exemplifies the calculation for the determination of 5% NiO:

$$\begin{aligned}\frac{x}{x+2} &= 5\% \rightarrow x = 0.05 * (x+2) & (9) \\ &\rightarrow x - 0.05x = 0.1 \\ &\rightarrow 0.95x = 0.1 \rightarrow x = 0.1 \text{ g}\end{aligned}$$

7.2 Ni-Al Co-Oxide

And, the following equation exemplifies the calculation for the determination of 20% NiO:

$$\begin{aligned} \frac{x}{x+2} = 20\% \rightarrow x &= 0.2 * (x+2) & (10) \\ \rightarrow x - 0.2x &= 0.4 \rightarrow 0.8x \\ &= 0.4 \rightarrow x = 0.5 \text{ g} \end{aligned}$$

Thus, to find the required molality of 5% Ni (0.1 g), we divide the specified amount by the molar mass of NiO (74.69 g/mol), represented in the following equation.

$$\begin{aligned} NiO &= \frac{0.1 \text{ g}}{74.69 \text{ g/mol}} & (11) \\ &= 1.33 * 10^{-3} \text{ mol} \end{aligned}$$

However, the precursor used in this case was $Ni(NO_3)_2 \cdot 6H_2O$ and this element has a molar mass of 290.81 g/mol and purity of 99%. For this dilution correction and purity, calculations were required.

$$290.81 \frac{\text{g}}{\text{mol}} * 1.33 * 10^{-3} \text{ mol} = 0.389 \text{ g} \quad (12)$$

Calculation of the required dilution:

$$\begin{aligned} 0.389 \text{ g} - 10 \text{ mL} & & (13) \\ x - 25 \text{ mL} \\ x &= 0.974 \text{ g} \end{aligned}$$

Purity Calculation:

$$\begin{aligned} 0.974 \text{ g} - 99\% & & (14) \\ x - 100\% \\ x &= 0.983 \text{ g of } Ni(NO_3)_2 \cdot 6H_2O \end{aligned}$$

Thus, to find the required molality of 20% Ni (0.5 g), we divide the specified amount by the molar mass of Al_2O_3 (101.9 g/mol) needed, the following procedure was performed:

$$Al_2O_3 = \frac{2 \text{ g}}{101.9 \text{ g/mol}} = 0.0196 \text{ mol} \quad (15)$$

However, in alumina, we have 2 mol aluminum, and in this case, we use $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the precursor, therefore the following calculations were performed:

$$\begin{aligned} \text{Al} &= 2 * 0.196 = 0.0392 \text{ mol} & (16) \\ 0.0392 \text{ mol} * 375.13 \text{ g} \\ &= 14.70 \text{ g of } \text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} \end{aligned}$$

This calculation also required correction of dilution:

$$\begin{aligned} 14.70 \text{ g} - 10 \text{ mL} \\ x - 25 \text{ mL} \\ x = 36.75 \text{ g} & (17) \end{aligned}$$

And correction of purity:

$$\begin{aligned} 36.75 \text{ g} - 98\% & (18) \\ x - 100\% \\ x = 37.5 \text{ g} \end{aligned}$$

7.3 Tubes and flange installation

- A. Place the tube inside the oven, on top. Support it comfortably at a height below.
Fit the fiber strap around the tube.

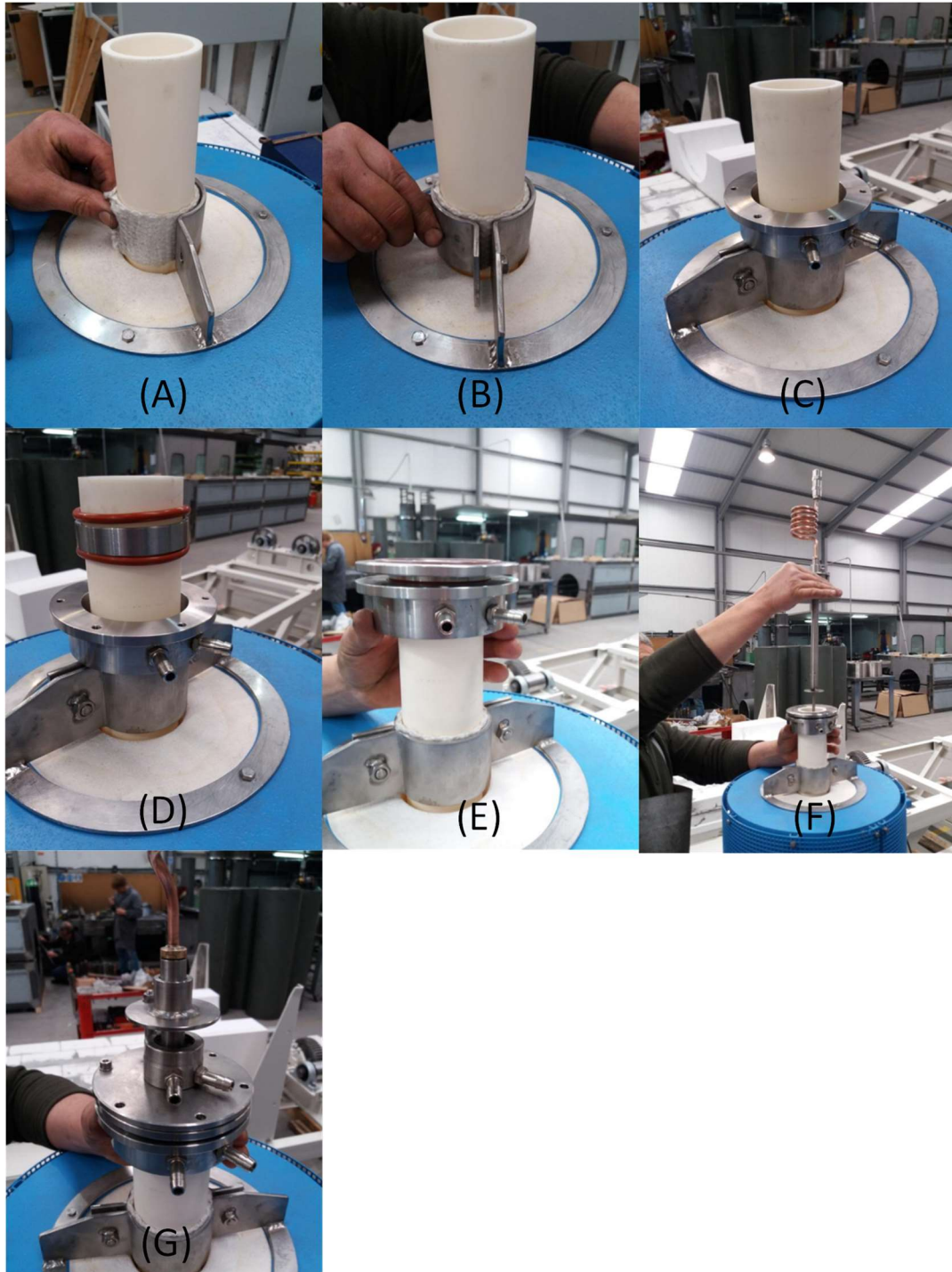


Figure 31: Steps about how to mount the flanges.

- B. Carefully place the removable part of the clamp and tighten the screws until the tube is secure.
- C. The next steps describe how to mount the flanges. Place the flange with the fittings for the water circuit.

- D. Place the first o'ring, the internal ring and the second o'ring.
- E. The above-described parts are adjusted so that the second o-ring is close to the end of the tube. Place the outer ring.
- F. Insert the cover assembly
- G. Tighten the screws. The same process is repeated for the lower flange.