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COMPARATIVE LIFE-CYCLE ASSESSMENT OF THE PRODUCTION OF 3YSZ BY CO-PRECIPITATION PROCESS AND EMULSION DETONATION SYNTHESIS

Dissertação no âmbito do Mestrado Integrado em Engenharia Mecânica, na área de Energia e Ambiente orientada pelo Professor Doutor Ricardo António Lopes Mendes e Doutor Carlos Miguel Baptista Ferreira apresentada ao Departamento de Engenharia Mecânica da Universidade de Coimbra.

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Comparative life-cycle assessment of the production of 3YSZ by co-precipitation process and emulsion detonation synthesis

A dissertation submitted in partial fulfilment of the requirements for the degree of Master in Mechanical Engineering in the speciality of Energy and Environment.

Comparação de ciclo de vida da produção de 3YSZ através do processo de co-precipitação e *emulsion detonation synthesis*

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Abstract

Nanomaterials are an emerging technology, as they display unique physio-chemical and mechanical properties due to their nanosize. This makes them useful to a multitude of industry sectors such as the healthcare, automotive, and electronics industries. A nanomaterial with very interesting properties and applications is zirconia doped with a 3% molar percentage of yttria, named yttria-stabilized zirconia (3YSZ). This material presents excellent mechanical, thermal and electrical properties such as high toughness and resistance to crack propagation, low thermal conductivity, and great ionic conductivity. This makes it useful to a wide array of applications, such as bioceramics, solid oxide fuel cells (SOFC) and thermal barrier coatings.

The nanotechnology global market is rapidly increasing, and with it, also their potential release into the environment. Concerns are raised, related with their potential ecotoxicity and health issues. Therefore, nanotechnology must be developed alongside sustainable strategies to allow its evolution and continued expansion. Comprehending the cause-effect relationship between nanomaterial production and the correlated environmental impacts is highly important. For that, the life-cycle assessment (LCA) methodology is incredibly useful, as it quantifies the environmental impacts associated with different products and systems, allowing industries to benchmark their production processes and sustainably evolve and develop.

The present study applies the LCA methodology for two different methods of 3YSZ production: the co-precipitation process and the emulsion detonation synthesis (EDS). First, a literature review was performed, in order to understand and define the goal and system boundaries of this study, along with an analysis of the production processes, in order to create a life-cycle inventory (LCI) for both methods and thus, to be able to quantify the environmental impacts associated with each process. For this study, a cradle-to-gate analysis was used, with the functional unit being defined as 1 kg of produced 3YSZ nanomaterial. The chosen LCIA method used was the ILCD 2011 Midpoint, where ten impact categories were selected.

Many data gaps existed in the *Ecoinvent* v3 database, so during this thesis, the inventory for 8 chemicals missing from the database were developed and assessed, in terms of their potential environmental impacts. This was possible, through extensive research and using mostly stoichiometric calculations and some assumptions. The missing chemicals were yttrium oxide, nitrate, and chloride; zirconyl chloride; zirconium basic carbonate and sulphate; sodium carbonate; and sodium zirconium silicate. This inventory creation and database strengthening was one of the main objectives of this thesis.

Finally, by assessing the potential impacts caused by the co-precipitation and EDS methods, an environmental comparison was possible and results were obtained. Overall, the EDS method presented environmental benefits in most of the relevant impact categories. However, for some impact categories, the EDS method is the most impactful of the processes, in particular the ozone depletion, human toxicity (non-cancer effects) and freshwater toxicity impact categories. The main contributors to the co-precipitation environmental impacts were zirconyl chloride, ethanol usage and energy consumption. Regarding the EDS method, the largest contribution came from zirconium basic carbonate and ammonium nitrate production. Therefore, co-precipitation is a very energy-intensive process and consumes large amounts of ethanol and water from the washing cycles. The EDS method does not present any of these characteristics, but the precursors it uses, especially zirconium basic carbonate and ammonium nitrate, contribute significantly to the impacts, being very harmful and detrimental to the environment.

Keywords: Life-cycle assessment (LCA), yttria-stabilized zirconia, co-precipitation, emulsion detonation synthesis (EDS), environmental impacts.

Resumo

Os nanomateriais são uma tecnologia emergente, pois apresentam propriedades físico-químicas e mecânicas únicas devido ao seu tamanho nano. Isso torna-os úteis para uma infinidade de setores da indústria, como saúde, automóvel e eletrónica. Um nanomaterial com propriedades e aplicações extremamente interessantes é a zircónia dopada com uma percentagem molar de 3% de ítria ou, simplesmente, zircónia estabilizada com ítria (3YSZ). Este material apresenta excelentes propriedades mecânicas, térmicas e elétricas, como alta tenacidade e resistência à propagação de fendas, baixa condutividade térmica e grande condutividade iónica, tornando-o útil para uma vasta gama de aplicações, como biocerâmica, *solid oxide fuel cells* (SOFC) e revestimentos para barreiras térmicas.

O mercado global da nanotecnologia está a crescer rapidamente e, com ele, também o potencial destes serem libertados no meio ambiente. Muitas preocupações são levantadas, relacionadas com a sua potencial ecotoxicidade e problemas de saúde relacionados. Dessa forma, a nanotecnologia deve ser desenvolvida em conjunto com estratégias sustentáveis , para conseguir evoluir e manter a sua expansão contínua. É muito importante compreender a relação causa-efeito entre a produção de nanomateriais e os seus impactes ambientais. Para tal, a metodologia de análise de ciclo de vida (ACV) é extremamente útil, pois quantifica os impactes ambientais associados a diferentes produtos e sistemas, permitindo que as indústrias desenvolvam os seus processos de produção de forma sustentável.

O presente estudo aplica a metodologia ACV em dois métodos diferentes de produção de 3YSZ: o processo de co-precipitação e a *emulsion detonation synthesis* (EDS). Especificamente, os impactes ambientais destes são estudados apenas na produção deste nanomaterial. Primeiramente, foi realizada a revisão de literatura, de maneira a entender e definir o objetivo e limites do sistema em estudo, juntamente com uma análise destes processos, para criar um inventário dos fluxos de materiais e energia (consumidos ou libertados) para ambos os métodos e, assim, poder quantificar os impactes ambientais associados. O método para avaliação de impactos utilizado foi o ILCD 2011 Midpoint, do qual foram analisadas dez categorias de impacto.

Devido à falta de algumas substâncias na base de dados *Ecoinvent* v3, durante o desenvolvimento desta tese, foram criados o inventário de 8 produtos químicos, para poder quantificar os seus potenciais impactes ambientais. Isso foi possível, através da extensa pesquisas e estudo de vários artigos de literatura e usando principalmente cálculos estequiométricos e algumas simplificações. Os produtos químicos em falta eram óxido, nitrato e cloreto de ítrio; cloreto e carbonato básico e sulfato de zircónio; carbonato de sódio; e *sodium zirconium silicate*. Esta criação de inventários e consequente fortalecimento das bases de dados era um dos principais objetivos desta dissertação.

Por fim, avaliando os potenciais impactes causados pelos métodos de co-precipitação e EDS, foi possível realizar uma comparação ambiental e obter resultados. No geral, o método EDS apresentou benefícios na maioria das categorias de impacte relevantes. No entanto, algumas apresentam o método EDS como o mais impactante dos dois, em particular as categorias de impacte de depleção da camada de ozono, toxicidade humana (efeitos não cancerígenos) e toxicidade aquática. Os maiores responsáveis para os impactes ambientais da co-precipitação foram o cloreto de zircónio, o consumo de etanol e consumo energético. Em relação ao método EDS, a maior contribuição veio da produção do carbonato básico de zircónio e do nitrato de amónio. Portanto, a co-precipitação é um processo muito intenso energeticamente e consome grandes quantidades de etanol e água deionizada nas suas lavagens. O método EDS não apresenta nenhuma dessas características, mas os precursores que utiliza, em especial o carbonato de zircónio e nitrato de amónio, contribuem enormemente para os impactes, sendo muito prejudiciais para o ambiente.

Palavras-chave: Análise de ciclo de vida (ACV), zircónia estabilizada com ítria, co-precipitação, *emulsion detonation synthesis* (EDS), impactes ambientais.

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ACRONYMS/ABBREVIATIONS

CO_2 – Carbon dioxide.

H_2O – Water.

H_2SO_4 – Sulfuric acid.

Na_2CO_3 – Sodium carbonate.

Na_2ZrSiO_5 – Sodium zirconium silicate.

Y_2O_3 – Yttrium oxide (Yttria).

3YSZ – 3% mol yttria-stabilized zirconia.

EDS – Emulsion detonation synthesis.

ENM – Engineered nanomaterials.

GWP – Global warming potential.

ICEV – Internal combustion engine vehicle.

LCA – Life-cycle assessment.

LCI – Life-cycle inventory.

LCIA – Life-cycle impact assessment.

LCT – Life-cycle thinking.

NGO – Non-governmental organizations.

R&D – Research and Development.

HCl – Hydrochloric acid.

$HDPE$ – High-density polyethylene.

HNO_3 – Nitric acid.

$NaCl$ – Sodium chloride.

$NaHCO_3$ – Sodium bicarbonate.

NH_4OH – Ammonium hydroxide.

SiO_2 – Silicon dioxide (Silica).

$Y(NO_3)_3 \cdot 6\,H_2O$ – Yttrium nitrate.

$YCl_3 \cdot 6\,H_2O$ – Yttrium chloride.

$Zr(OH)_2CO_3 \cdot ZrO_2$ – Zirconium basic carbonate.

$Zr(SO_4)_2 \cdot 4\,H_2O$ – Zirconium sulphate.

ZrO_2 – Zirconium oxide (Zirconia).

$ZrO(NO_3)_2 \cdot 6\,H_2O$ – Zirconyl nitrate.

$ZrOCl_2 \cdot 8H_2O$ – Zirconyl chloride.

$ZrSiO_4$ – Zirconium silicate (Zircon).

1. INTRODUCTION

1.1. Nanomaterials and Yttria-stabilized Zirconia

1.1.1. Nanomaterials and Properties

Nanotechnology promises to bring many benefits to a multitude of industry fields. It is an emerging technology that is thought by many as having the potential to completely change the way we live. The rising advances and growth of the nanomaterials market can be associated with their wide scope of applications in various industry sectors. To be able to achieve the most revolutionary applications that nanotechnology is envisioned to reach, ample research and development (R&D) is required by engineers and investigators, who will face many challenges [1].

Nanomaterials have brought the enhancement of many products and systems, pushing countries forward towards technological and economic progress. For instance, nanotechnology has generated new and growing opportunities in a wide range of sectors: from the chemical, healthcare, energy, electronics, construction and agriculture sectors to aerospace and defence industries. Additionally, methods of synthesis which focus on environmental and healthcare protection are being progressively carried out [2].

Since their development, nanomaterials have been recognized for possessing enhanced or even unique optical, catalytic, and mechanical properties, primarily because of their nano size. Over the past decade, there has been an exponential growth in the development of new manufactured or engineered nanomaterials, such as nanopowders, nanofibers, nanowires and nanosheets. The abovementioned excellent physio-chemical properties and rising applications are causing a global increase in demand of these materials [3], [4].

Engineered nanomaterials (ENM's) are increasingly taking a notable portion of global economy's material flows. These are already providing many benefits, such as: reduction in material usage; improvements in energy efficiency; and better performance in various existing and new applications [5]. However, nanomaterials also present some disadvantages, such as their high cost and their potential (but rather unknown) environmental impacts, which future regulations may hamper the growth of the market.

Since the investments in the nanotechnology industry are increasing, its market is rapidly growing, along with the number of scientific studies, articles and patents regarding this topic. Between 2000 and 2016, the average annual increase of the number of these publications was about 15%, which is a reflection of nanotechnology development [6]. Furthermore, there is also an annual increase in the number of companies and the volume of marketed products, related to nanotechnology and nanomaterials. The average annual increase of the nanopowders industry is 15%, being the most developed commercial sector of the nanomaterials market. Also, metal oxide powders are the main type of nanomaterials produced, as seen in Figure 1.1 [7].

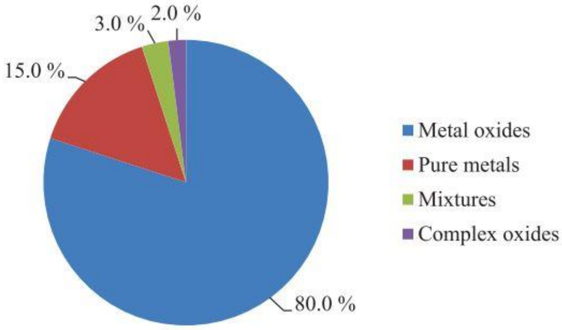

Figure 1.1. Nanopowders in the world market for nanomaterials [7].

It is expected that the nanomaterial market size is going to continue its rapid expansion. The *"Nanomaterials Market Size, Market Share, Application Analysis, Regional Outlook, Growth Trends, Key Players, Competitive Strategies and Forecasts, 2021 to 2029"* report states that the global nanomaterials market, in 2020, accounted for \$10.3 billion, and it is anticipated to grow to \$38.2 billion by 2029. That indicates a compound annual growth rate (CAGR) of 18% during that period. [4].

The escalating needs of the nanoscience and nanotechnology fields, the increasing development of different tools and methods for nanomaterial production, coupled with the support from governments and larger funding by organizations towards R&D (e.g., BASF, a leading nanotechnology company, spent almost €2.03 billion in R&D activities in 2021), is positively influencing the progress and growth of the global nanomaterials market [4].

1.1.2. Sustainability in Nanomaterials

Our understanding of nanomaterials is quickly advancing, and it can be cited from Andy *et al.* (2012) [3] that "*their use may be limited only by one's imagination*". This knowledge will surely help the growth of products and systems that use nanomaterials. Thus, a proportional increase in nanoparticle releases to the environment will likely occur. Research on this issue is vital and, therefore, a characterization of nanoparticle environmental behaviour and an accurate understanding of their potential environmental impacts is essential [3].

Numerous articles raise awareness to the potential environmental issues associated with nanomaterial production. On the topic of energy consumption, Khanna *et al.* (2008) [8] found that the life-cycle energy requirements for carbon nanofibers are 13-50 times that of traditional materials like primary aluminium and steel. In terms of health issues, Oberdörster (2004) [9] demonstrates that manufactured nanomaterials such as fullerenes present potential toxicity towards aquatic organisms, through body absorption and contamination. In addition, Ge *et al.* (2011) [10] evaluated the effects of the exposure of metal oxide nanoparticles like titania (TiO_2) and zinc oxide (ZnO) on soil bacterial communities, and found that it reduced microbial biomass and diversity and changed their compositions. According to Wang *et al.* (2017) [11] silver nanoparticles in plants, mainly silver sulfide (Ag_2S) were studied and found that exposure and absorption of these particles may have caused decreased plant growth. Also, Ghosh *et al.* (2017) [12] studied TiO_2 nanoparticles and confirmed its potential for damaging DNA material in both plant and human lymphocytes. Furthermore, Adams *et al.* (2006) [13] studied TiO_2, ZnO and silica (SiO_2) nanomaterials and showed they were hazardous to all tested organisms (bacteria and cells), with toxicity increasing with particle concentration. However, further research is required to fully understand and assess these problems while an LCA approach is required, as to decide if the benefits of nanomaterials outweigh the potential drawbacks.

Nanotechnology has been transitioning from academic and laboratory settings to the commercial markets, gradually invading the global economy. This justifies the need to understand their environmental implications, which requires the gathering of relevant information on these impacts, since there are still considerable uncertainties and data gaps on this subject. When better information and knowledge is gathered, the framework for estimating their emissions can be easily improved [5]. Therefore, the scientific efforts must be directed towards the development of sustainable strategies, tools and policies, that will ensure safe, responsible and efficient use of nanotechnology, especially in environmental terms [14].

1.1.3. Yttria-stabilized Zirconia

The main focus of this thesis will be towards a specific type of nanomaterial, which is zirconium oxide (ZrO_2) doped with 3% molar percentage of yttrium oxide (Y_2O_3). This material corresponds to 3% mol yttria-stabilized zirconia (3YSZ). The main goal of this study is to determine and evaluate the environmental impacts of producing 3YSZ and compare those impacts between two different methods of producing it.

Zirconium oxide or zirconia (ZrO_2) is a white crystalline metal oxide. It arises in nature as the mineral baddeleyite and can also be commonly obtained with zirconium recuperation from zircon ($ZrSiO_4$) as an intermediate product. Additionally, it can also be obtained by calcination (thermal decomposition) of zirconium compounds like zirconium carbonate or zirconium hydroxide [15].

Zirconia crystals have three polymorphic forms at atmospheric pressure: monoclinic (M), cubic (C), and tetragonal (T), with the monoclinic crystal structure presented at room temperature and the cubic and tetragonal crystal structures corresponding to high-temperature phases. Nonetheless, these high-temperature structured phases (T and C) can be stabilized through the addition of soluble oxides such as MgO, CeO_2, Al_2O_3, CaO and Y_2O_3, which are the most commonly used. As the concentration of the doping oxide is raised, monoclinic zirconia transforms into tetragonal form (partially-stabilized zirconia) and then into cubic form (fully-stabilized zirconia), retaining those respective structures at room temperature [16]. By preserving the tetragonal phase, it is possible to control the stress induced tetragonal-to-monoclinic (T ⟶ M) phase transformation, efficiently impeding crack propagation and therefore augmenting the toughness of the zirconia material [17]. This phenomenon is known as transformation toughening [18].

For the purpose of this study, we will be focusing on zirconia stabilized by the addition of yttrium oxide or yttria (Y_2O_3) and hence, it can be named yttria-stabilized zirconia (YSZ). In this case, a molar percentage of 3% yttria is added, creating a partially stabilized zirconia nanoceramic and can be written as $Y_{0.06}Zr_{0.94}O_{1.97}$ or 3YSZ.

Since phase stabilization is set out by doping ZrO_2 with Y_2O_3, the Y^{3+} atoms replace part of the Zr^{4+} atoms, being incorporated into the zirconia structure. This stabilizes the high-temperature polymorphic modifications of ZrO_2 and avoids the volume changes caused by phase transformations. Moreover, this creates a large number of oxygen vacancies, which immensely increases ionic conductivity, giving the material its electrolyte properties and making it useful in oxygen sensors and fuel cells [19, 20]. Also, 3 mol% yttria-stabilized zirconia (3YSZ) has been extensively applied in structural components and used in bioceramics with improved mechanical properties [21].

There are many different manufacturing processes for YSZ, which will be reviewed and discussed in Section 2.2. For this study, we only focus on two different methods of synthesis: the co-precipitation process, a more traditional, established and current process; and a recent and innovative technology named emulsion detonation synthesis (EDS method). Since this thesis intends to enhance and promote sustainability and environmental awareness, by using a life-cycle assessment (LCA) approach, we will be able to evaluate and compare the environmental impacts of both these processes.

1.2. Motivation

Sustainability has been one of the most emerging and discussed subjects in recent years. As climate change, resource depletion and pollution increasingly affect us, research and advances in technology have been directed towards ecological progress, in the sense of reducing our impacts on the environment.

Sustainable development was defined by the Brundtland Commission, formally known as the World Commission on Environment and Development (WCED), as being the *"development that meets the needs of the present without compromising the ability of future* *generations to meet their own needs"* [22]. For that purpose, more and more information is necessary to heed change and tackle these issues. For that reason, comprehending the cause-effect relationship between industries or product manufacturing and their environmental footprint and its repercussions is of great importance. To assess this, the life-cycle assessment (LCA) methodology can be very helpful.

The LCA methodology works as a structured approach to analyse material and energy flows. It sets sight on identifying and quantitatively comparing environmental impacts associated with different products, processes, and services. This way, LCA studies are an informative tool for decision-makers and authorities, allowing them to find better solutions for environmental improvement and lead to more sustainable practices and policies. Applying LCA to industries can also instigate companies to improve their sustainability actions, strive for better efficiency and allow them to benchmark the environmental performance of their products and services. The growing concerns of consumers regarding sustainability practices will reinforce the need for these positive changes [23].

In the foreseeable future, life-cycle thinking (LCT) and LCA studies will continue to grow in importance and relevance. The range of industry sectors using them and their applications has been expanding, progressing from academic context to being implemented in environmental policy-making. Sala *et al.* (2021) [24] shows us that LCT and LCA have been increasingly mentioned in European Union (EU) policies and communications. Examples of this are the *EU Ecodesign Directive* [25], the *EU Eco-label* [26], which is applied in situations such as the ease of product disassembly [27], the United Nations (UN) *"10 Year Framework of Programmes on Sustainable Consumption and Production Patterns (10YFP)"* [28] and the *UN Sustainable Development Goals* [29]. That growing trajectory can be predicted to continue for future policy developments.

Furthermore, LCA may well be gradually entering the political world, as even the European Parliament has suggested the development of life-cycle-oriented product policies (such as regulations, providing financial incentives for LCA studies or by improving access to data on public registers, linking companies and their products back to their emissions and impacts) [30].

Consumers, non-governmental organizations (NGO's) and governmental authorities have been requesting LCA studies for more rigorous eco-labelling. Industry sectors and companies are aware of these requests and acknowledge the possibilities for LCA in minimizing emissions, as well as reducing resources and energy depletion. LCA studies might not only apply as an instrument for environmental improvement but can also benefit industries in terms of saving costs. Considering the consumer interest on sustainability, LCA can also function as a marketing tool and bring competitive advantage [30].

Nanotechnology is quite a recent development and nanomaterials are intended to developed in accordance with the ever-evolving sustainable development ideas and regulations, due to many concerns on their environmental behaviour, discussed in Section 1.1.2. Therefore, this thesis sets sight on applying the LCA methodology towards the quantification of the environmental impacts of nanomaterials.

1.3. Aim and Research Objectives

The present thesis aims to assess and compare the life-cycle environmental impacts of the production of 1 kg of 3% mol yttria-stabilized zirconia (3YSZ) nanopowders, by two distinct methods of synthesis: the more traditional process of co-precipitation; and the innovative process of emulsion detonation synthesis (EDS). For that purpose, a life-cycle inventory for both processes was developed, considering their respective materials and energy flows.

The main reason for this study, is that nanomaterials aspire to be on the forefront of technology and, therefore, environmental research and practices must be taken into account in order to achieve a sustainable development. This master thesis can contribute to the increasing relevance of LCA studies in the nanopowder industry, since no LCA study were found about zirconia production by any of the two assessed processes. Therefore, this study intends to obtain answers to these main objectives:

- Assess the environmental impacts of producing 1 kg of 3YSZ nanopowders.

- Considering two different methods of synthesis (co-precipitation and EDS method), compare their results, considering a cradle-to-gate analysis on a wide range of impact categories, applying the ILCD 2011 Method.
- Discover which material or energy flow is the highest contributor to each process's environmental impacts.

1.4. Document Structure

With the posed questions in need of an answer, along with the aim of this study in mind, this thesis has been structured in five distinct chapters, which are presented as follows:

Chapter 2 reviews the literature of the most important concepts of this study, including nanotechnology, more specifically zirconia and yttria-stabilized zirconia; and the production processes for this material – co-precipitation process and emulsion detonation synthesis (EDS).

Chapter 3 focuses on presenting the LCA methodology, describing and explaining its use. The first steps of this LCA are also accounted for, defining the goal and scope of this study and the impact categories to be analysed. Then, the life-cycle inventories (LCI's) of the material and energy flows for both processes are created and developed. Then, these LCI's are converted into the predefined impact category indicators, allowing the life-cycle impact assessment phase (LCIA) to be started.

Chapter 4 is where the results of the preceding chapters are presented and interpreted, evaluating the impacts of both production processes, comparing and discussing those results in order to reach conclusions, as well as identifying the environmental hotspots of each process, which is the stage or process of the life-cycle that accounts for the biggest contribution to the total environmental impacts of the defined functional unit, and is the focus of action towards improving the environmental performance of the product system.

Chapter 5 summarizes the main findings related to the abovementioned research objectives, draws conclusions, and foments discussion of the results while also providing recommendations for future research.

2. LITERATURE REVIEW

2.1. Nanomaterials and Nanotechnology

Nanotechnology has been extensively praised and predicted to be the *"defining technology for the 21st century"* [31] and an increase in various economic sectors for the market and applications of nanomaterials can be foreseen. Its origin is regularly pointed to a speech given by Richard P. Feynman, in December of 1959, entitled *"There's Plenty of Room at the Bottom"* [32], hinting at the numerous possibilities, on a microscopic scale, for technological advances and evolution. From that day forward, various articles aiming to define 'nanomaterial' and other related terms have been published.

The *European Commission* (EC) defines 'nanomaterial' as a *"natural, incidental or manufactured material containing particles"* if 50% or more of its particles have a length of between 1 nm and 100 nm, for one or more of their external dimensions [33]. This definition is in accordance with other definitions worldwide, namely by the ISO/TS 80004-1:2015, which defines the term 'nanomaterial' as a *"material with any external dimension in the nanoscale"* or *"having internal structure or surface structure in the nanoscale"*. The term 'nanoscale' is then defined as a *"length range approximately from 1 nm to 100 nm"* [34].

By simply modifying their scale, shape or composition, nanoparticles can combine specific characteristics, unlike traditional materials. Presently, due to these features and their reduced size, nanoparticles are increasingly crucial throughout several industry sectors and have been expanding to new fields, by bringing in the latest applications. Various industry sectors are now employing nano-enabled products in applications, ranging from the electronics, automotive and national defence sectors to healthcare and environmental remediation [35].

Despite current efforts and research, there are still many knowledge gaps involving the environmental safety of nanomaterials. For emerging technologies to succeed, it is necessary that the concerns in terms of effects and impacts they have on health and the environment to be addressed. Therefore, only through appropriate research and collecting data can these gaps be filled, in order to find answers that are increasingly demanded by consumers and industries and for policies and regulations to be defined [26, 27].

Nanotechnology has the potential to address many sustainability-related problems globally. Yet, that must be weighed against the existing uncertainties related to the environmental and health effects of nanomaterials. As it will be seen during this thesis, the synthesis of nanomaterials generally depends on multi-step, energy intensive production methods and often rely upon the use of limited resource materials and solvents. Thus, these factors lead to questions on the potential environmental impacts and create sustainability challenges for these processes [38].

In order to tackle these challenges posed by emerging nanotechnologies, the life-cycle assessment (LCA) methodology is increasingly recommended, since it can help guide decision-makers towards more sustainable actions and assess the nanomaterials' environmental performance. However, there is a scarce number of published studies to date that include all life-cycle stages, because of various knowledge gaps and a high degree of uncertainty regarding the releases and impacts of engineered nanomaterials [39]. Consequently, most nano LCA studies so far have a cradle-to-gate approach and therefore do not include the use-phase and end-of-life treatment and emissions thereof [35]. This also increases the concerns about the safety of ENM's in environmental terms [40].

2.2. Yttria-stabilized Zirconia

The name "Zirconia" is derived from the word *"Zragum"*, meaning "gold-coloured" in Persian language, and corresponds to zirconium oxide [41]. Zirconium (Zr) is the 17th most abundant element in the Earth's crust. The primary source is from the mineral zircon ($ZrSiO_4$) and it can also be found in igneous rocks in the form of the mineral baddeleyite, which is a natural form of zirconia [42]. Zirconia (ZrO_2) is a white crystalline powder with interesting properties, suitable for many uses in a variety of ceramics and coatings.

ZrO_2 is a polymorphic ceramic metal oxide presenting three different crystal structures: monoclinic (M), tetragonal (T) and cubic (C). These phases can be observed in Figure 2.1. Considering pure undoped $\mathrm{ZrO_2}$, these thermodynamically stable phases, which are reversible, correspond to the following intervals: at temperatures below 1170ºC it presents a monoclinic phase; from 1170ºC to 2370ºC it is tetragonal; and above 2370ºC it transforms into a cubic form, until reaching melting temperature (2715ºC) [20].

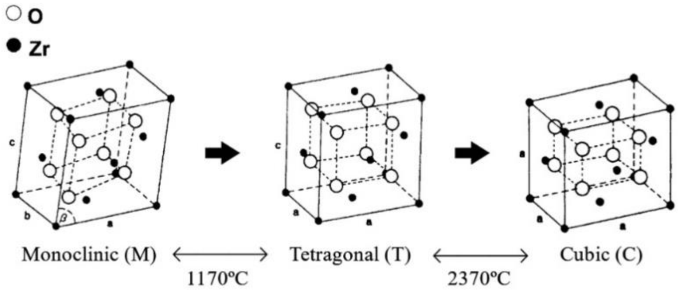

Figure 2.1. Crystal structures of zirconia and transformation temperatures (adapted from [18]).

When cooling to room temperature, this is, when a tetragonal-to-monoclinic (T ⟶ M) phase transformation occurs, it is accompanied by a 3–5% volume expansion. This limits the use of undoped zirconia materials in high-temperature applications or in applications involving frequent temperature variations [43], which is the biggest drawback of pure undoped ZrO_2.

However, by adding a certain quantity of a doping oxide to zirconia, its high-temperature phases can be stabilized. This stabilization is based on the formation of a solid solution, using ions with lower valence than zirconium, creating vacancies in the anion's network. There are numerous doping oxides used in zirconia stabilization, with the most frequent being MgO, CaO, CeO_2 and Y_2O_3. When a high content of stabilizing oxide is doped into zirconia, we obtain fully-stabilized zirconia (FSZ) which is presented in the cubic form. When a lower content is doped, we obtain partially-stabilized zirconia (PSZ) which is presented in the tetragonal form as the primary phase [43]. This study considers the use of 3% mol yttria-stabilized zirconia (3YSZ), which can be defined in the following way,

$$\mathbf{0.03\,Y_2O_3 + 0.97\,ZrO_2 \Rightarrow Y_{0.06}Zr_{0.94}O_{1.97} \Rightarrow 3YSZ}$$

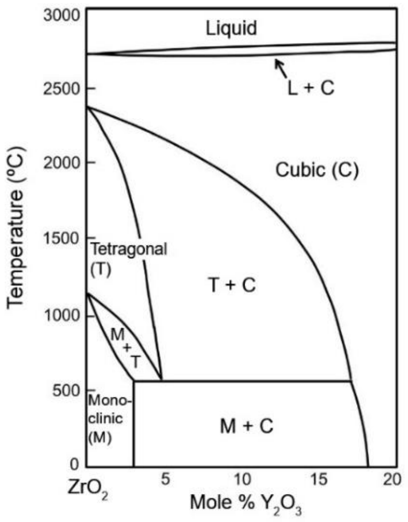

Figure 2.2. ZrO_2–Y_2O_3 phase diagram: L=liquid; F=cubic; T=tetragonal; M=monoclinic (adapted from [44]).

Doping zirconia with a low amount of yttria has the advantage of more effectively retaining its tetragonal form at room temperature, when compared with other stabilizing oxides, as seen in Figure 2.2. Yttria stabilization causes Zr^{4+} ions to be replaced by Y^{3+} ions, as well as four O^{2-} ions that are replaced by three O^{2-} ions, which influences ionic conductivity [43]. Retaining its tetragonal form is important because it presents improved features for ceramics.

Yttria-stabilized zirconia (YSZ) is presently one of the most studied combinations for stabilized zirconia, due to its excellent mechanical, thermal, electrical, ion conducting, optical and catalytic properties, which are better than other zirconia combinations [45]. This makes them important for various industrial applications, such as:

- **Biomedical and Bioceramics ⟶** Thanks to high chemical, corrosion and fracture resistance, and high toughness, YSZ ceramics have excellent biocompatibility, making them suitable for dental implants and other biomedical applications [17].
- **Solid oxide fuel cells (SOFC) ⟶** Using high-performance materials like YSZ in solid electrolytes, due to its great ionic conductivity, has been a key factor in increasing the efficiency of energy conversion [19], [41].
- **Oxygen sensors ⟶** YSZ shows high ionic conductivity, particularly for oxygen ions.

- **Thermal Barrier Coatings ⟶** Ceramic coatings are necessary to protect metallic materials at high temperatures, functioning as thermal barriers, giving great use to its very low thermal conductivity and refractory capability [21], [41].
- **Jewelry.**

2.2.1. Transformation Toughening

3% mol yttria-stabilized zirconia (3YSZ) is a pre-stressed material, which results from the 3% volume increase that occurs in tetragonal-to-monoclinic phase transformation (T ⟶ M) [46]. Therefore, a propagating crack can release the stresses on neighbouring grains, causing them to transform from the metastable tetragonal state into the monoclinic structure. With this, the expansion that occurs results in compressive stress on the edge of the crack tip, and makes it more difficult for the crack to propagate further, as extra energy would be necessary for that to happen [46]. This phenomenon is extremely important since it gives the material high toughness and mechanical strength, and is known as transformation toughening [47]. This can be seen in the representation shown in Figure 2.3.

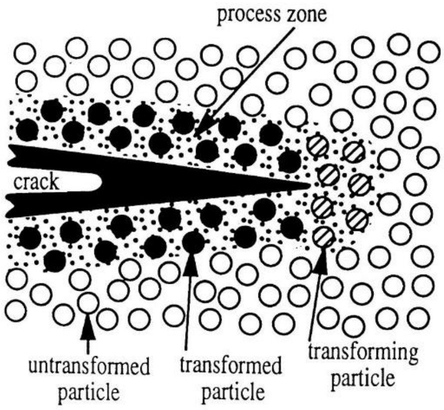

Figure 2.3. Representation of stress-induced transformation toughening in 3YSZ, where the white circles correspond to tetragonal 3YSZ and the black circles to monoclinic 3YSZ [48].

Due to the wide range of possible uses and applications for 3YSZ, in addition to the lack of data in terms of the disposal and end-of-life of this ceramic nanomaterial, this study will only employ a cradle-to-gate approach. Therefore, the use and end-of life phases of the 3YSZ life-cycle will not be considered. Hence, we will only be focusing and accounting for the environmental impacts of the raw material extraction and manufacturing stages.

As reported in literature [11, 36, 38] it is possible to find a wide variety of articles that studied different routes or methods of synthesis for ZrO_2 and YSZ. These consist of a vast array of conventional processes, already established in the industry, such as: sol-gel, [39–41]; hydrothermal synthesis, [42–45]; solvothermal [57]; spray pyrolysis [58]; plasma spray synthesis [59]; combustion synthesis, [38, 49, 50]; and co-precipitation [51–53].

The employment of these different methods and their varying conditions plays a major role in the different features and properties of the produced material, with each method having advantages and disadvantages. Of all the mentioned processes, co-precipitation seems the most favourable, as it is one of the most commonly applied process in the ceramic nanopowder industry. Therefore, it is important to use it in comparison with the innovative method of emulsion detonation synthesis (EDS method) which is described in Section 2.4.

This study intends to do a comparative environmental analysis of these two different manufacturing processes (co-precipitation and EDS method) for the production of 3YSZ.

2.3. Co-Precipitation Process

The co-precipitation process is the most common and simplest method for synthesizing most metal oxide nanoparticles. It typically involves the use of aqueous solutions of the precursor salts (e.g., chlorides, nitrates) and the addition of a base like ammonium hydroxide (NH_4OH). During the liquid-phase, water-insoluble salts are formed and when a certain pH level is reached, the solution becomes saturated, nucleation starts precipitation of metal hydroxide nanoparticles occurs. Then, after several washing cycles and drying and calcination processes, we are able to achieve the desired material with the appropriate properties [65].

The conditions of all processes involved (reactant concentration, pH level, processes' duration and temperature) mould the composition, size and morphology of the final product. Optimization of these conditions is necessary to attain the desired properties of the nanoceramic particles [66]. These are enumerated and discussed in Section 102.2.

Co-precipitation is a common method of synthesis and one of the most adopted routes, since: it uses cheap chemicals, being cost effective; it is quite a simple process; it presents good bio-compatibility; it does not produce numerous by-products; and it has large-scale production capability [36, 51, 56] compared with other chemical processes for producing 3YSZ, co-precipitation has superior fine grain size, appropriate chemical homogeneity and precise control of its composition [63]. Although the co-precipitated powders often resulted in agglomerated powder, the use of ethanol washing was shown to considerably reduce the extent of agglomeration [68].

Nevertheless, nanopowders produced by co-precipitation often present some disadvantages, namely its difficulty in constantly maintaining and controlling particle shape and size. Also some agglomeration between particles occurs during synthetic processing [51, 58]. Additionally, it is difficult to verify the quality of the co-precipitated product during the reaction.

For this thesis, since it aims to produce 3% mol yttria-stabilized zirconia (3YSZ) through the co-precipitation process, simultaneous precipitation of zirconia and yttria is required. For this, numerous precursor salts could be chosen as the reactants. Considering literature such as [63], [70] the chosen precursors for zirconium and yttrium were zirconyl chloride and yttrium chloride, respectively. These salts are used in their hydrated forms, corresponding to $ZrOCl_2 \cdot 8\,H_2O$ and $YCl_3 \cdot 6\,H_2O$. Precipitation of the respective hydroxides is caused by the addition of a base. The most common is ammonium hydroxide (NH_4OH), which is also the one considered for this thesis.

Considering all reactants required for co-precipitation, along with the washing, drying and calcination processes, the following aggregate reaction is obtained, considering stoichiometric rules:

$$0.06\,YCl_3 \cdot 6H_2O + 0.94\,ZrOCl_2 \cdot 8\,H_2O + 2.06\,NH_4OH$$
$$\longrightarrow$$
$$Y_{0.06}Zr_{0.94}O_{1.97} + 2.06\,NH_4Cl + 8.91\,H_2O$$

Figure 2.4 shows a simple flowchart of a typical co-precipitation process. In this study, aqueous solutions of zirconyl chloride and yttrium chloride are mixed with the ammonium hydroxide base, creating the liquid-phase solution. At a certain pH level, precipitation occurs, and the hydroxide precipitates are filtered from the solution. After several different washing processes prior to drying and calcination, we obtain 3YSZ and other products which in this case are ammonium chloride and wastewater.

The material and energy inputs, temperature values and timespans for each process, along with the outputs (amount of final product and by-products obtained) will be discussed in Section 3.3.

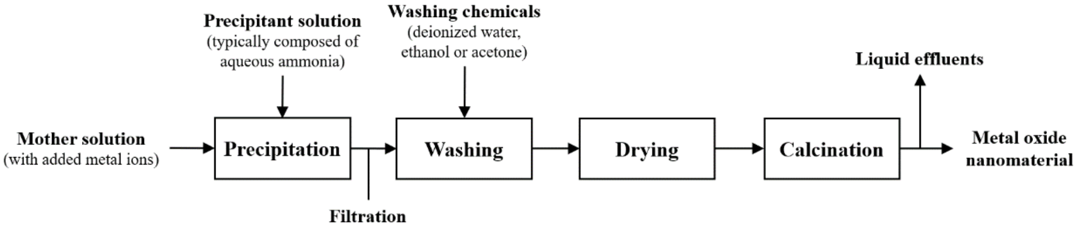

Figure 2.4. Flowchart of the co-precipitation process depicting the material flows, with the final product being typically a nanomaterial composed of metal oxides, after the washing, drying and calcination processes.

2.3.1. Particle Size

Considering values found in literature, we can create estimates and a defined sample for the particle size of 3YSZ produced by co-precipitation process. However, some articles were not very clear on defining it the referred sizes correspond to particle or grain size and, therefore, a clear conclusion is not possible to made, in comparison with particle sizes from other processes such as the EDS method.

Table 2.1. Articles studying co-precipitation process and their results on particle size for the nanomaterials considered.

Co-Precipitation Articles	**Particle Size Results**
[69]	YSZ produced by urea hydrolysis exhibited a particle size in the 10–30 nm range.
[70]	3YSZ, when heat treated at 500ºC, presented a particle size from 5 – 10 nm.
[71]	From Table 1, an average of all 7 valued samples gave a particle size of 5.03 nm. The actual article's results were an average particle size of 4.46 nm.
[72]	$Y_{0.16}Zr_{0.84}O_{1.92}$ powder with the average particle size of 14.8 nm was obtained when calcined at 800ºC for 4 h.
[73]	Zirconia nanopowders that went through a calcination process at 700ºC presented an average particle size of 32.9 nm.

2.4. Emulsion Detonation Synthesis (EDS Method)

Emulsion detonation synthesis (EDS) technology is a recent gaseous-phase method of synthesis. It was designed to synthesise spherical oxide powders under unique thermodynamic conditions, which normally present nanocrystalline structure (dimensions inferior to 100 nm).

The EDS process for 3YSZ nanopowders production begins with a two water-in-oil (W/O) emulsion. This emulsion is composed of two different phases: an internal aqueous phase, which acts as the oxidizer; and an external oil-based phase, which works as the combustible fuel. Typically, metallic precursors are homogeneously dissolved in this emulsion. Subsequently, the emulsion goes through a detonation process, that can be described as an immediate release of energy at extremely high pressures and temperatures (approximately 1400°C and 10GPa) in an extremely short time. Due to the shock wave caused by the extreme thermodynamic conditions (high temperature and pressure, plus rapid quenching), it triggers chemical reactions of the metallic elements, which react and combine exothermically with oxygen, within microseconds. During the expansion process of detonation, spherical metal oxide products are condensed and formed. Afterwards, they go through an incredibly rapid quenching process, allowing the formation of the desired final product – ultrafine ceramic nanopowders – and allowing them to retain their small grain size and thus achieve high sinterability [63, 64].

The high-pressure chemical reactions that occur in microseconds in the EDS Method, would take hours to complete in other methods. Therefore, EDS enables the synthesis of large quantities of the desired nanoproduct in a short amount of time. Also, the physio-chemical properties resulting from this method seem to be extremely favourable for nanopowders and for metastable phases.

2.4.1. 3% mol Yttria-stabilized Zirconia

The EDS technology first emerged and was patented in 2005 [76]. However, in 2012 this method was scaled-up to industrial levels and patented by Innovnano, in order to develop, manufacture and commercialize different types of oxides. Now, they are working and projecting the second-generation version of this technology, that will allow a 4N purity level (> 99.99%) to be reached.

An essential aspect of EDS is to incorporate metals in the emulsion's composition, through the dissolution of metallic salts in the oxidant phase, such as nitrates, acetates, carbonates or sulphates. During detonation, the respective metal oxide is formed through the reaction between the metallic element and oxygen [77].

For this thesis, the synthesis of 3% mol yttria-stabilized zirconia (3YSZ) ceramic nanoparticles is studied, by means of detonation of a zirconium- and yttrium-doped, ammonium nitrate-based explosive emulsion. The metallic salts implemented into the emulsion composition are zirconium basic carbonate $(Zr(OH)_2CO_3 \cdot ZrO_2)$ and yttrium nitrate $(Y(NO_3)_3 \cdot 6\,H_2O)$. These will lead to the formation of their respective oxides: zirconia (ZrO_2) and yttria (Y_2O_3). The produced yttria will work as a doping oxide, stabilizing the produced zirconia and forming the desired product, 3% mol yttria-stabilized zirconia (3YSZ). It is important to mention that the EDS method contributes greatly to zirconia stabilization, due to the energetic nature of the process [78], and it is capable of providing high chemical homogeneity, with uniform yttria distribution.

2.4.2. Properties of EDS Method Products

EDS is an efficient, adjustable, and simple method. It generally provides precise control of purity, morphology, particle size and other properties of the desired product. This makes EDS exceptionally useful for producing ultrafine oxide nanoceramic powders, as it offers improved quality, uniformity, cost-effectiveness and industrial-level production capability [66, 67].

This method appeals to many researchers and investigators, due to its capacity to produce a large amount of numerous oxide nanomaterials. Normally, the nanopowders resulting from EDS present improved structural properties, such as high hardness, flexural strength, fracture toughness and resistance to thermal shock.

The mutual control of the temperature, pressure and quenching of the EDS process makes it possible to adjust the design of the particles' properties to specific requirements, providing great manufacturing customization. Beyond this, EDS presents multiple other benefits, such as:

- Single-step synthesis.
- Highly efficient and self-sustained (since detonation is an exothermic reaction).
- Instantaneous reaction times for human perception.
- Cost-effective process.
- High purity of the nanoparticles produced (> 99.9%).
- Uniform small grain sizes with increased specific surface area (since rapid quenching minimizes particle growth).
- Increased physio-chemical properties and high mechanical resistance [77, 80].

All advantages and enhancements of the EDS Method are due to the combination of three important aspects: high temperature, high dynamic pressures, and rapid quenching. These can be seen in the three stages of the nanoparticle synthesis in the gaseous phase of this process:

i) Firstly, the desired product is created in the vapor phase at high temperatures, which results in dense and spherical particles;
ii) Secondly, the desired product condensates and forms nanocrystalline material of small particle size and with the desired crystalline phase, due to high pressure;
iii) Finally, quenching/rapid cooling helps preserve and control their small size, the particles deagglomerated state and increases their specific surface area [64, 68].

There are several reasons as to why this technology is unique and sets itself apart from other processes: i) due to the high homogeneity between phases, the water-in-oil emulsion presents the necessary structure to conduct complete chemical reactions during detonation; ii) it has great adaptability in terms of the possible metallic precursor choices to use, allowing extensive control over the chemical composition, morphology, final properties and purity of the resulting nanoceramic; iii) due to its high water content, the emulsion is stable and very safe towards frictions and shocks [77].

The EDS technology allows the synthesis of compounds that were otherwise difficulty to obtain from other, more common, methods (either difficulty in production at industrial scales or because of entailed massive costs) [80].

The nanomaterial market and industry have an ever-increasing need for new materials, to meet the demands of technology's continual improvements. Production processes that promote the design and development of new and exciting materials, with enhanced or even unique properties, are necessary to stimulate innovation. The EDS method offers this opportunity by being very adaptable and flexible, allowing a customizable production that is easily adjustable to numerous different precursors and experimental reaction conditions [75]. Figure 2.5 depicts a simple flowchart of the EDS method, considering all inputs and outputs of the process.

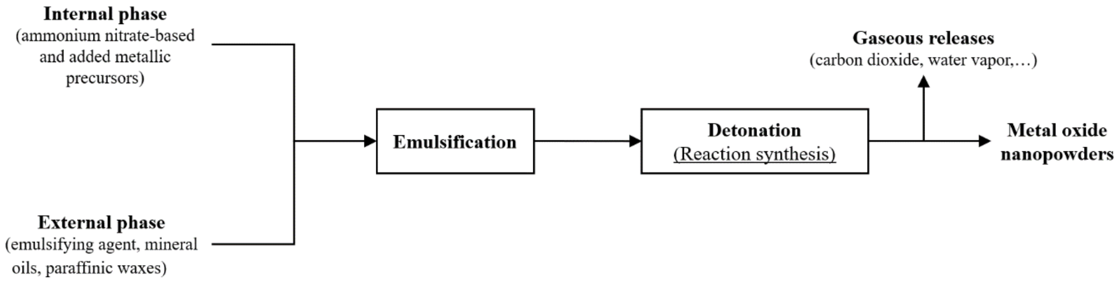

Figure 2.5. Flowchart of the EDS method production process, depicting the material flows, with the detonation resulting in the desired nanopowders and gas emissions.

2.4.3. Particle Size

Considering values found in literature, it is possible to define and select some samples for the particle size of materials, typically zirconia, produced by EDS method, and from there create estimates for the possible size of the 3YSZ nanopowders of this study. However, since most articles from Table 2.1 were not very clear on the particle and grain size, not many conclusions can be retrieved from this information.

Table 2.2. Articles studying EDS method and their results on particle size of the nanomaterials considered.

EDS Method Articles	Particle Size Results
[79]	ZrO_2 powder was composed of agglomerated spherical particles with average diameter of 20 nm.
[77]	Particle size inferior to 40 microns.
[81]	Example 1, which corresponds to ZrO_2, presents a particle size of 15 nm.
[82]	Zirconia powder with a typical particle size of 5-6 nm is synthesized by an explosive method.

2.5. Life-Cycle Assessment (LCA)

2.5.1. Definition and Methodology

Society is getting increasingly aware of the dangers of climate change and resource depletion, and how vital our need to decrease emissions and implement sustainable practices is in order to protect our environment. To understand and assess those impacts, whether that may be to quantify them or for comparison purposes, a methodology that addresses such effects is life-cycle assessment (LCA).

The concept of LCA is defined by the international standards ISO 14040:2006 and ISO 14004:2016 as a *"compilation and evaluation of the inputs, outputs, and potential environmental impacts of a product system throughout its life cycle"* [83]. These standards allow for more consistency, reliability of results and easier comparison between LCA studies. However, to be able to compare different LCA studies, the functional unit must be defined. It is a measure of the functional system, a quantified description of the product in study and works as the reference unit for the relation between inputs and outputs.

LCA gives knowledge and information to decision-makers in industries, organizations and governments by identifying, through relevant indicators of environmental performance, opportunities in some stages of a product's life-cycle to decrease its impact on the environment and make it more ecological. LCA can also function as a marketing tool, through eco-labelling or by composing an environmental product declaration. The goal of the life-cycle assessment (LCA) methodology is to transform gathered data into information, which in turn becomes knowledge, and for this knowledge to be passed on to understanding and, finally, to actions [84].

Since 3YSZ nanomaterial and the EDS method have only recently been researched and investigated, no LCA studies were found in literature, which could provide any results or additional information regarding this material and production process.

2.5.2. Future of LCA and Sustainable Policies

Tackling climate change, pollution and resource depletion is our generation's biggest fight. In response to the enormous task ahead, the *European Green Deal* was signed. In this treaty, the EU committed itself to achieving no-net emissions of greenhouse gases by 2050. Besides the goal of reaching climate neutrality in 2050, it intends to reduce greenhouse gas emissions by a minimum of 50% and towards 55% by 2030, compared with 1990 levels. For that reason, decisions and actions must be taken quickly and consistently throughout the next decades. Knowledge of the environmental impacts of most, if not all, industry sectors is fundamental to this, along with government policies for sustainable products. A transition to circular economy, life-cycle thinking (LCT) and LCA studies will be an elementary component to commit and complete this deal [85].

The *European Green Deal* comes as a guideline, with instructions to follow, in order for Europe's economy to align with the sustainability needs of the future, and towards fulfilling the goal set in the *Paris Agreement*. This international treaty set the goal of holding the increase in global average temperature to below 2ºC above pre-industrial levels, with the main objective being not to surpass 1.5ºC, to halt climate change. It also makes reference to strengthening environmental studies such as, for example, LCA's when it cites *"strengthening scientific knowledge on climate, including research, systematic observation of the climate system and early warning systems, in a manner that informs climate services and supports decision-making"* [86].

Considering the abovementioned information, it is possible to imagine that in the foreseeable future, political policies will have sustainability concerns and new product development will most likely have mandatory information (or require LCA studies) about environmental impacts of those products, since consumer demand is transitioning to environmentally-friendly solutions and paying close attention to eco-labelling. Thus, the industries and manufacturers will adapt to these conditions, modifying the market for these products [87].

2.5.3. Life-cycle Stages and Cradle-to-gate Approach

An LCA approach allows us to know quantitively the environmental impacts of the life-cycle of a product, process or service throughout all its stages: starting from raw material extraction, production, use-phase and end-of-life treatment (e.g. recycling, waste disposal). Between these stages, transportation can also be considered. By doing this, we get a holistic view of the impacts and can prevent shifting the burden towards other life-cycle stages or impact categories [88].

Due to the wide possibilities of application for 3YSZ, which are discussed in Section 2.2, this study will employ a cradle-to-gate approach, whereas the use-phase and disposal of this material will not be considered. An example of a cradle-to-gate approach is showed in Figure 2.6. Therefore, we will only be focusing on impacts caused during the raw material extraction and manufacturing stages of the life-cycle.

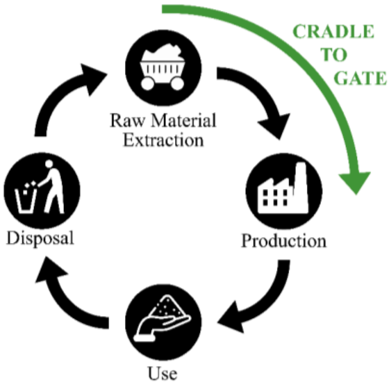

Figure 2.6. Example of a cradle-to-gate approach on the life-cycle of a product (adapted from [88]).

An LCA study is comprised of four interconnected phases:

1. **Goal and scope definition** – The aim of the study, what is analysed, the scope and the system boundaries are defined. The functional unit of the LCA and the impact categories are also defined. In this phase, the whole LCA is detailed, to ensure that the study is headed towards the right direction.

2. **Inventory analysis** – By gathering necessary information and collecting reliable data on the materials and energy flows, we can quantify the inputs and outputs of the product system, creating an inventory related to the functional unit. This includes all types of inputs, outputs or emissions across the life-cycle of the product.
3. **Impact assessment** – Life-cycle impact assessment (LCIA) begins with dividing and converting the material and energy flows and releases (compiled during the LCI phase) into specific impact indicators, associated with each impact category. The LCI is converted into the impact categories selected – named characterisation. This allows a better understanding of the magnitude of environmental impacts caused by the life-cycle inventory and allows comparisons between processes.
4. **Interpretation** – In this phase, the results are summarized and discussed in relation to the defined goal and scope, as a basis for conclusions, recommendations and decision-making.

Figure 2.7 shows the interconnection of the abovementioned phases.

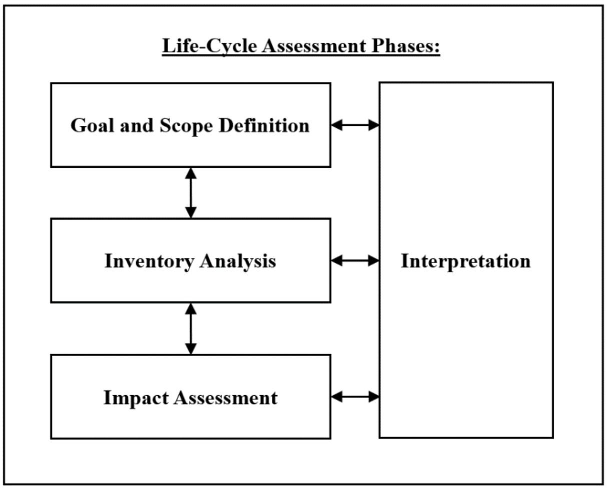

Figure 2.7. Framework of a life-cycle assessment study (adapted from [23]).

2.5.4. Necessity for LCA studies and life-cycle Thinking (LCT)

With consumers and policy-makers increasing the demand for sustainability, businesses and industries have started using a marketing scheme referred as "greenwashing", whereas a product, service or company's aims are deceptively stated as "green" or "eco-friendly". However, in most cases, the life-cycle impacts of those products and services are not at all considered. To actually affirm something as sustainable or environmentally-friendly, one must have a holistic view of it and assess its whole life-cycle.

Most often, if an LCA approach is not applied, a change in the production process that decreases environmental impacts in a certain stage of the process may be viewed as desired and applicable. However, that change might be simply shifting the burden, which means it could be generating more impacts in another life-cycle stage, or generating other (possibly worse) types of environmental impacts. Therefore, one singular isolated improvement does not necessarily mean that it offsets the life-cycle impacts originating from all other stages and processes.

Therefore, the purpose of this study is to avoid this situation from happening with nanomaterial production and launch its sector towards ecological development. Since nanotechnology is quite recent, LCA studies may have an even bigger impact on its industry.

The most used tool to model an LCA study is the *SimaPro* software, which will also be used in this study. *SimaPro 9.1.1.7* is a software that models the life-cycle and enables the assessment of environmental impacts, by introducing and calculating the values from the inventory of materials used, energy consumption and effluents released. To create the necessary LCI for both processes, the *Ecoinvent* v3 database was used, as it contains the information of most materials required to complete the LCI phase of an LCA study. When a certain compound did not exist in this database, extensive research and stoichiometric calculations were necessary and are depicted in Section 3.2 and Appendix A.

3. LIFE-CYCLE ASSESSMENT OF 3YSZ PRODUCTION

To be able to perform a life-cycle assessment (LCA), all of its 4 stages must be taken into account. This section presents in detail the four stages of an LCA study for a cradle-to-gate analysis of the production of 3% mol yttria-stabilized zirconia (3YSZ) nanopowders.

3.1. Goal and Scope Definition

This study intends to assess and compare the environmental impacts of the 3% mol yttria-stabilized zirconia (3YSZ) nanopowders production, by two different methods of synthesis: co-precipitation process and emulsion detonation synthesis (EDS method). The functional unit of this assessment corresponds to 1 kg of 3YSZ produced.

In terms of the system boundaries, the life-cycle stages considered are the raw material extraction and transformation, and the manufacturing of the 3YSZ nanoparticles. The use and end-of-life phases were not considered, since they are indifferent to the production method used. In other words, as the 3YSZ created by one method or the other can be considered as almost equal, then they both can have the same uses and be disposed in the same fashion. Thus, the focus of the study will only be until the production phase.

During the goal and scope stage of an LCA, the impact categories of interest to the study must be selected, along with the definition of the assumptions and limitations necessary, either due to knowledge gaps, to avoid excessive complexity or to achieve easily comparable and reliable results.

3.1.1. Impact Categories

During the life-cycle of a product or system, the abovementioned flows (their spending and releases) have an affiliated environmental impact. Therefore, after completing the LCI phase, the total inventory of the life-cycle of 3YSZ production for both processes in study can be converted to the respective environmental impacts, through the use of characterization factors. However, this impact conversion varies according to the method used and it is dependent of the impact categories chosen or deemed important for the study. Although the environmental studies typically focus on impacts such as global warming, acidification, eutrophication and abiotic depletion, it is also equally important to quantify the impacts in terms of human and environmental toxicity, considering those concerns towards nanomaterials.

The ILCD 2011 Midpoint+ method was selected to assess the environmental and toxicological impacts. This LCIA method follows the recommendations from the ILCD guidance document [89] and bases itself on applying the recommended 16 impact categories from various LCIA methods (e.g., ReCiPe, CML, USEtox). This thesis will only focus on studying the impact categories depicted in Table 3.1.

Table 3.1. Impact categories from ILCD 2011 Midpoint considered in this thesis (adapted from [89, 90]).

Impact category	***Default LCIA method***	***Indicator***	***Details***
Climate change	Baseline model of 100 years of the IPCC 2007	Radiative forcing as Global Warming Potential (GWP100)	Calculates the potential contribution of substances for the greenhouse effect.
Ozone depletion	Steady-state ODPs 1999 as in WMO assessment	Ozone Depletion Potential (ODP)	Calculates the destructive effects on the stratospheric ozone layer.
Human toxicity, cancer effects	USEtox model	Comparative Toxic Unit for humans (CTUh)	Expresses the estimated increase in morbidity in the total human population per unit mass of a chemical emitted (cases per kilogramme).
Human toxicity, non- cancer effects	USEtox model	Comparative Toxic Unit for humans (CTUh)	Expresses the estimated increase in morbidity in the total human population per unit mass of a chemical emitted (cases per kilogramme).
Photochemical ozone formation	LOTOS-EUROS as applied in ReCiPe	Tropospheric ozone concentration increase	Expression of the potential contribution to photochemical ozone formation (only for Europe).
Acidification	Accumulated Exceedance	Accumulated Exceedance (AE)	Damage to ecosystem quality, as a result of emission of acidifying substances to air.
Eutrophication, freshwater	EUTREND model as implemented in ReCiPe	Fraction of nutrients reaching freshwater end compartment (P) or marine end compartment (N)	The increase in concentration of nutrients in ecosystems due to P and N emissions.
Freshwater Ecotoxicity	USEtox model	Comparative Toxic Unit for ecosystems (CTUe)	The impact of toxic substances on aquatic ecosystems.

Water Resource Depletion	Model for water consumption as in Swiss Ecoscarcity	Water use related to local scarcity of water	Scarcity-adjusted amount of freshwater used.
Mineral, fossil & renewable resource depletion	CML 2002	Scarcity	Scarcity of mineral resources. Refers to abiotic depletion, from both the impact of depletion and due to extraction of resources.

3.1.2. Assumptions and Limitations

Data gaps are a typical issue for LCA studies, as they largely depend on knowledge from a vast array of subjects. Furthermore, theses gaps typically increase when the study's focus is on developing technologies. Since this thesis is focused on nanopowders and considers the innovative production method of emulsion detonation synthesis, data gaps were considerable. Therefore, some standardization and simplifications had to be made to ease the complexity of this study, make it more easily understandable and for both processes in question to be consistent with each other.

The life-cycle inventories created for both processes require the use of information, in terms of the type and quantity of materials used and released, along with the energy consumption of those methods. This data came mostly from literature sources or, if there were knowledge gaps, assumptions were made and limitations accounted for. Being an integral part of an LCA study, it is important that they are described in the goal and scope definition. This information must be presented to the readers, to allow the results to be deemed reliable and well-founded, as well as accurate enough, without creating an excessively complex system [91]. The specific assumptions and limitations related to this thesis are presented below:

a) Cradle-to-gate Approach:

This LCA study will only focus on a cradle-to-gate analysis of the product system. Therefore, although it accounts for the impacts of raw material extraction, the manufacturing of the precursors used and the 3YSZ production by the two different processes, it will not consider any environmental impacts from the use-phase of the 3YSZ nanopowders or its end-of-life.

b) *Ecoinvent* Data Gaps and Limitations on Yttrium and Zirconium Compounds:

Although the majority of product life-cycles involve chemicals, only a small portion of the chemicals produced today are included in the accessible databases. This makes it extremely challenging to obtain production information on most chemicals, since chemical companies are very protective of their production data, due to confidentiality concerns.

This thesis used the *EcoInvent* v3 database from the *SimaPro* software, highly acknowledged as the largest and most reliable LCI database available. However, the quantification of the environmental impacts of yttrium and zirconium compounds, which is vital for this thesis, does not exist in this database. As a result, an extensive amount of research was necessary in order to investigate and calculate the impacts of the precursors used in this study. This was done by exploring literature, in order to create the required life-cycle inventories.

In conclusion, the materials that are non-existent in the *Ecoinvent* v3 database were modelled mostly based on literature, and typically through the calculation of the stoichiometry of chemical reactions. The developed LCI’s can be seen in Section 3.2 and Appendix A.

c) Assumptions for Material Losses and Energy Consumption:

The articles used to describe the materials missing from the *Ecoinvent* v3 database, in order to complete the LCI’s needed, often had scarce information in relation to efficiency of chemical reactions, input losses and energy consumption. Since calculating all energy consumption, levels of efficiency and input losses for all the materials used and for all the chemical reactions would be an extremely time-consuming process and would lead to high uncertainty and complexity, these had to be simplified.

A good way to achieve simplification is through estimation performed with consistency for all materials. Therefore, the constructed LCI’s consider the estimation approach developed by Hischier *et al.* (2005) [92], as done in many other LCA studies [93], [94][93–95]. This approach suggests: i) an efficiency level of 95 % for the stoichiometric chemical equation, which basically means considering 5% losses for raw materials consumption; ii) the heat and electricity consumptions of 2 MJ and 0.333 kWh per 1 kg of product produced, respectively (based on average values typical of the chemical industry); iii) of the input materials, 0.2 % were estimated to be emitted into the air.

d) <u>Assumptions for Co-precipitation Process:</u>

During the washing process of the precipitates, the water and ethanol used can be quantified in the material inputs of the LCI, but it is not possible to consider these as discarded into the environment. This is because in “real” industries, these materials have to be reused, recycled or sent to wastewater treatment, since ammonium chloride is extremely detrimental to the environment. Therefore, these substances are considered outside the scope of the product system because the final destination of these materials is not known, so they cannot be quantified as an output in the co-precipitation inventory.

3.2. Preparation of Precursors Non-existent in the *Ecoinvent* Database

To accurately quantify the impact of producing 3YSZ, all the materials required for its production must be available in the *SimaPro* software. Since nanomaterials are a recent technology, the *EcoInvent* v3 database used in this study has a quite large data gap concerning many of them, in particular yttrium and zirconium compounds. That created quite a challenge since both studied processes require the quantification of environmental impacts for those materials.

A description of their synthesis had to be reviewed extensively in the accessible literature, which was sometimes scarce and/or outdated. The purpose of this was, firstly, to assemble a life-cycle inventory (LCI) for each non-existent compounds in the database, and secondly, to insert those LCI’s in the *SimaPro* software, in order to quantify their environmental impacts, considering a functional unit of 1 kg of the respective compound.

Therefore, due to the numerous data gaps in the *Ecoinvent* v3 database, during the work of this thesis, a total of 8 processes were created for the *SimaPro* software. Those missing chemicals were:

- Yttrium oxide, nitrate, and chloride.

- Zirconyl chloride.
- Zirconium sulphate, and basic carbonate.
- Sodium carbonate.
- Sodium zirconium silicate.

By adding these LCI's to *SimaPro*, their environmental impacts could now be quantified, and thus, be used to create the LCI's for 3YSZ production, by co-precipitation and EDS method. All assumptions and simplifications considered during these inventory calculations are described in Section 3.1.2.

3.2.1. Necessary Precursors for the Co-precipitation Process

For the co-precipitation process, the required precursors that do not exist in the *Ecoinvent* v3 database are yttrium chloride and zirconyl chloride.

3.2.1.1. Yttrium chloride hexahydrate ($YCl_3 \cdot 6\ H_2O$) production

To produce yttrium chloride hexahydrate, yttria can be dissolved in hydrochloric acid, which is then filtered and evaporated until the salt crystallizes [96, 97]. The chemical reaction can be written as such,

$$Y_2O_3 + 6\,HCl \longrightarrow 2\,YCl_3 + 3\,H_2O$$

In a simplified way, by adding deionized water to the precursors, the immediate production of hydrated yttrium chloride can be considered to form as such,

$$Y_2O_3 + 6\,HCl + 9\,H_2O \longrightarrow 2\,YCl_3 \cdot 6\,H_2O$$

However, (Y_2O_3) is also not quantified in the *EcoInvent* database, in terms of its environmental impacts. Since no literature was found on its production or extraction, an oxidation reaction between yttrium (Y) and oxygen (O) was considered in the *SimaPro* software. The yttrium chloride hexahydrate LCI is shown in Table 3.2. Throughout this thesis, the energy consumed was assumed to be of medium voltage, with an electricity mix equal to the one consumed in Portugal.

Table 3.2. Life-cycle inventory for the production of yttrium chloride hexahydrate, and the intermediate production of yttria.

Level 1	Level 2
Yttrium chloride hexahydrate production (1 kg)	
Components:	
Hydrochloric acid (0.3793 kg)	
Deionized water (0.2811 kg)	
Yttrium oxide (0.3915 kg)	**Yttrium oxide production (1kg)**
	Components:
Energy:	Yttrium (0.8284 kg)
Electricity {PT} (0.333 kWh)	Oxygen (0.2236 kg)
Steam (2 MJ)	
	Energy:
	Electricity {PT} (0.333 kWh)
	Steam (2 MJ)

3.2.1.2. Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8\ H_2O$) production

Zirconyl chloride can be produced by hydrochloric acid leaching of a by-product of the decomposition of zircon (zirconium silicate) through caustic fusion [98–100]. Therefore, this chemical reaction can be written as such,

$$Na_2ZrSiO_5 + 4\ HCl \longrightarrow 2\ NaCl + ZrOCl_2 + SiO_2 + 2\ H_2O$$

where zirconyl chloride is formed along with sodium salts, silica gel and water. To be able to consider the hydrated compound, a simplified way was considered for a simple reaction such as,

$$ZrOCl_2 + 8H_2O \longrightarrow ZrOCl_2 \cdot 8H_2O$$

However, to quantify the environmental impacts of $ZrOCl_2 \cdot 8\ H_2O$ production, all its precursors must exist in the *Ecoinvent* database, but sodium zirconium silicate

(Na_2ZrSiO_5) does not. Therefore, a life-cycle inventory for its production must be assessed, and it is described in Appendix A, as well as the also necessary sodium carbonate production.

After reaching a production process where all materials are included in the database, the life-cycle inventory of $ZrOCl_2 \cdot 8\,H_2O$ can be assembled, in relation to the defined functional unit of 1 kg of that desired material produced.

Table 3.3. Life-cycle inventory for the production of zirconyl chloride octahydrate, considering the hydrating reaction.

Level 1	Level 2
Zirconyl chloride octahydrate production (1 kg)	
Components:	
Deionized water (0.4705 kg)	
Zirconyl chloride (0.5815 kg)	**Zirconyl chloride production (1kg)**
Energy:	*Components:*
Electricity {PT} (0.333 kWh)	Sodium zirconium silicate (1.4486 kg)
Steam (2 MJ)	Hydrochloric acid (0.8613 kg)
	Emissions to water:
	Sodium chloride (0.6562 kg)
	Silicon dioxide (0.3373 kg)
	Water (0.2023 kg)
	Energy:
	Electricity {PT} (0.333 kWh)
	Steam (2 MJ)

3.2.2. Necessary Precursors for the EDS Method

For the EDS method, the required precursors that do not exist in the *Ecoinvent* v3 database are yttrium nitrate and zirconium basic carbonate.

3.2.2.1. Yttrium nitrate hexahydrate $(Y(NO_3)_3 \cdot 6\,H_2O)$ production

Yttrium nitrate can be obtained through the reaction between yttria and nitric acid, in a stirred mixture of deionized water [63, 97, 98]. The corresponding production can be represented as,

$$Y_2O_3 + 6\,HNO_3 + 9\,H_2O \longrightarrow 2\,Y(NO_3)_3 \cdot 6\,H_2O$$

The inventory developed for yttria can be seen in Appendix A.

Table 3.4. Life-cycle inventory for the production of yttrium nitrate hexahydrate, and the intermediate production of yttria.

Level 1	Level 2
Yttrium nitrate hexahydrate production (1 kg)	
Components:	
Nitric acid (0.5192 kg)	
Deionized water (0.2227 kg)	
Yttrium oxide (0.3101 kg)	**Yttrium oxide production (1 kg)**
Energy:	*Components:*
Electricity {PT} (0.333 kWh)	Yttrium (0.8284 kg)
Steam (2 MJ)	Oxygen (0.2236 kg)
	Energy:
	Electricity {PT} (0.333 kWh)
	Steam (2 MJ)

3.2.2.2. Zirconium basic carbonate $(Zr(OH)_2CO_3 \cdot ZrO_2)$ production

The US Patent [103], more specifically, the information of Example 1 in terms of the materials and processes required for producing $Zr(OH)_2CO_3 \cdot ZrO_2$, considers the use of known amounts of zirconium sulphate, deionized water, sodium chloride, sodium carbonate and concentrated hydrochloric acid as the reactants. These materials form a basic zirconium sulphate that, after some heating and filtration, is suspended once again in deionized water. With the addition of sodium hydrogen carbonate to this suspension, an unknown amount of pure, white zirconium basic carbonate is obtained. By calcining it at about 1000ºC, 122 to 124 g of zirconium oxide of high purity is obtained.

The stoichiometric calculations were based on the values mentioned in Example 1, and in two different relations that can be noted:

a) The relation between the mass values for the precursors mentioned, with the stated mass of calcined zirconium oxide presented as a final product.
b) The relation between zirconium basic carbonate and zirconium oxide, if its decomposition through calcination is presented in chemical equation, as such,

$$Zr(OH)_2CO_3 \cdot ZrO_2 \longrightarrow 2\ ZrO_2 + H_2O + CO_2.$$

Considering these two relations, the quantity of reactants needed to produce 1 kg of zirconium basic carbonate was calculated, through stoichiometry and proportional relations., The subsequent calcination process mentioned was not of interest for this study and was, therefore, not considered. In Table 3.5, the total life-cycle inventory for zirconium basic carbonate production, calculated considering the functional unit of 1 kg, is presented.

All materials except zirconium sulphate and sodium carbonate are already present in the *EcoInvent* database. Therefore, a life-cycle inventory for both these materials is necessary, as described in Appendix A.

Table 3.5. Life-cycle inventory for the production of zirconium basic carbonate, and the intermediate production of zirconium sulphate and sodium carbonate.

Level 1	Level 2
Zirconium basic carbonate production (1 kg)	
Components:	
Zirconium sulphate tetrahydrate (2.4367 kg)	**Zirconium sulphate tetrahydrate production (1 kg)**
	Components:
	Zirconium oxide (0.3647 kg)
	Sulfuric acid (0.5806 kg)
	Deionized water (0.1066 kg)

	Energy:
	Electricity {PT} (0.333 kWh)
	Steam (2 MJ)
Sodium carbonate (1.014 kg)	**Sodium carbonate production (1 kg)**
	Components:
	Sodium bicarbonate (1.6676 kg)
	Emissions to air:
	Water (0.17 kg)
	Carbon dioxide (0.4152 kg)
	Energy:
	Electricity {PT} (0.333 kWh)
	Steam (2 MJ)
Hydrochloric acid (0.4032 kg)	
Sodium hydrogen carbonate (0.6888 kg)	
Sodium chloride (0.82 kg)	
Deionized water (23.9159 kg)	
Energy:	
Electricity {PT} (0.333 kWh)	
Steam (2 MJ)	

3.3. Life-cycle Inventory (LCI) for the Co-precipitation Process

3.3.1. Steps for the Co-precipitation Process

The co-precipitation process has numerous possibilities and variations that can be attributed to it: different precursors, different final products, the number of washing cycles and chemicals used, and different drying and heat treatment (calcination) process values of temperature and time.

This process has been briefly described in Chapter 2.3. There, it is possible to see that the sources for zirconium and yttrium ions are zirconyl chloride octahydrate and yttrium chloride hexahydrate ($ZrOCl_2 \cdot 8H_2O$ and $YCl_3 \cdot 6H_2O$), respectively [58, 65]. These are soluble salts that are dissolved in deionized water to create an aqueous solution, which can be referred to as the mother solution (deionized water with Y^{3+} and Zr^{4+} ions). To initiate the precipitation process, the addition of a base is necessary. One of the most commonly used bases for most studies, like the ones in Table 3.6, is an ammonium hydroxide or aqueous ammonia (NH_4OH) solution, which acts as a pH adjuster and can be referred to as the precipitant solution.

With both solutions created, the precipitant solution is added dropwise into the recipient with the mother solution under vigorous stirring. As the solution is mixed and heated to the desired reaction temperature, this continuous addition slowly changes the pH level of the mother solution. When the required level is reached, a reaction occurs which forms the respective hydroxides, corresponding to $Zr(OH)_4$ and $Y(OH)_3$. Since these are insoluble salts, they therefore precipitate. These precipitates are then filtrated out of the solution, and the only products left of the chemical reaction are wastewater and ammonium chloride. The precipitates must then be washed to remove all Cl^- ions and undesired substances. Afterwards, they are dried and calcined in order to obtain the desired final product, 3YSZ. The system boundaries of this LCI can be seen in Figure 3.1.

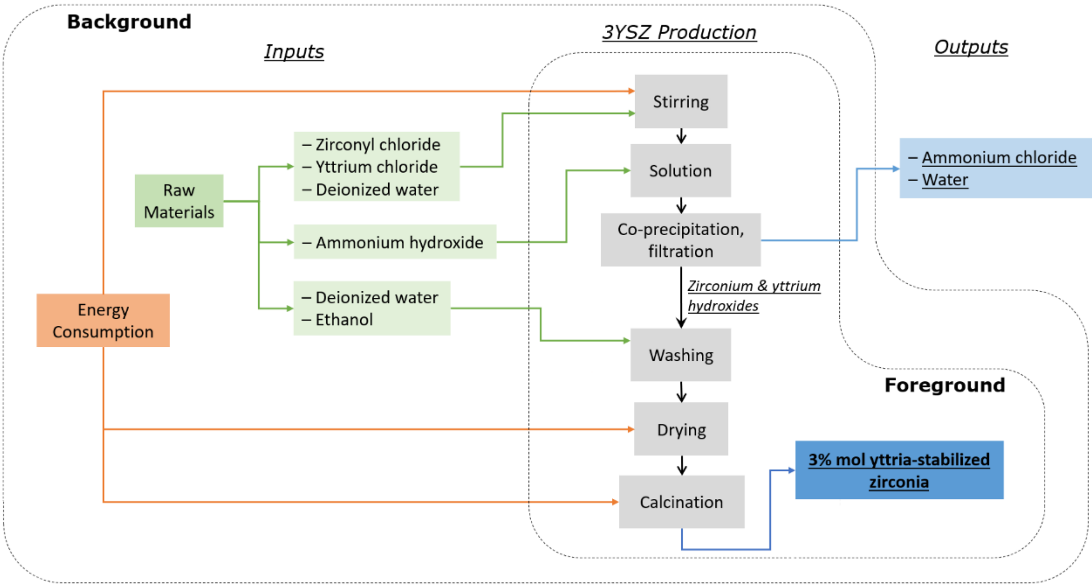

Figure 3.1. Framework of 3YSZ produced by co-precipitation, depicting the system boundaries.

3.3.2. Relevant Literature for the Co-precipitation Process

A decision on the characteristics and values of the washing, drying and calcination processes applied to the precipitates is necessary, since these will be accounted for in terms of materials and energy consumption to complete the co-precipitation LCI and then converted into the resulting environmental impacts. Many articles were gathered and their details of production are described in Table 3.6. From there on, the average values were assumed for this LCA study. Therefore, the co-precipitation process was considered to include:

- **Stirring:** Assumed 1 hour of vigorous stirring with a hotplate magnetic stirrer, in order to mix the emulsion and raise its temperature to the desired reaction temperature, in order for precipitation to fully occur.
- **Washing:** The washing process considered was 4 washes with deionized water followed by 2 washes with ethanol, to purify the precipitates. Ethanol is used because some literature reports have pointed out its importance in producing deagglomerated calcined powders [68]. The amounts of deionized water and ethanol consumed per wash is discussed in Section 3.3.4.
- **Drying:** The drying process is conducted at 100ºC for 24 hours in an oven.
- **Calcination:** The calcination process occurs at 800ºC for 2 hours in a furnace.

Table 3.6. Different co-precipitation articles that depict the details of the process.

Articles	Reactants and Final Product	Time Stirring	Number of Washings Cycles	Drying Process	Calcination Process
[72]	$Y_{0.16}Zr_{0.84}O_{1.92}$	-	Washed 4 times with deionized water, then rinsed 2 times with ethanol.	70ºC for 20h.	800ºC for 4h.
[47]	3YSZ	-	Washed with water until no residual Cl^- was present. Then, washed with ethanol.	Oven-dried at 80ºC for 24h.	800ºC for 1h.
[62]	$Y_{0.08}Zr_{0.92}O_{1.96}$	60 min.	Washed by deionized water and then by ethanol for several times.	60°C.	Different temperatures (300, 400, 500, and 600 °C) for 2h.

[68]	3YSZ	2h.	Washed with distilled water until Cl^- ion was completely removed. Then, treated with ethanol	100ºC.	470, 600, 700, 800 and 900ºC separately.
[63]	*8% mol YSZ*	30 min.	Continuously washed by deionized water until the chloride ions had disappeared. After that, the solid product was further washed twice by ethanol.	Naturally, at room temperature.	500°C for 2h.
[104]	*3YSZ*	-	Washed repeatedly with deionized water to remove anions (NO_3^-, Cl^-). Then, washed with ethanol 3 times.	24h in an oven.	Different temperatures for 2h (examples of 800 and 1100ºC).
[105]	YSZ/Al_2O_3	-	Washed with distilled water 5 times to remove Cl^- and washed with ethanol for 3 times to remove the residue water.	120ºC for 24h.	Predetermined temperature for 2h (examples of 1000 and 1300ºC).
[16]	*YSZ*	50°C for 30 min.	Washed with distilled water and acetone.	24h at 100°C in air.	-
[106]	*YSZ*	Total of 1h.	Repeatedly rinsed and filtered with a large amount of deionized water to remove residual Cl^-.	90ºC.	Different temperatures (300–1200ºC) for 2h.

3.3.3. Stoichiometry

Since the desired final product is $Y_{0.06}Zr_{0.94}O_{1.97}$, which represents a relation between molar percentages of 3% yttria and 97% zirconia, it is possible to use that relation in order to calculate the number of moles of the reactants.

The following 2-step chemical reaction representing the co-precipitation process is considered: the first depicting the calculated stoichiometry for the hydroxide precipitation, and the second creating the desired 3YSZ nanopowders and other products, after the washing, drying and calcination processes.

$$0.06\,YCl_3 \cdot 6\,H_2O \;+\; 0.94\,ZrOCl_2 \cdot 8\,H_2O \;+\; 2.06\,NH_4OH$$

$$\xrightarrow[co-precipitation]{}$$

$$0.94\,Zr(OH)_4 \;+\; 0.06\,Y(OH)_3 \;+\; 2.06\,NH_4Cl \;+\; 6.94\,H_2O$$

$$\xrightarrow[washing,\;\; drying\ and\ calcination]{}$$

$$Y_{0.06}Zr_{0.94}O_{1.97} \;+\; 2.06\,NH_4Cl \;+\; 8.91\,H_2O$$

This was possible by balancing the relationship between reactants and products, considering all elements that participate in the chemical reaction. Knowing the number of moles and molar masses of each compound, it is possible to calculate the inventory of a single co-precipitation reaction, as seen in Table 3.7.

The intermediate products were not considered in terms of their environmental impacts, because they are only formed in an intermediate phase of the co-precipitation process. In fact, these products will only serve in this study for the calculation of energy and water consumption, since the zirconium and yttrium hydroxides are the materials that undergo the washing, drying and calcination processes.

Table 3.7. Amount of reactants used and products created during a single co-precipitation process.

	Name	**Chemical Formula**	**Molar Mass (g/mol)**	**Mole Number (mol)**	**Mass (g)**
Reactants	Zirconyl chloride	$ZrOCl_2 \cdot 8\,H_2O$	322.25	0.94	302.92
	Yttrium chloride	$YCl_3 \cdot 6\,H_2O$	303.36	0.06	18.20
	Ammonium hydroxide	NH_4OH	35.05	2.06	72.19
	Total Mass				**393.31**
Intermediate Products	Zirconium hydroxide	$Zr(OH)_4$	159.25	0.94	*149.70*
	Yttrium hydroxide	$Y(OH)_3$	139.93	0.06	*8.40*
	Ammonium chloride	NH_4Cl	53.49	2.06	110.19
	Water	H_2O	18.02	6.94	125.03
	Total Mass				**393.31**
Final Products	*3YSZ*	$Y_{0.06}Zr_{0.94}O_{1.97}$	122.60	1.00	*122.60*
	Ammonium chloride	NH_4Cl	53.49	2.06	110.19
	Water	H_2O	18.02	8.91	160.52
	Total Mass				**393.31**

The values from Table 3.7 represent the quantity of materials consumed and produced in order to obtain 122.60 g of 3YSZ. However, since the functional unit of this study is 1 kg of produced 3YSZ, the inventory must correspond to the inputs and outputs required to obtain that amount. To achieve this, the process must be performed several times. Hence, to reach the desired functional unit, the reaction must be performed 8.16 times. Therefore, by proportionally multiplying the values of material flows of Table 3.7, the total LCI of this method is obtained, as shown in Table 3.8.

Simply for means of comparison, the reaction's efficiency can be studied by calculating the fraction of 3YSZ produced, per the amount of reactants required to produce it. This delivered a total conversion efficiency of 31.17%, when considering all reactants. In relation only to the amount of zirconium and yttrium precursors used, 38.18% formed 3YSZ.

3.3.4. Water and Energy Consumption

3.3.4.1. Water and ethanol consumption of the washing cycles

The washing process, which is necessary for the co-precipitation method, requires the use of great amounts of water and ethanol. The estimates taken from Table 3.6 are that firstly, the precipitated hydroxides are washed 4 times with deionized water, considering the amount of water used to be 2 times the mass of the precipitates. Thereafter, they are washed again, but with ethanol, a total of 2 times, considering the amount of ethanol per wash to be 2.5 times the mass of the water washed precipitates. To calculate this water and ethanol consumption, all that is left is knowing the mass of the precipitates.

The quantity of precipitates can be retrieved from Table 3.7 as being 158.09 grams (149.70 g of $Zr(OH)_4$ and 8.40 g of $Y(OH)_3$). However, those values equate, from stoichiometry, to the exact mass of those compounds. In reality, these precipitates are typically hydrated and the emulsion already contains water. It is imperative to the results that we can estimate the mass of the precipitates considering a real situation.

Therefore, our efforts were based on Patil and Bhargava, (2012) [68], where it is cited that *"this amount of water in precipitate was reproducibly seen to be around 93% of the filtered coprecipitated mass"*. This shows that the water hydrating the precipitates corresponds to 93% of its weight. In other words, from 158.09 g of precipitates, we can estimate that these are hydrated with 147.03 g of water. Therefore, the hydrated precipitates that go through the washing process are estimated to weigh around 305.11 g.

In accordance with this, a total of 19.91 kg of deionized water is need for the 4 washes and a total of 12.44 kg of ethanol for the 2 washes, to obtain the defined functional unit of 1kg of 3YSZ.

3.3.4.2. Energy consumption of stirring, drying and calcination processes

To calculate the energy consumption of the co-precipitation process, the appropriate equipment for the occurring processes must be specified. An oven and a furnace for the drying and calcination processes, were selected respectively, from the Carbolite Gero 30-3000ºC *"Laboratory & Industrial Ovens and Furnaces"* catalogue. These can be seen in Annex A.

For the drying process, the selected laboratory oven was the *PN 30*, which has a slow airflow for powder drying along with a maximum temperature of 300ºC. It also presents characteristics necessary for the energy consumption calculation, such as:

- Heat-up time of 52 minutes.
- Maximum power of 0.75 kW.
- Holding power of 0.30 kW.

For the calcination process, the chamber furnace *AAF 12/18* was chosen, due to it being suitable for heat treatment of metals and presenting a maximum continuous operating temperature of 1200 ºC. It also presents the following characteristics:

- Heat-up time of 70 minutes.
- Maximum power of 7.08 kW.
- Holding power of 3.50 kW.

Considering the power of the equipment selected and multiplying it by the amount of time they are functioning (24 hours of drying and 2 hours of calcination), the energy consumption can be calculated. However, the holding power and heat-up time of the equipment were measured at different temperatures than the desired ones. Through proportional calculations and estimates, the holding power and heat-up times for the drying and calcination processes at 100ºC and 800ºC, respectively, were:

$$P_{drying,holding@100ºC} = 240\ W = 0.24\ kW$$

$$\Delta t_{drying,heat-up@100ºC} = 18.9\ min = 0.315\ h$$

$$P_{calcination,holding@800ºC} = 5600\ W = 5.6\ kW$$

$$\Delta t_{calcination,heat-up@800ºC} = 50.9\ min = 0.848\ h$$

Using these values, it is possible to calculate the amount of energy that the oven and chamber furnace consumed during their working periods.

Drying process:

For the drying process, the oven will consume energy while heating up to the desired temperature of 100ºC and also during the 24 hours that it is drying the precipitates. Therefore,

$$E_{drying,heat-up} = P_{drying,máx} * \Delta t_{drying,heat-up@100ºC} = 0.75 * 0.315 = 0.236\ kWh$$

$$E_{drying,holding} = P_{drying,holding@100ºC} * \Delta t = 0.24 * 24 = 5.76\ kWh$$

This gives us the final value of energy consumption for the drying process,

$$E_{drying\ process} = E_{drying,heat-up} + E_{drying,holding} = 0.236 + 5.76 = 5.996\ kWh$$

Calcination process:

For the calcination process, the chamber furnace will consume energy while it is heating up to the desired temperature of 800ºC, and also during the 2 hours of keeping that temperature and heat-treating the precipitates, in order to produce the desired 3YSZ nanopowders. Therefore,

$$E_{calcin,heat-up} = P_{calcin,máx} * \Delta t_{calcin,heat-up@800ºC} = 7.08 * 0.848 = 6.004\ kWh$$

$$E_{calcin,holding} = P_{calcin,holding@800ºC} * \Delta t = 5.6 * 2 = 11.2\ kWh$$

This gives us the final value of energy consumption for the calcination process:

$$E_{calcination\ process} = E_{calcin,heat-up} + E_{calcin,holding} = 6.004 + 11.2 = 17.204\ kWh$$

Stirring process:

While the precipitation reaction is occurring, the emulsion is under constant vigorous stirring. Considering the estimates from Table 3.6, the mixture is estimated to be stirred for approximately 1 hour at the required reaction temperature. To do this, a hotplate magnetic stirrer from the *"Thermo Scientific Round Top Hotplate Stirrers"* catalogue was also selected, with the *Thermo Scientific RT2 Advanced Hotplate Stirrer* being the chosen equipment. It presents a heating power of 600 W and, likewise, we can calculate its energy consumption,

$$E_{stirring} = P_{hotplate\ stirrer} * \Delta t = 0.6 * 1 = 0.6\ kWh$$

In order to obtain 1 kg of produced 3YSZ, the co-precipitation process must be performed 8.16 times. Although the drying and calcination process can be performed in only one go, since the precipitates can be accumulated, the stirring process has to be done every time the co-precipitation process occurs. Therefore,

$$\Leftrightarrow E_{stirring,total} = 0.6 * 8.16 = 4.896\ kWh$$

Total energy consumption:

By adding all these calculated values, the total energy consumption for the defined function unit will be of $28.096\ kWh$. However, to increase the reliability of the results, a 95% efficiency was considered for these equipments, corresponding to,

$$E_{Co-Precipitation} = \frac{28.096}{0.95} = 29.575\ kWh$$

3.3.5. Inventory Results

Considering all the information above, the total life-cycle inventory for the co-precipitation process, considering the production of 1 kg of 3% mol yttria-stabilized zirconia is presented in its totality in Table 3.8.

Table 3.8. Life-cycle inventory of the co-precipitation process (per 1 kg of 3YSZ produced).

Constituents	Amount
Inputs:	
Zirconyl chloride	2.4707 kg
Yttrium chloride hexahydrate	0.1485 kg
Ammonium hydroxide	0.5888 kg
Washing:	
Deionized water	19.91 kg
Ethanol	12.44 kg
Outputs:	
3% mol yttria-stabilized zirconia	*1.0000 kg*
Ammonium chloride	0.8988 kg
Water	0.1309 kg
Energy:	
Electricity {PT}	29.575 kWh

It is important to note that ammonium chloride is extremely detrimental and causes severe harm to the environment and, thus, cannot be directly emitted into the environment. It must be treated, recycled, or even used as such being considered a reaction by-product and therefore require impact allocation. Due to the lack of information regarding the function of this substance in the process, the ammonium chloride output was considered outside the scope of this study.

3.4. Life-cycle Inventory (LCI) for the EDS Method

3.4.1. Steps for EDS Method

The production of 3YSZ nanopowders through an emulsion detonation synthesis is briefly explained in Section 2.4. In synthesis, this process consists in a water-in-oil emulsion made from two different phases (an internal aqueous phase and external oil-based phase), which through vigorous stirring at a reaction temperature of 95ºC were emulsified.

This emulsion is then inserted into a cartridge which is made from high-density polyethylene (HDPE), weighing only 10g and having a capacity for 1.2kg of emulsion. When the cartridge is placed in a secure place and ready for the detonation phase, the emulsion is ignited. As detonation occurs at high temperatures and pressures in microseconds, the precursors are quickly decomposed under the shockwave effect and suffer an oxidation reaction, forming the desired zirconium and yttrium oxides. After expanding and cooling to room temperature, these nanopowders are collected.

Shown in Figure 3.2 are the material and energy flows of this process, depicting all inputs incorporated into the emulsion, along with the detonation products which is mainly the desired 3YSZ nanopowder, but also gaseous emissions.

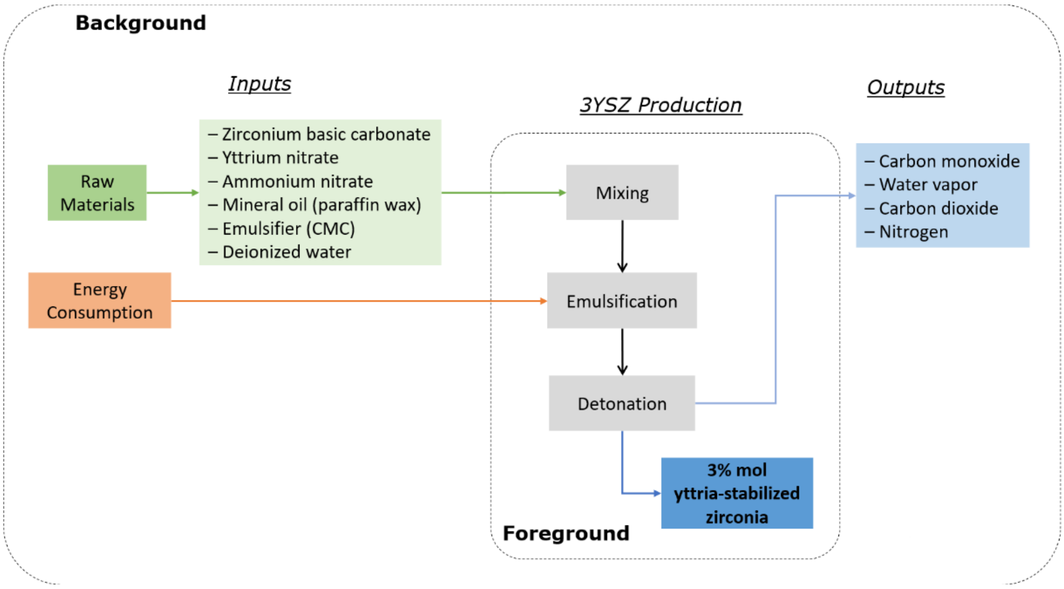

Figure 3.2. Framework of 3YSZ produced by EDS method, depicting the system boundaries.

3.4.2. Stoichiometry

The production of 3YSZ by EDS method presents completely different conditions, materials and processes when compared with the co-precipitation process. The reactants used in this study are provided by a European company that is representative of this sector and produces this material through this method of synthesis.

From the information supplied, it was possible to know the composition of the 1.2 kg emulsion, which is constituted by 35% of zirconium basic carbonate. Considering this and the yttrium-zirconium proportional relation of the final product (3% molar of yttria and 97% of zirconia), using stoichiometric calculations the content of yttrium nitrate represents 5.55% of the total amount. It is also known that 5% of the emulsion is composed of deionized water and 7% is a mixture of mineral oil and emulsifier – this latter is made of 70% mineral oil in the form of paraffin wax and 30% of carboxymethyl cellulose (CMC) as the emulsifying agent. The rest of the emulsion is composed of ammonium nitrate, corresponding to 47.45% of the total emulsion. Since its composition is known, along with the total mass of the emulsion, the amount of each reactant can be calculated and their number of moles, by stoichiometric calculations.

Considering that the EDS method works with a detonation reaction, the synthesized products, besides the desired metal oxides, are gas effluents typical of a combustion, like water vapor (H_2O), nitrogen (N_2), carbon monoxide (CO) and carbon dioxide (CO_2). This method typically occurs as an unfinished combustion, wherein the formation of CO occurs prioritized in relation to CO_2, which is only be produced if there is excess oxygen in the reaction.

Through various stoichiometric calculations, it was confirmed that there is indeed excess oxygen, which can react with CO to form some amount of CO_2. Then, by recalculating the stoichiometry of the reaction but now accounting the formation of CO_2 in the products, the following chemical reaction was obtained:

$$1.36\ Zr(OH)_2CO_3 \cdot ZrO_2\ +\ 0.17\ Y(NO_3)_3 \cdot 6\ H_2O\ +\ 7.11\ NH_4NO_3$$
$$+\ 0.21\ C_{20}H_{42}\ +\ 0.10\ C_8H_{16}O_8\ +\ 3.33\ H_2O$$
$$\longrightarrow$$
$$2.90\ Y_{0.06}Zr_{0.94}O_{1.97}\ +\ 25.17\ H_2O\ +\ 5.96\ CO\ +\ 7.37\ N_2\ +\ 0.41\ CO_2$$

Since the number of moles for the detonation products are now known, along with their molar masses, it is possible to calculate their masses and create the life-cycle inventory for the EDS method. Also, each detonation requires the use of one cartridge made of high-density polyethylene (HDPE), with a mass of 10 g, which will also be considered in the inventory.

Table 3.9. Material flows for the EDS method, considering a cartridge with 1.2 kg of emulsion.

	Name	Chemical Formula	Molar Mass (g/mol)	Mol	Mass (g)
Reactants	Zirconium basic carbonate	$Zr(OH)_2CO_3 \cdot ZrO_2$	308.47	1.36	420.00
	Yttrium nitrate	$Y(NO_3)_3 \cdot 6\ H_2O$	383.01	0.17	66.57
	Ammonium nitrate	NH_4NO_3	80.04	7.11	569.43
	Mineral oil (Paraffin wax)	$C_{20}H_{42}$	282.55	0.21	58.80
	Emulsifier (CMC)	$C_8H_{16}O_8$	240.21	0.10	25.20
	Deionized water	H_2O	18.02	3.33	60.00
	Total Mass				**1200.00**
Products	3YSZ	$Y_{0.06}Zr_{0.94}O_{1.97}$	122.60	2.90	*355.17*
	Water vapor	H_2O	18.02	25.17	453.49
	Carbon monoxide	CO	28.01	5.96	166.81
	Nitrogen	N_2	28.01	7.37	206.59
	Carbon dioxide	CO_2	44.01	0.41	17.93
	Total Mass				**1200.00**

Table 3.9 reveals that, per each detonation, 355.17 g of 3YSZ nanomaterial is produced. The defined functional unit for this study is 1 kg of 3YSZ produced, so the detonation process was performed several times for the desired amount to be obtained, and the inventory was also adapted for the functional unit selected. This LCI can be observed in Table 3.10, after also calculating the energy consumption.

Simply for means of comparison, the reaction's efficiency can be studied, by calculating the fraction of 3YSZ produced per the amount of reactants required to produce it. The total amount of reactants delivered a converting efficiency of 29.60%. In relation only to the amount of zirconium and yttrium precursors used, 73.00% formed 3YSZ.

3.4.3. Energy Consumption

The only energy consuming process necessary for the production of 3YSZ nanopowders, during the EDS process, is in the emulsification, where the two phases are thoroughly stirred for 10 minutes and heated to 95ºC, in order to cause total emulsification of all the materials. To do this, considering the "*Thermo Scientific Round Top Hotplate Stirrers"* catalogue [107], a hotplate stirrer was chosen (with capacity to heat while stirring the emulsion), and the selected equipment was the *Thermo Scientific RT2 Advanced Hotplate Stirrer*, which has a heating power of 600 W. Thus, the energy consumed by this equipment was converted to the functional unit, corresponding to 0.282 kWh.

3.4.4. Inventory Results

Considering all the information mentioned above, a life-cycle inventory of the EDS method can be established, in relation to the defined functional unit of 1 kg of produced 3% mol yttria-stabilized zirconia. This LCI can be observed in Table 3.10.

Table 3.10. Inventory for the process of emulsion detonation synthesis (per 1 kg of 3YSZ produced).

Constituents	Amount
Inputs:	
Zirconium basic carbonate	1.1825 kg
Yttrium nitrate hexahydrate	0.1874 kg
Ammonium nitrate	1.6032 kg
Mineral oil (Paraffin wax)	0.1656 kg
Emulsifier (CMC)	0.0710 kg
Deionized water	0.1689 kg
Packaging:	
High-density polyethylene	0.0282 kg
Outputs:	
3% mol yttria-stabilized zirconia	*1.0000 kg*
Water vapor	1.2768 kg
Carbon monoxide	0.4697 kg
Nitrogen	0.5817 kg
Carbon dioxide	0.0505 kg
Energy:	
Electricity {PT}	0.282 kWh

4. RESULTS OF LIFE-CYCLE IMPACT ASSESSMENT

This section presents the Life Cycle impact Assessment (LCIA) results associated with the 3YSZ production by the co-precipitation process and EDS method. Since these are two completely distinct methods of production, their life-cycle inventories will look very dissimilar, as their consumptions and emissions differ from each other. This, therefore, translates into different categories and quantities of potential environmental impacts and allows comparable results to be interpreted and conclusions to be drawn, which is the aim of this thesis and, therefore, the focus of the following sections.

4.1. Environmental Comparison of Co-precipitation Process and EDS Method

The comparison between the potential environmental impacts of the co-precipitation and the EDS method, for the selected impact categories, can be examined in Table 4.1 and a more schematic comparison can also be observed in Figure 4.1.

Table 4.1. Comparison between the co-precipitation and EDS method environmental impacts, for the functional unit of 1 kg of produced 3YSZ nanopowders.

Impact category	**Unit**	**Co-Precipitation**	**EDS Method**
Climate change	kg CO_2 eq	3.14E+01 ***(100%)***	2.25E+01 *(71.9%)*
Ozone depletion	kg CFC-11 eq	2.07E-06 *(77.6%)*	2.66E-06 ***(100%)***
Human toxicity, non-cancer effects	CTUh	6.87E-06 *(94.1%)*	7.30E-06 ***(100%)***
Human toxicity, cancer effects	CTUh	1.38E-06 ***(100%)***	9.31E-07 *(67.6%)*
Photochemical ozone formation	kg NMVOC eq	1.24E-01 ***(100%)***	8.31E-02 *(66.8%)*
Acidification	molc H+ eq	1.95E-01 ***(100%)***	1.79E-01 *(91.9%)*
Freshwater eutrophication	kg P eq	1.32E-02 ***(100%)***	6.10E-03 *(46.1%)*
Freshwater ecotoxicity	CTUe	4.90E+02 *(92.7%)*	5.28E+02 ***(100%)***
Water resource depletion	m^3 water eq	1.46E-01 ***(100%)***	8.16E-02 *(55.7%)*
Mineral, fossil & ren resource depletion	kg Sb eq	4.35E-02 ***(100%)***	4.31E-02 *(99.1%)*

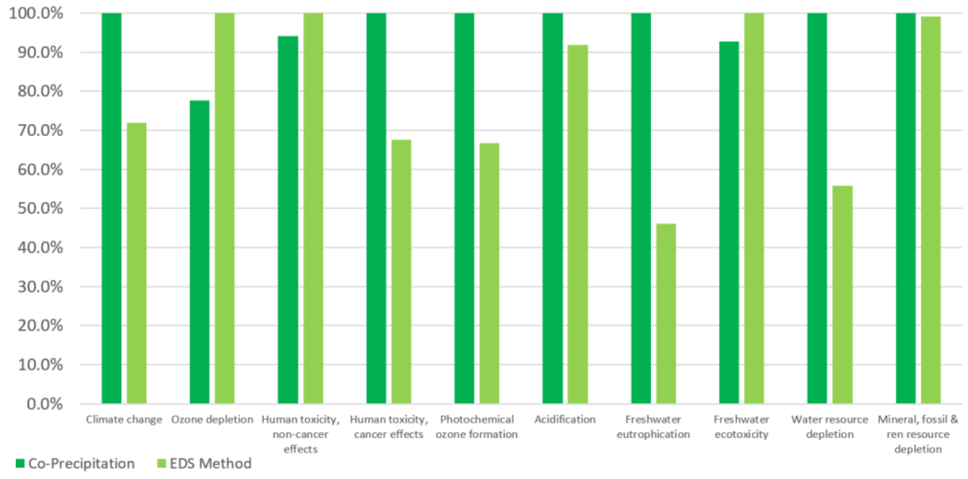

Figure 4.1. Environmental comparison between co-precipitation process and EDS method.

It can be observed that the EDS method presents lower environmental impacts for the following impact categories: climate change, human toxicity (cancer effects); photochemical ozone formation, acidification, freshwater eutrophication and water resource depletion. The category which seems to be the biggest beneficiary of using the EDS method is freshwater eutrophication, since it only causes 46.1% of the impacts produced by co-precipitation process. However, a trade-off can be observed. In this case, the EDS method presents higher impacts when considering the following impact categories: ozone depletion, human toxicity (non-cancer effects), and freshwater toxicity. In terms of the mineral, fossil and renewable resource depletion impact category, a very small difference is observed and, therefore, both processes can be considered as equally impactful.

To better understand these results, an individual assessment is performed. By looking into the individual processes of each method or, in other words, by examining the environmental impacts caused by all material and energy flows within their LCI’s, the inputs or outputs which are most impactful can be identified. Thus, the co-precipitation process and EDS method will be explored in Sections 4.1.1 and 4.1.2, respectively.

4.1.1. Contributions to the Impacts Associated with the Co-precipitation Process

In terms of the potential environmental impacts of the co-precipitation process, it can be observed in Figure 4.2 that there are three main contributors, which in combination are responsible for an average of 96.3% of the total impact for all impact categories (excluding the mineral, fossil and renewable resource depletion). These three main contributors are:

i) Zirconyl chloride, one of the main precursors consumed in this process, presents an impact ranging from 16.0% for climate change, to 46.9% for ozone depletion.

ii) The co-precipitation is a very energy-intensive process, as seen in Section 3.3.4.2. Therefore, the energy consumed from a typical electricity mix in the country of Portugal, corresponds to a contribution ranging from 23.8% to 47.6% in the freshwater ecotoxicity and acidification categories, respectively.

iii) The ethanol used in the washing cycles applied to the precipitates causes a significant portion of the co-precipitation impacts, contributing from 16.3% to 56.5% of the total environmental impacts, across the selected categories, being most impactful in the photochemical ozone formation and less impactful in the ozone depletion.

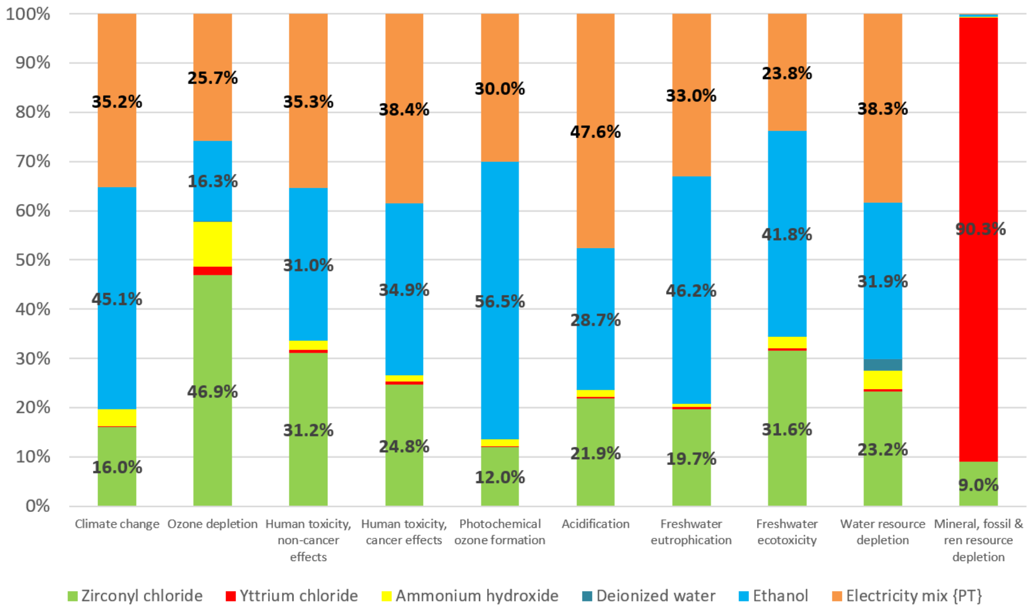

Figure 4.2. Environmental impacts of the production of 3YSZ nanomaterial through the co-precipitation process. Material and energy consumption contributions.

The only exception to the main contributors to the total impact is observed for the mineral, fossil and renewable resource depletion. It must be noted that yttrium chloride is produced using yttria as a precursor. The yttria was developed using yttrium (Y) as a raw material in an oxidation reaction, contributing to the depletion of raw materials. Due to this, this category is dominated by the potential environmental impacts of yttrium chloride.

4.1.2. Contributions to the Impacts Associated with the EDS Method

In terms of the EDS method, two main contributors to the total impacts can be observed in Figure 4.3, which are responsible for an average of 93.9% of the total impacts across the various impact categories (excepting, once again, the mineral, fossil and renewable resource depletion impact category). These impactful flows are:

i) Zirconium basic carbonate, since it is one of the most consumed materials for the EDS process. It must be noted that the inventory for the production of this substance was created in this work, based on literature research. The impact contribution of zirconium basic carbonate ranges from 35.5% to 75% in the climate change and freshwater eutrophication categories, respectively.

ii) Ammonium nitrate, which accounts for 21.1% to 60.6% of the potential total environmental impacts to the EDS method, in which the lower and higher impact contribution are for freshwater eutrophication and climate change, respectively.

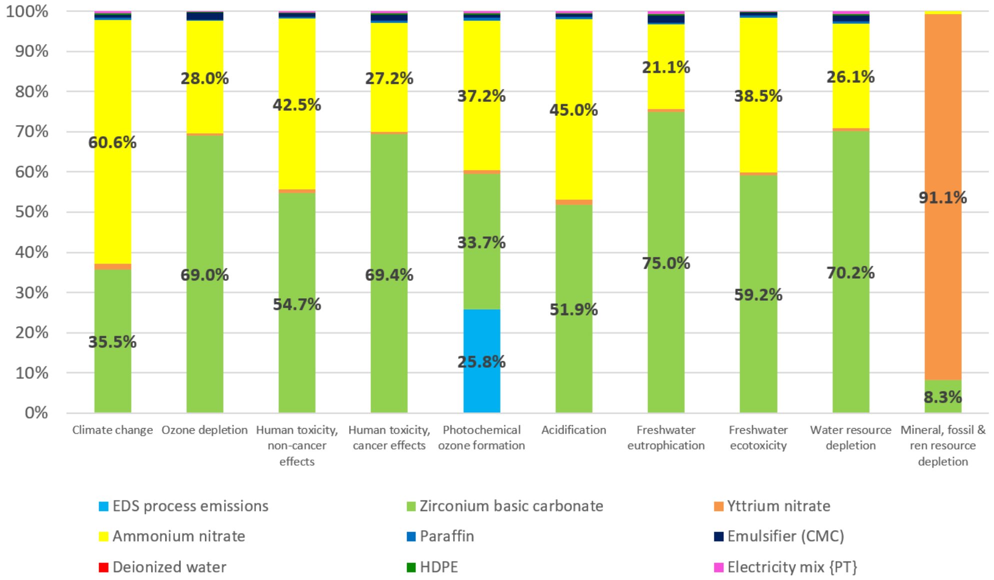

Figure 4.3. Environmental impacts of the production of 3YSZ nanomaterial by the co-precipitation process, with material and energy consumption contributions.

There are two other noticeable results worth mentioning. Firstly, the distinctly dominance of the environmental impacts of yttrium nitrate production for the mineral, fossil and renewable resource depletion category. This could be explained because the yttrium nitrate production consumes yttria as a raw material.

Secondly, the gaseous emissions during the emulsion detonation of the EDS method, which causes 25.8% of the potential environmental impacts, in terms of photochemical ozone formation. This most likely occurs due to the considerable formation and release of N_2 and CO during the detonation.

4.1.3. Comparison Between Zirconyl Chloride and Zirconium Basic Carbonate

One of the largest contributors to the environmental impacts of both processes originates from their respective zirconium precursor (zirconium chloride for co-precipitation and zirconium basic carbonate for EDS). Therefore, to understand their significance and their environmental behaviour, a comparison of the impact of both materials was made and can be observed in Table 4.2. These impacts were quantified based on a functional unit of 1 kg of produced zirconyl chloride and 1 kg of produced zirconium basic carbonate, respectively.

Table 4.2. Comparison between the potential environmental impacts caused by zirconyl chloride and zirconium basic carbonate, considering a functional unit of 1 kg of produced material.

Impact category	Units	Zirconyl chloride	Zirconium basic carbonate
Climate change	kg CO_2 eq	2.03E+00 *(30.1%)*	6.76E+00 ***(100%)***
Ozone depletion	kg CFC-11 eq	3.92E-07 *(25.2%)*	1.55E-06 ***(100%)***
Human toxicity, non-cancer effects	CTUh	8.67E-07 *(25.7%)*	3.38E-06 ***(100%)***
Human toxicity, cancer effects	CTUh	1.38E-07 *(25.3%)*	5.46E-07 ***(100%)***
Photochemical ozone formation	kg NMVOC eq	6.02E-03 *(25.4%)*	2.37E-02 ***(100%)***
Acidification	molc H+ eq	1.73E-02 *(22.0%)*	7.84E-02 ***(100%)***
Freshwater eutrophication	kg P eq	1.06E-03 *(27.3%)*	3.87E-03 ***(100%)***
Freshwater ecotoxicity	CTUe	6.27E+01 *(23.7%)*	2.64E+02 ***(100%)***
Water resource depletion	m^3 water eq	1.38E-02 *(28.4%)*	4.84E-02 ***(100%)***
Mineral, fossil & ren resource depletion	kg Sb eq	1.59E-03 *(52.6%)*	3.03E-03 ***(100%)***

From these results, it is possible to understand how much more impactful the zirconium basic carbonate is, relative to zirconyl chloride. One must note, however, that both these materials are not available in the *Ecoinvent* database and were created based on extensive literature research. For instance, the data for zirconium basic carbonate was mostly derived from an outdated patent. This could mean that the inventory was calculated on the basis of less-advanced technology with less efficiency control and the use of obsolete materials relating to nanomaterial production. This could influence the reason why zirconium basic carbonate is more impactful in comparison with zirconyl chloride.

4.1.4. Material Contributions to Zirconium Basic Carbonate Production

Zirconium basic carbonate greatly contributes to the environmental impacts of the EDS method. So, a deeper analysis for this material was performed. It is possible to see in Figure 4.4 that the highest contributors to the impacts of zirconium basic carbonate production are zirconium sulphate tetrahydrate and sodium carbonate – materials which were also missing from the *Ecoinvent* database and were created in this thesis (these can be seen in Appendix A).

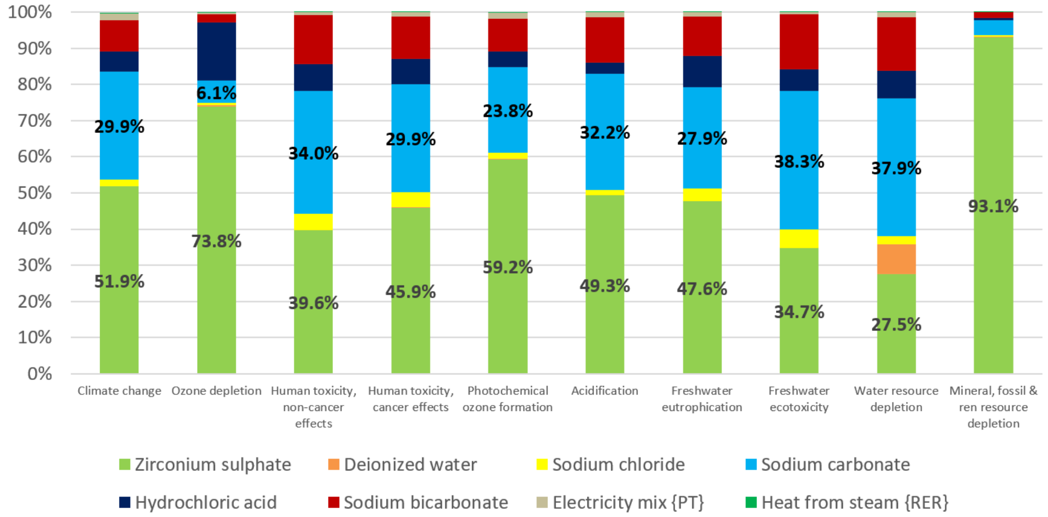

Figure 4.4. Environmental impacts of the production of zirconium basic carbonate, with material and energy consumption contributions.

To better understand the processes or materials which originate these potential environmental impacts, zirconium sulphate was also assessed, which can be seen in Appendix B. Most of the impacts from zirconium sulphate originate from zirconium oxide (zirconia) production. However, this specific zirconia production is an already existing process in *Ecoinvent*, but it is unlike the zirconia produced by the two studied processes of this thesis. This is because the 3YSZ produced in this thesis is nanosized, therefore presenting better properties, efficiency and wider range of possible uses.

4.1.5. Material Contributions to Zirconyl Chloride Production

Zirconyl chloride tetrahydrate is one of the biggest contributors to the environmental impacts of the co-precipitation process, so the main contributors to those impacts were assessed. It is possible to see in Figure 4.5 that the highest contributors to the total environmental impact is sodium zirconium silicate and hydrochloric acid. The sodium zirconium silicate is the most impactful of the two, and it is also a material which was missing from the *Ecoinvent* database and was created in this thesis (see Appendix A).

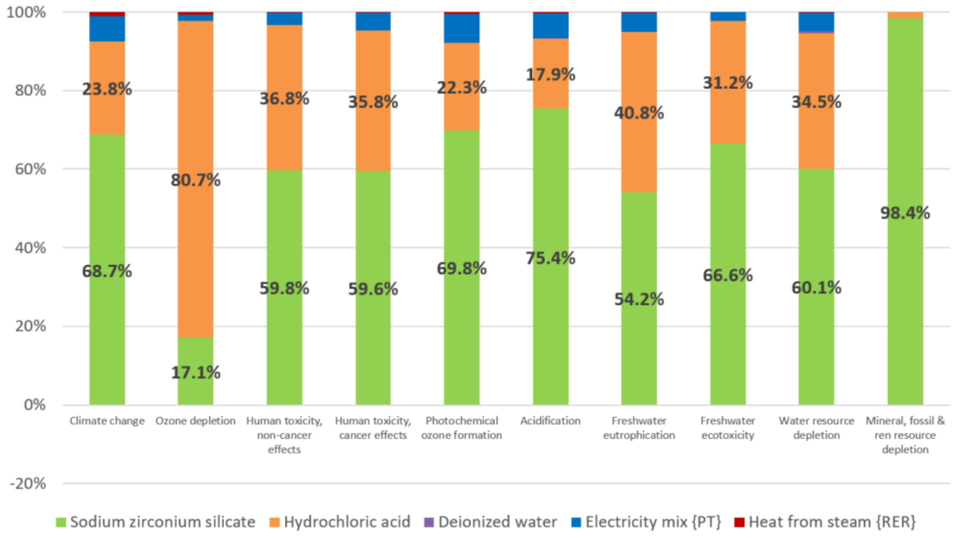

Figure 4.5. Environmental impacts of the production of zirconyl chloride, with material and energy consumption contributions.

To understand from which process in the database the environmental impacts of sodium zirconium silicate originate from, an assessment of the material contributions was performed. The major contributors were zircon (with 50% of zirconium content), and sodium carbonate.

Since sodium carbonate was also a process created in this thesis (see Appendix A), a deeper analysis was performed, which found that all their environmental impacts came from sodium bicarbonate production. All the abovementioned analysis can be examined in Appendix B.

4.1.6. Comparison Between Ammonium Hydroxide and Ammonium Nitrate

Another material contribution of the EDS method to the total environmental impact that stands out is ammonium nitrate. Since the co-precipitation process also utilizes an ammonium-related product, a comparison was performed and it can be observed in Table 4.3.

Table 4.3. Comparison between the potential environmental impacts caused by ammonium hydroxide and ammonium nitrate, considering a functional unit of 1 kg of produced material.

Impact category	Units	Ammonium hydroxide	Ammonium nitrate
Climate change	kg CO_2 eq	1.82E+00 *(21.4%)*	8.52E+00 ***(100%)***
Ozone depletion	kg CFC-11 eq	3.17E-07 *(68.0%)*	4.65E-07 ***(100%)***
Human toxicity, non-cancer effects	CTUh	2.11E-07 *(10.9%)*	1.93E-06 ***(100%)***
Human toxicity, cancer effects	CTUh	3.00E-08 *(19.0%)*	1.58E-07 ***(100%)***
Photochemical ozone formation	kg NMVOC eq	2.88E-03 *(14.9%)*	1.93E-02 ***(100%)***
Acidification	molc H+ eq	4.65E-03 *(9.3%)*	5.02E-02 ***(100%)***
Freshwater eutrophication	kg P eq	1.32E-04 *(16.4%)*	8.03E-04 ***(100%)***
Freshwater ecotoxicity	CTUe	1.88E+01 *(14.8%)*	1.27E+02 ***(100%)***
Water resource depletion	m^3 water eq	9.31E-03 *(70.2%)*	1.33E-02 ***(100%)***
Mineral, fossil & ren resource depletion	kg Sb eq	2.69E-05 *(16.9%)*	1.59E-04 ***(100%)***

From the results, it is possible to understand that ammonium nitrate presents higher impacts than ammonium hydroxide. The only categories where ammonium hydroxide presents a minor difference in the impacts compared to ammonium nitrate is for ozone depletion and water resource depletion. In all other impact categories, ammonium nitrate presents more than five times the quantity of environmental impacts of ammonium hydroxide. This is one of the major reasons the co-precipitation and EDS processes do not show a higher discrepancy in their environmental impacts.

5. CONCLUSIONS AND FUTURE RESEARCH

5.1. Key Findings and Contribution

This dissertation aimed to implement the life-cycle assessment (LCA) methodology in the production of 3YSZ nanopowders, by two distinct methods (co-precipitation and EDS), as a means to quantify and evaluate their potential environmental impacts. This allowed a comparative assessment between both processes. Therefore, this dissertation was able to obtain results and draw conclusions, while addressing the main objectives previously defined in Section 1.3, by carrying out the following steps:

In Chapter 2, various concepts were reviewed in literature, including the properties of nanomaterials and specifically 3YSZ. Also, an analysis of both production methods was performed, by identifying the materials used and relevant processes, to be able to define the steps and workflow of each method. The LCA methodology was also described, related to the motivation of this thesis, as it aspired to put emphasis on the sustainable development of nanotechnology.

In Chapter 3, the LCA study was performed with the goal and scope defined, along with the system boundaries and relevant impact categories. A cradle-to-gate approach was considered, since the focus of this thesis was on the production phase of 3YSZ.

A significant contribution of this thesis arises from the fact that the *Ecoinvent* v3 database has extensive data gaps in terms of various required chemicals. Thus, eight life-cycle inventories were created for the chemicals non-existent in the database, seen in Section 3.2 and Appendix A. The data gathering necessary to develop these inventories were very laborious, as the research literature was either mostly scarce, quite incomplete or outdated. Through stoichiometric calculations and some simplifications based on Hischier *et al.* (2005) [92] to promote consistency between processes and grant more certainty to the results, these life-cycle inventories were created and added to the database, closing some of those data gaps.

In Chapter 4, the life-cycle impact assessment (LCIA) stage is approached. The two major LCI's were converted into their potential environmental impacts, using the ILCD 2011 Midpoint+ method, and results were gathered.

These results allowed the conclusion that the EDS method, overall, presented a better environmental impact, relative to the co-precipitation process, for the production of 3YSZ nanomaterials. In terms of each impact category, it can be noted that in 4 of the 10 studied impact categories, both processes present similar results, with less than a 10% relative difference – EDS presents better results in acidification (91.9%) and abiotic depletion (99.1%), relative to the co-precipitation impacts; while the co-precipitation process presents better results in the human toxicity (non-cancer) (94.1%) and freshwater ecotoxicity (92.7%), relative to the EDS method.

Regarding the other impact categories, EDS is less environmentally impactful in terms of the following categories: climate change (71.9%), human toxicity (cancer) (67.6%), photochemical ozone formation (66.8%), freshwater eutrophication (46.1%), and water resource depletion (55.7%). However, a trade-off occurs concerning ozone depletion, where the co-precipitation process only causes 77.6% of the environmental impacts of EDS.

For the co-precipitation process, the major contributors to the total environmental impacts were zirconyl chloride (23.6%), ethanol (33.3%) and electricity consumption (30.7%), In terms of the EDS method, the biggest contributors are zirconium basic carbonate (52.7%) and ammonium nitrate (32.7%). These percentages correspond to the average contribution of the respective material or process, across all the studied impact categories.

An aspect worth mentioning is the importance of yttrium compounds in relation to the abiotic depletion category. For co-precipitation, yttrium chloride contributes with 90.3% of the total environmental impacts, while yttrium nitrate contributes 91.1% in the EDS method.

Additionally, one can conclude that the co-precipitation process is highly energy-intensive and consumes large amounts of ethanol and deionized water in its washing process. Despite presenting none of these impactful characteristics, the EDS method does not present an enormous impact difference from the co-precipitation process, although it does seem more environmentally beneficial. This arises from the fact that, although the EDS method does not consume large amounts of electricity and materials, the precursors it does consume have a large impact on the environment, such as zirconium basic carbonate and, especially, ammonium nitrate.

5.2. Limitations and Topics for Future Research

One important limitation of this thesis was the lack of data or accessible literature for both production processes. For instance, the possible outputs of ammonium chloride in the co-precipitation process, where no information could be found that could define the destination of the produced ammonium chloride. All that is known, is that ammonium chloride could not possibly be released into the environment, due to their hazardous behaviour. Due to the lack of information and constrains of time, this material was considered out of the scope of the study. However, in the future, various scenarios can be proposed (e.g., treating ammonium chloride in wastewater, re-using ammonium chloride in other processes; consider a by-product of the process and therefore allocate the calculated environmental impacts with 3YSZ production) to ascertain the influence of these changes to the total impact.

Also, an incredibly important aspect for nanomaterials is their nanosize. Although the literature was not very clear on the size difference between 3YSZ produced by co-precipitation and by EDS, the co-precipitation process could originate a high particle size in comparison with the EDS method. It can be noted that a thermal treatment stage such as a calcination process (which occurs in the co-precipitation process) leads to an evident growth of the crystallite, being difficult to obtain crystals inferior to 0.5 microns [77]. The higher sized particles of 3YSZ produced by the co-precipitation process would require an additional process such as milling. Some articles in literature (see Table 3.6) refer to the use of milling processes for the co-precipitation process, which would also increase the electricity consumption of the process. Therefore, the size of the particles from both processes requires more research, in order to include the same yield in the function unit, which can influence the final results.

For the zirconium basic carbonate production, an outdated US patent [103] was considered in order to create its life-cycle inventory, since no recent literature, which was extensive or clear enough to be able to create an LCI, was found. However, since technology is in constant evolution, a newer and more efficient manner of producing zirconium basic carbonate in comparison with this patent most likely exists.

Therefore, a larger contribution from the chemical industry to provide more data is necessary, even if limited or concealed, so that information referent to most important materials such as yttrium and zirconium compounds and others could be accessible. That collaboration from the industry would strengthen the databases and allow for inventories to be constructed with more reliable information, for better results to be obtained and conclusions drawn. This would greatly improve the environmental impact assessment studies such as LCA for chemical productions.

Another aspect that could be approached in future research is the substitution of the ammonium nitrate used in the EDS method, by a similar material with the same reactiveness and capacity for detonation, but with a better environmental performance. That would allow different scenarios to be explored.

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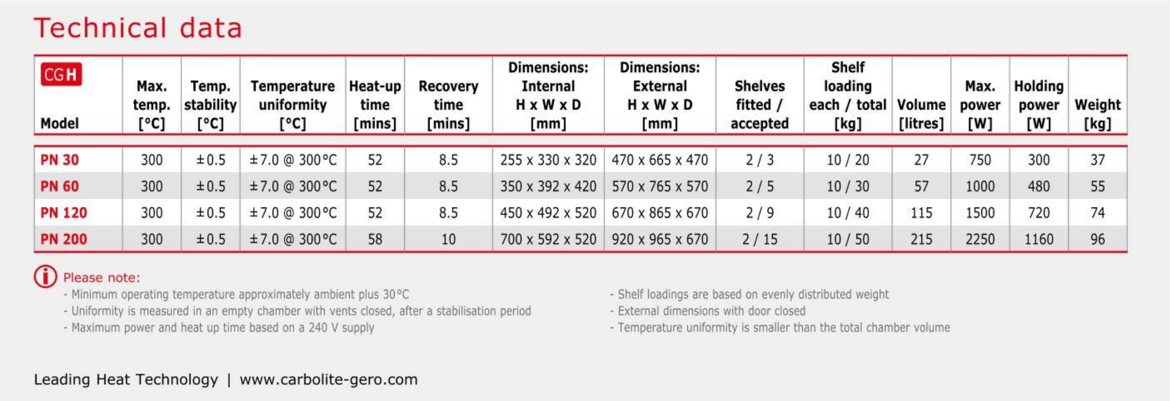
ANNEX A – OVEN, FURNACE AND HOTPLATE STIRRER CATALOGUES



Technical data

CGH Model	Max. temp. [°C]	Temp. stability [°C]	Temperature uniformity [°C]	Heat-up time [mins]	Recovery time [mins]	Dimensions: Internal H x W x D [mm]	Dimensions: External H x W x D [mm]	Shelves fitted / accepted	Shelf loading each / total [kg]	Volume [litres]	Max. power [W]	Holding power [W]	Weight [kg]
PN 30	300	±0.5	±7.0 @ 300°C	52	8.5	255 x 330 x 320	470 x 665 x 470	2 / 3	10 / 20	27	750	300	37
PN 60	300	±0.5	±7.0 @ 300°C	52	8.5	350 x 392 x 420	570 x 765 x 570	2 / 5	10 / 30	57	1000	480	55
PN 120	300	±0.5	±7.0 @ 300°C	52	8.5	450 x 492 x 520	670 x 865 x 670	2 / 9	10 / 40	115	1500	720	74
PN 200	300	±0.5	±7.0 @ 300°C	58	10	700 x 592 x 520	920 x 965 x 670	2 / 15	10 / 50	215	2250	1160	96

Please note:
- Minimum operating temperature approximately ambient plus 30°C
- Uniformity is measured in an empty chamber with vents closed, after a stabilisation period
- Maximum power and heat up time based on a 240 V supply
- Shelf loadings are based on evenly distributed weight
- External dimensions with door closed
- Temperature uniformity is smaller than the total chamber volume

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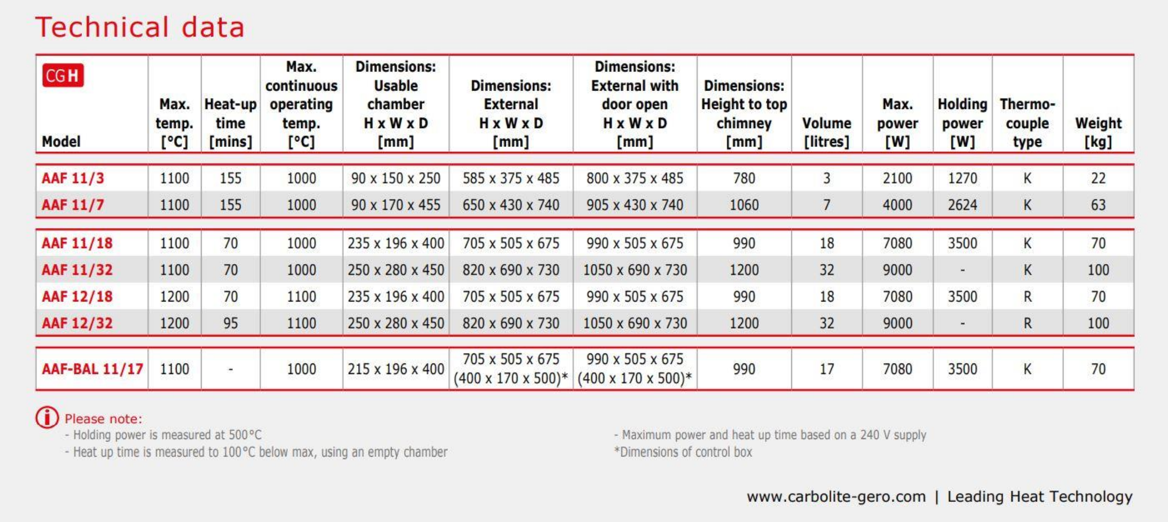
Figure A.1. Table of properties for the *PN 30* natural convection oven used in the co-precipitation process for drying (from [109]).



Technical data

CGH Model	Max. temp. [°C]	Heat-up time [mins]	Max. continuous operating temp. [°C]	Dimensions: Usable chamber H x W x D [mm]	Dimensions: External H x W x D [mm]	Dimensions: External with door open H x W x D [mm]	Dimensions: Height to top chimney [mm]	Volume [litres]	Max. power [W]	Holding power [W]	Thermo-couple type	Weight [kg]
AAF 11/3	1100	155	1000	90 x 150 x 250	585 x 375 x 485	800 x 375 x 485	780	3	2100	1270	K	22
AAF 11/7	1100	155	1000	90 x 170 x 455	650 x 430 x 740	905 x 430 x 740	1060	7	4000	2624	K	63
AAF 11/18	1100	70	1000	235 x 196 x 400	705 x 505 x 675	990 x 505 x 675	990	18	7080	3500	K	70
AAF 11/32	1100	70	1000	250 x 280 x 450	820 x 690 x 730	1050 x 690 x 730	1200	32	9000	-	K	100
AAF 12/18	1200	70	1100	235 x 196 x 400	705 x 505 x 675	990 x 505 x 675	990	18	7080	3500	R	70
AAF 12/32	1200	95	1100	250 x 280 x 450	820 x 690 x 730	1050 x 690 x 730	1200	32	9000	-	R	100
AAF-BAL 11/17	1100	-	1000	215 x 196 x 400	705 x 505 x 675 (400 x 170 x 500)*	990 x 505 x 675 (400 x 170 x 500)*	990	17	7080	3500	K	70

Please note:
- Holding power is measured at 500°C
- Heat up time is measured to 100°C below max, using an empty chamber
- Maximum power and heat up time based on a 240 V supply

*Dimensions of control box

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Figure A.2. Table of properties for the *AAF 12/18* standard ashing furnace used in the co-precipitation process for calcination (from [109]).

Ordering Information and Specifications

Cat. No.	**88880006**	**88880005**
Plug Configuration		
Temperature Range	Ambient 50°C to 350°C / 122°F to 662°F	
Heating Control	Feedback Control with PID / Scale	
Stirring Speed Range	30 to 2000rpm	
Maximum Load (vessel)	25kg / 55.1lbs	
Stirring Capacity (H_20)	20L	
Body Material	Aluminum	
Top Plate Material	Ceramic coated aluminum	
Top Plate Dimensions	140mm / 5.5in diameter	
Overall Dimensions (WxDxH)	161 x 290 x 100mm 6.34 x 11.42 x 3.94in	
Heating Power	600W	
Power	120V, 60Hz	230V, 50/60Hz
Certifications	CE, cCSAus	
Warranty	2 Years	

Accessories for RT2 Advanced Hotplate Stirrer	**Cat. No.**
Heating Bath	**88880141**
Transparent Shield (PC)	**88880142**
Support Rod (Ø12mm, 400mm, M10)	**88880143**
Temperature Probe (PT 100, SN-8-4 connector sensor)	**88880147**
C-5, Clamp Holder (PP body, Ø12 mm)	**88880148**
3 Prong Clamp (60mm grip)	**88880149**
Temperature Probe (PT100, A Class, 400°C)	**88880150**

Includes Temperature Probe
(PT 100, SN-8-4 connector sensor)

Figure A.3. Table of properties for the *RT2 Advanced Hotplate Stirrer* used in the EDS Method for mixing and heating the emulsion and for the stirring necessary in the co-precipitation process (from [107]).

APPENDIX A – PREPARATION OF THE REACTANT'S PRECURSORS

Yttria (Y_2O_3) production:

Since no literature on its production was found, the yttria production process was considered, in the *SimaPro* software, by using yttrium in the form of a raw material, while oxygen was considered through an existing process of cryogenic air separation. Therefore, the basic chemical reaction was of an oxidation as follows,

$$4\,Y \;+\; 3\,O_2 \longrightarrow 2\,Y_2O_3$$

With this being a simple reaction and since the molar masses of these elements and molecules are known, if their masses are calculated in accordance with a functional unit of 1 kg of Y_2O_3 produced, a life-cycle inventory is accomplished, as seen in Table 3.2 and Table 3.4.

Zirconium sulphate tetrahydrate ($Zr(SO_4)_2 \cdot 4\,H_2O$) production:

From Houchin, (1992) [110], we have that zirconium sulphate tetrahydrate can be produced through leaching of a low-silica-containing zirconiferous material, considered in most of the examples of the article as zirconia (ZrO_2), with sulfuric acid (H_2SO_4). This reaction occurs in the form of an acid leach slurry, which also contains some amount of deionized water. Therefore, considering stoichiometry rules, the following chemical reaction was considered,

$$ZrO_2 \;+\; 2\,H_2SO_4 \;+\; H_2O \;\rightarrow\; Zr(SO_4)_2 \cdot 4\,H_2O$$

Sodium zirconium silicate (Na_2ZrSiO_5) production:

For sodium zirconium silicate, it is known that it is a by-product of decomposing zircon. Considering a variant of the caustic fusion process, seen in [98] we can produce an acid-soluble sodium zirconium silicate as seen in,

$$ZrSiO_4 + Na_2CO_3 \longrightarrow Na_2ZrSiO_5 + CO_2$$

Zirconium silicate ($ZrSiO_4$) occurs in nature as zircon, which is already quantified in terms of environmental impacts in the *SimaPro* software. However, sodium carbonate (Na_2CO_3) does not exist in the *Ecoinvent* database and, therefore, we must understand how it is produced, in order to create its life-cycle inventory and add it to the database.

- **Sodium carbonate (Na_2CO_3) production:**

To produce sodium carbonate, we can consider the *Solvay Process*. In this process, Na_2CO_3 is produced from sodium chloride ($NaCl$) and limestone ($CaCO_3$) by participation of ammonia (NH_3) [111]. Focusing on only one of the equations of this article, we can understand that sodium bicarbonate ($NaHCO_3$) can be decomposed by heating, forming the required sodium carbonate, H_2O and CO_2. This occurs by a calcination process, represented in the following chemical equation,

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

The total life-cycle inventory of Na_2ZrSiO_5 can be seen in Table A.1, considering as the defined functional unit a 1kg of produced material. Since this inventory required the reviewing of sodium carbonate production, its life-cycle inventory is also accounted for in the table, with its corresponding functional unit.

Table A.1. Inventory for the process of sodium zirconium silicate production, and the intermediate production of sodium carbonate.

Level 1	Level 2
Sodium zirconium silicate production (1 kg)	
Components:	
Zircon (0.7862 kg)	
Sodium carbonate (0.4546 kg)	**Sodium carbonate production (1 kg)**
Emissions to air:	*Components:*
Carbon dioxide (0.1794 kg)	Sodium bicarbonate (1.6676 kg)
Energy:	*Emissions to air:*
Electricity {PT} (0.333 kWh)	Water (0.17 kg)
Steam (2 MJ)	Carbon dioxide (0.4152 kg)
	Energy:
	Electricity {PT} (0.333 kWh)
	Steam (2 MJ)

APPENDIX B – *SIMAPRO* GRAPHICS OF MATERIAL CONTRIBUTION TO ENVIRONMENTAL IMPACTS

Material contributions to zirconium sulphate environmental impacts:

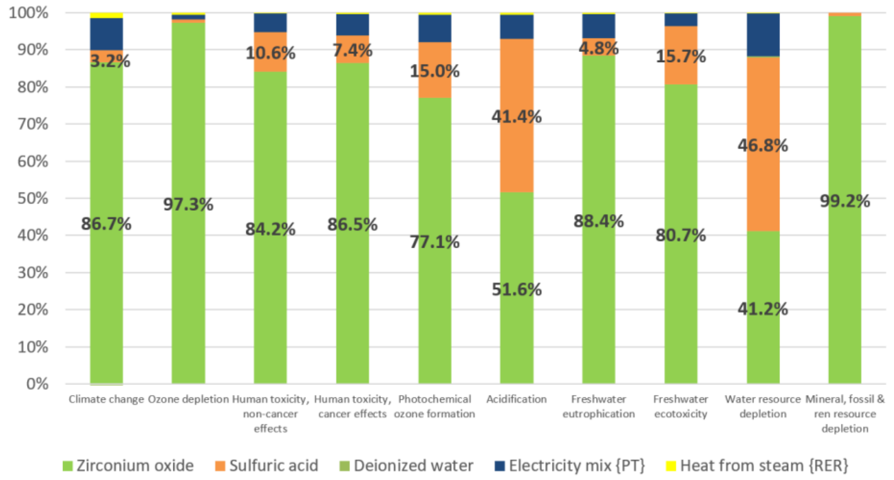

Figure B.1. Environmental impacts of the production of zirconium sulphate, with materials and energy consumption contributions.

Material contributions to sodium zirconium silicate environmental impacts:

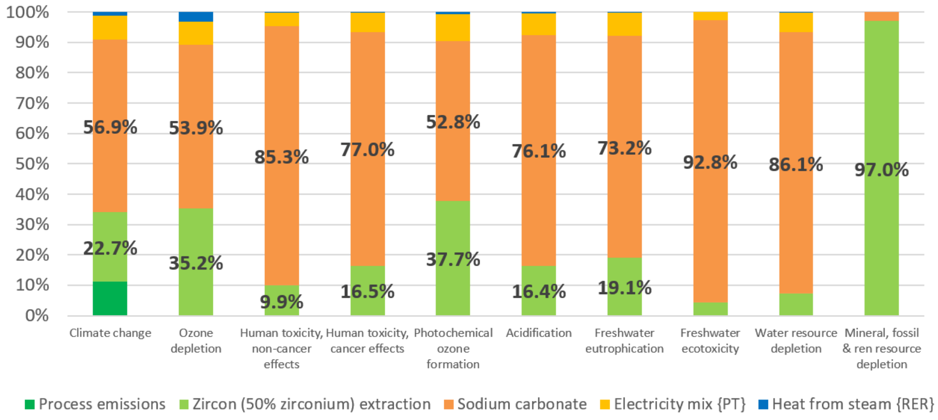

Figure B.2. Environmental impacts of the production of sodium zirconium silicate, with materials and energy consumption contributions.

Material contributions to sodium carbonate environmental impacts:

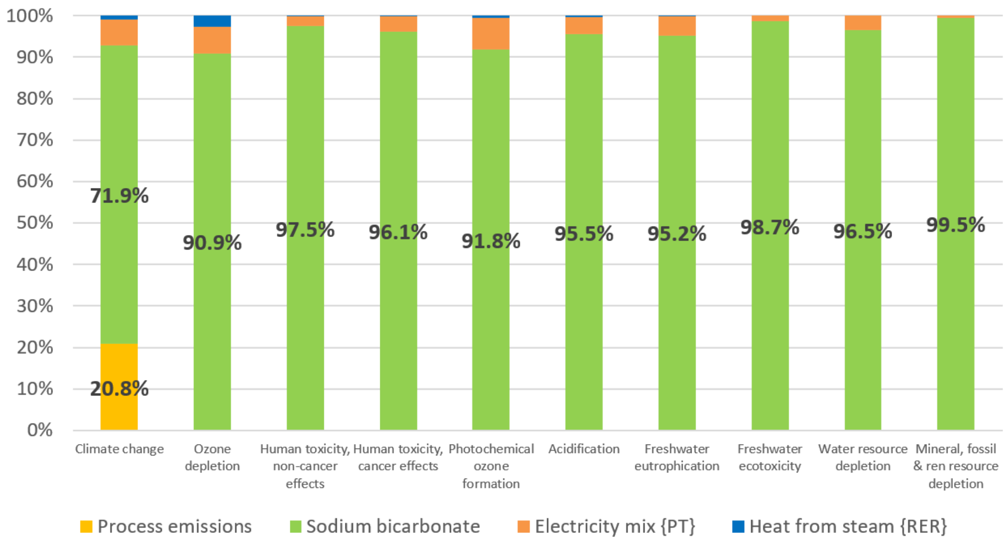

Figure B.3. Environmental impacts of the production of sodium carbonate, with materials and energy consumption contributions.