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Can nanomaterials be a solution for application on alternative vehicles? – A review paper on life cycle assessment and risk analysis

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ABSTRACT

Nanomaterials may have a key role since they can be applied in several vehicle components (such as H₂ storage, vehicle structure, batteries), but there is the concern that some nanomaterials may lead to relevant environmental impacts. This paper addresses a revision of the environmental impacts of different types of nanomaterials applied to alternative vehicles in order to reduce energy use (and consequently the global greenhouse gases emissions). A literature review is performed in order to analyze the recent improvements in nanomaterials applied to alternative vehicles. This revision will be based on life cycle assessment and risk analysis.

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Introduction and objectives

The world interest in Hydrogen (H₂) has grown over the years. Fossil fuels and environmental impacts of carbon-based energy systems are the main pointed reasons to the development of the hydrogen economy [1,2]. Despite this verdict, Mcdowall and Eames [3] emphasize the uncertainties and the contested views of sustainability in the hydrogen economy. There are three main aspects to take into account in the hydrogen economy: i) production source, ii) the vehicle type and their characteristics (such as weight) and iii) transport and storage.

The type of the feedstock for H₂ generation is crucial to establish the benefits of H₂ compared to conventional vehicles. Renewable energy sources are cited as the environmentally friendly way to produce hydrogen [2,4,5]. The hydrogen production stage is not thoroughly discussed in this study.

Regarding the second aspect, fuel cell vehicles (FCVs) show higher efficiency than vehicles with internal combustion engines (ICE) [6], however the use of nanomaterials on lightweight vehicles can contribute to improve the fuel economy. There has been an intensive investigation in order to replace the common metal (typical carbon steel) for new materials with lightweight, good strength and low-cost. These material have a great potential, the use of glass-reinforced polymers as

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structural components could yield a 20–35% reduction in vehicle weight. On the other hand, the use of carbon fiber-reinforced materials could yield a 40–65% reduction [7]. Nanocomposites can be applied in non-critical parts of the vehicle (such as front and rear fascia) and a billion kilograms of weight can be saved per year [8]. Presting and König [9] predicted that a 30% improvement in car-weight might reduce the fossil fuel consumption and consecutively the CO₂ emissions by 15%.

The nanomaterials may have a crucial role in the development of hydrogen vehicles. The high investment in the study and development of nanomaterials demonstrates the great interest in its development. In United States, in 2013, the investments in nanomaterials were \$ 1.6 billion [10]. These investments provide a demand of new and advanced materials in automotive applications. It is expected that in 2015, the consumer products with nanotechnology applications will value \$1 trillion on the world market [11]. However it is imperative to know what is the impact of these new materials in the environment and its risk to human health. Regarding to the nanomaterial's investment in 2013, in United States, only 6.3% was related to study and analysis the environmental and human health impact [10].

On the other hand, the H₂ storage is another key element to define the H₂ benefits compared to conventional vehicles [4,12,13]. Actually, the most common ways to store the hydrogen is in gaseous and liquid state. The hydrogen liquefaction requires more energy than the gasification. However, the low density of gaseous H₂ provides that the energy consumption in transport is very sensitive to the distance [4]. There are critical factors in the on-board hydrogen storage system, such as the dimension, weight and safety. These factors have boosted the use of nanomaterials for hydrogen storage. Some authors, such as Li et al. [14] explored the H₂ storage in nanomaterials by Mg atoms adsorbed boron fullerene (B80). Di Profio et al. [15] have carried out a study on ways to store hydrogen in order to assess characteristics and performance. For the storage in carbon nanotubes (CNTs) there is developed research [16], but they did not consider the costs of nanotubes production and regeneration.

Life Cycle Assessment (LCA) is a tool to quantify the environmental impact of a product, service or process. In a typical product LCA the raw materials acquisition, manufacture, use, and end of life treatment are considered. So, LCA considers all stages throughout the life of a product, from extraction of raw materials to the final stage where the residues are returned to the earth or recycled. This methodology is defined by a set of standards [17,18]. In addition the emissions are categorized according to their impact on climate change, stratospheric ozone depletion, tropospheric ozone (smog) creation, eutrophication, acidification, toxicological stress on human health and ecosystems, depletion of resources, water use, land use, and noise [19]. In this sense, the LCA is a good methodology to assess the environmental impacts of nanomaterials. In addition, the Quantitative Risk Assessment (QRA) is a good tool to demonstrate the risk caused by the handling or use a product. This methodology can provide relevant information to the competent authorities in order to enable that they take the best decisions. The methods used in a QRA were defined by Committee for the Prevention of Disasters (CPR) in three

reports. The 'Red Book' describing methods for determining the probability of undesired events, the effects they cause and any damage which may develop from those effects [20], 'Yellow Book' define methods for the calculation of physical effects resulting from releases of hazardous materials [21] and finally the 'Green Book' that describes the methods for determining of possible damage to people and objects resulting from releases of Hazardous Materials [22]. QRA can be an interesting tool to evaluate the potential risk caused by nanomaterials.

This paper aims to address the contribution of the nanotechnologies in vehicles, in order to choose the best ways to improve the production of recent models with less fossil fuels dependence and a reduction in the environmental impacts. Namely, the state of art of the life cycle assessment and risk assessment of nanotechnology applications on the lightweight, batteries and H₂ storage in vehicles are analyzed in detail. Also challenges and weaknesses to guide further research in order to anticipate magnitude and nature of the impact of specific nanotechnology-based innovations in the automotive industry are outlined.

This paper is organized in five main sections. First an introduction will be presented and then the nanomaterials applications to transport sector. Third chapter will focus on the LCA and risk assessment studies of nanomaterials. Next some research strategies will be presented and finally the main conclusions will be stated.

Transportation sector and nanomaterials

Nanotechnology has been appointed as an opportunity to influence the properties of materials in a way that smaller but more capable and more intelligent systems [23], however nanomaterials can differ from those of bulk materials [24]. The nanomaterials interest has been great in the different sectors, and in the last five years, in the U.S., there had been an investment of \$ 9 billion in the investigation and development of nanomaterials [10].

The transportation sector is one of the areas that have had benefits with nanomaterials. The use of nanomaterials is not exclusive in cars, airplanes, motorcycles and bicycles are other examples of transportation means that have had great impact with the nanotechnology evolution. Fig. 1 shows an overview of the most common applications of nanomaterials in transportation sector.

According Bidmon et al. [25], the design and conception of buses, light and heavy vehicles can be affected by nanotechnology and the related technologies in up to 60% in 10 years.

Several researchers have attempted to demonstrate the benefits of using nanomaterials in energy-related applications [26–29]. The review performed by Serrano et al. [28] demonstrated that hydrogen and new generation batteries are the most significant examples of the contributions of nanotechnology in the energy sector. Zhang et al. [29] verified through a literature review several advantages of nanomaterials using in energy applications, particularly in batteries and hydrogen storage systems. The authors enumerated three great benefits for the application of nanomaterials in energy-related applications, namely:

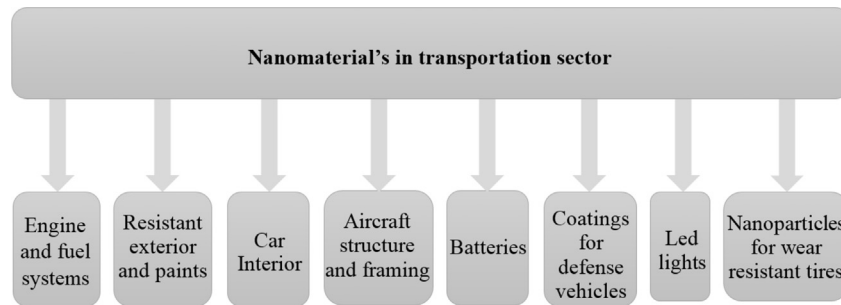


Fig. 1 – Examples of application fields of nanotechnology in transportation sector.

- 1) To provide a large surface area to boost the electrochemical reaction or molecular adsorption occurring at the solid–liquid or solid–gas interface;
- 2) To generate optical effects to improve optical absorption in solar cells;
- 3) To give rise to high crystallinity and/or porous structure to facilitate the electron or ion transport and electrolyte diffusion.

Despite of the broad range of applications of nanotechnology in the transportation sector, the next subchapters will focus primarily on the application of nanotechnology in batteries, fuel storage and vehicle structure in order to weight reduce and optimize the wear.

Special focus on the LCA and risk analysis evaluation studies on nanotechnology applications in the above referred components, applied in electric and hydrogen vehicles will be given.

Nanotechnology: application in batteries

One of the problems with the use of batteries as a way of storing energy in vehicles (hybrid electric vehicles and electric vehicles) is the weight that they represent relatively to the autonomy that they offer. Due to their small dimensions, the nanomaterials have been associated to the development of batteries in order to reduce the vehicle weight the battery dimension. Various types of materials have been suggested for use in the cathode and anode of the lithium batteries [30].

The anode and cathode material choices are a key for battery cost [31]. However the choice of these materials will also influence the safety and the battery storage capacity, so their choice will determine the value of the global battery efficiency. Nevertheless for vehicle manufactures the first thing in the anode and cathode material selection is to know if it is safe. If these chemicals are considered safe, next goal will be to improve the battery lifetime and reduce the final cost.

The most promising materials for anode are the carbon nanotubes and the nanosized transition-metal. On the other hand, the nanosized LiCoO_2 , LiFePO_4 and LiMn_2O_4 show higher capacity and better cycle life as cathode materials [32]. However some authors warn to the restrictions in the production of the used materials in batteries, such as for example, the total dependence on imports of cobalt by the USA [33]. On the other hand, Aurbach et al. [34] verified that

vanadium oxides (VO_x) compounds exhibit relatively fast kinetics, high capacity ($>200 \text{ mAh/g}$) and stability upon charge/discharge cycling in commonly used electrolyte solutions for Li-ion batteries. They affirm that VO_x compounds are promising cathodes for lithium batteries. Andersson and Råde [35] alert for the few locations where lithium, rare-earth elements, vanadium and cobalt are concentrated. So, these materials are very volatile, causing some uncertainty regarding to technological and economic development. The increased demand of these materials due to the mass production of batteries for electric vehicles and hybrid electric vehicles may trigger rising prices and monopolistic behavior.

Zhang et al. [36] use a carbon-coated graphene metal oxide anode and verified a significantly improvement in cycling performance relatively to graphene metal oxide and carbon-coated metal oxide anodes.

On the other hand, non-aqueous metal–air battery technology has been considered one good solution for long-range electric vehicles, due to the electrochemical energy storage with the highest specific energy density [37]. Nevertheless the air cathode shows some hurdles, such as the limited capacity to accommodate a significant amount of metal oxide. The high charge overvoltage, low life cycle and low power capability of the cell are other hurdles of this technology.

The development of nanomaterials for application in batteries in order to use in vehicles is in progress. However, other considerations must be taken in addition to the safety, cost and storage capacity in the selection of nanoproductions to the cathode and anode. In next chapter LCA studies of nanomaterials will be covered.

Nanotechnology: application in vehicle structure

The nanomaterials use in vehicle structure is another potential application of nanoproductions in order to reduce the vehicle weight and accordingly his consumption/autonomy. Nanotechnology has provided developing lighter vehicles, thus reducing fuel consumption without compromising vehicle safety. Ning et al. [38] demonstrated that it is possible a reduction of 55% in a bus weight using thermoplastic composite body panel instead of a conventional bus with aluminum skin and supporting steel bars. Other authors have analyzed the thermoplastic application in the body of buses. Vaidya et al. [39] demonstrated that a 40% weight reduction can be achieved if the conventional metal/plywood material

in the floor structure of buses is replaced by glass/PP woven tape forms. A thermoplastic composite for an air conditioning cover roof door on a mass transit bus was evaluated by Ning et al. [40]. They found that the using of thermoplastic composite instead to the metallic counterpart, can lead a reduction of 39% and 42% in weight and free-standing deflection, respectively. Nevertheless, Garcés et al. [8] claim that on average the thermoplastic composite allow a 25% reduction in vehicle weight. Thus, in accordance with Presting and König [9], which states that a 15% reduction in fuel consumption can be obtained with a 30% reduction in vehicle weight, in average a 12.5% reduction in fuel consumption can be obtained with the using of thermoplastic composite in vehicles.

The glass mat thermoplastic is generally associated to a low cost, good recoverability and excellent mechanical property. So, Li et al. [41] evaluate the high strain rate mechanical property of one glass mat thermoplastic. They verified that a small impact on automobile body crashworthiness and strength was obtained when the conventional body material (steel) was replaced to the studied glass mat thermoplastic (30% fiberglass reinforced polypropylene). In addition Li et al. [41] demonstrate that, with glass mat thermoplastic, a body weight reduction by 41 kg can be obtained, maintaining the automobile body crashworthiness and strength.

Despite the demonstrated great characteristic of glass fiber reinforced plastic in terms of cost, recoverability and mechanical properties, the carbon fiber reinforced plastic shows lower density, higher specific strength and superior impact resistance. Thus the carbon fiber reinforced plastic has been applied in the body of some super sport cars, such as Lamborghini. The Murciélago model of Lamborghini with a carbon/epoxy body (except for the doors and roof structure) presents 40% less weight (34 kg) than its predecessor, Diablo (that have the same components in aluminum) [42]. Liu et al. [43] analyze the lightweight EV body structure made of carbon fiber reinforced plastic and verified that the crashworthiness of body structure has been increased considerably in comparing with the glass fiber reinforced plastic body, despite the 28% reduction in weight. Parka et al. [44] demonstrate that a 41% weight reduction can be obtained with a replacing of steel front side panels to the glass fiber-reinforced plastic panels. However the total cost of plastic fender is higher than steel fender due to the cost of the plastic material.

The weight reduction is an important way in order to develop the more green vehicles. Presting and König [9] demonstrate that the weight reduction in vehicles is directly related to the reduction of the fuel consumption and therefore the CO₂ emissions reduction. So the weight reduction is a key for more sustainable vehicles, since around 87% of energy consumption and greenhouse gases emissions in a LCA is due to the vehicle operation step [4].

Nanotechnology: application in fuel cells

There are several types of fuel cells, nevertheless the polymer exchange membrane fuel cell (PEMFC) as the most likely candidate for transportation applications. The PEMFC requires cathodes and anodes with high electro catalytic activity in order to improve their efficiency.

Zhiania et al. [45] fabricated and evaluated several Nafion–Polyaniline nano-composite modified cathodes for use in PEMFC. They verified that the existence of polyaniline nanofibers in the catalyst layer before adding Nafion solution, improves the homogeneity distribution of the ionomer in catalyst layer, change the morphology of electrode and increase the performance of gas diffusion electrodes in oxygen reduction reaction. Liu et al. [46] compare the platinum catalyst with zirconia particles (Pt₄ZrO₂/C) with the commercial carbon supported platinum (Pt/C) in terms of the durability as cathode catalyst in PEMFC, and verified that Pt₄ZrO₂/C is a good candidate for achieving longer cell life-time and higher cell performance. Despite platinum be the mostly used element in catalysts for fuel cell technology, its high price has led to the search for other low cost solutions. Fiala et al. [47] analysis if the platinum doped cerium oxide is an alternative solution for use in PEMFC anode. They demonstrate that this thin film catalyst preparation represents an alternative solution due to very low loading. On the other hand, Tsudaa et al. [48] evaluate the hydrogenase-based nanomaterials for use as anode electrode catalysts in PEMFC and conclude that it nanomaterial can manipulate to exhibit the catalytic activity equivalent to the well-known platinum catalyst.

There are several studies on the application of nanomaterials as catalysts in fuel cells, including carbon nanomaterials as metal-free catalysts [49]. However it is necessary to know the real impacts (on human health and the environment) of these new solutions.

Nanotechnology: application in H₂ storage

H₂ is the most common energy vector when we talk in nanotechnology applied for fuel storage. H₂ storage is one of the most peculiar stages of the H₂ complete chain [4,50]. The use of nanomaterials, in particular carbon nanotubes (CNT), is presented as a solution. Several studies have been conducted in order to store H₂ in nanomaterials. One of the most common solid state complex hydrides for hydrogen storage is the magnesium hydride. Magnesium is cheap, light weight and abundant in addition to the H₂ storage capacity (~7.6wt.%) [51]. However the very slow hydrogenation/dehydrogenation and the very high temperatures for hydrogen desorption limit the use of magnesium in practical applications [52]. Nevertheless, some studies in order to reduce the hydrogen desorption temperature of the magnesium hydride have been conducted. Gasan et al. [51] verified that a 40–50 °C reduction can be achieved with the magnesium (Mg) hydride powder mechanically milled with 5 wt.%M (Vanadium (V), Niobium (Nb), Titanium (Ti) and Graphite). Several additives to magnesium have been studied in order to improve hydrogen absorption/desorption [53–57]. Shao et al. [58] perform a review of the nano-processing methods for Mg-based hydrogen storage and verified that the desorption thermodynamics does not change with nanosize above 5 nm.

However other solid state complex hydrides have been studied in order to store H₂. The lithium aluminum hydrides [59–62] and the sodium aluminum hydrides [63–66] are two examples of these complex hydrides. Vittetoe et al. [62] verified the great capacity of lithium aluminum hydrides in hydrogen storage (10.5 wt.%) and found that the reversibility

could be realized. On the other hand, Krishnan et al. [63] observed the reversibility of sodium aluminum hydride in the presence of microwaves. Senoh et al. [61] compared the lithium aluminum hydride with the sodium aluminum hydride and verified that besides the many similarities, the lithium aluminum hydride present best results in terms of molar conductivity; ionic transfer number of cation and activation upon cycles beyond 1.0 V.

Other two solid state complex hydrides for H₂ storage are the lithium borohydrides [67–72] and the lithium amides [73–75]. Some authors shows that lithium borohydrides have great properties for hydrogen storage [70–72]. However Lai et al. [76] evaluate the nanoconfinement of borohydrides in CNT and in copper sulfide (CuS) hollow nanospheres and verified an improvement in hydrogen storage properties. In addition they conclude that the nanoconfinement of borohydrides in CuS have great proprieties for H₂ storage, since no decrease in capacity for H₂ storage was observed, unlike to the nanoconfinement in CNT.

Dillon et al. [77] verified the great capacity of CNT to H₂ storage applications. Since then, several studies regarding the H₂ storage in CNT have been prepared [78–81]. Niemann et al. [27] through a literature review demonstrated the great potential for H₂ storage in nanomaterials. They highlight the high-surface area and the several advantages for the physicochemical reactions, such as surface interactions, adsorption in addition to bulk absorption, rapid kinetics, low-temperature sorption, hydrogen atom dissociation, and molecular diffusion via the surface catalyzt.

Despite the wide variety of methods using nanotechnology for H₂ storage, there are very few studies that evaluate the environmental and human health impacts of these storage methods.

Life cycle assessment and nanomaterials

Nanomaterials have had a strong development and it is even mentioned by some authors as the technology of the 21st century [82].

However the fast growing of nanomaterials has triggered a gap between the launch of nanoproducts and the time when nanowastes reach the environment. So, the knowledge between the nanowaste and their impact on environment and human health remains ambiguous. The LCA can be used in order to analyses not only the impact of the nanomaterials production but also the nanowaste and nanomaterials recycling impact in environment and human health. LCA is divided in four phases and the results of one phase will be dictate the conclusions of the next phase [17,18], see Fig. 2.

In the last decade the concern about the potential impacts of nanomaterials on environment and human health has been increasing. So, several LCA studies have emerged, however the majority do not consider the end-of-life due to the difficulty to find its data.

Khanna el al [83] perform a life cycle of energy consumption and environmental impacts of carbon nanofiber (CNF), and verified that despite CNF have 13–50 times more energy consumption than aluminum and a great life cycle impact in all categories, in given applications the CNF may be greener

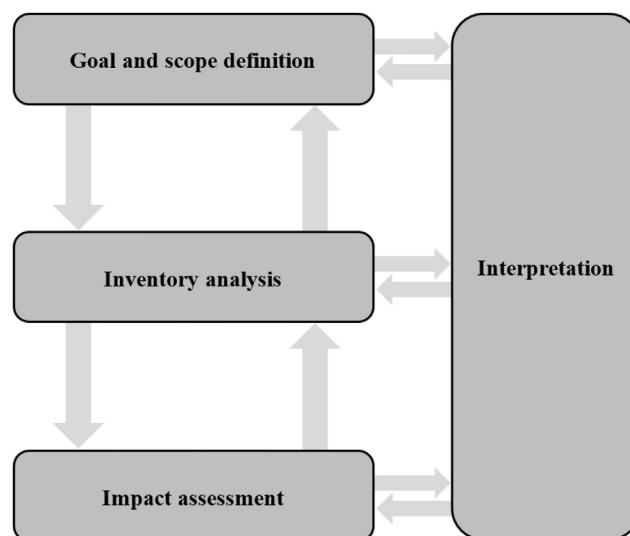


Fig. 2 – Overview of life cycle assessment phases.

than alternatives. However these authors do not analyze the end-of-life phase of CNF. Kushnir and Sandén [84] elaborated an LCA in terms of energy requirement of carbon nanoparticle production and show that carbon nanoparticles are 2–100 times more energy-intensive than aluminum. On the other hand, Isaacs et al. [85] perform an environmental assessment of single-walled carbon nanotubes (SWNT) production and found that electricity consumption during synthesis processes is the major contributor to the environmental burden. However they alert to the absence of the data in order to evaluate an environmental and human health impacts of SWNT particles. In addition Healy et al. [86] analyses the environmental impacts of three SWNT production processes and concluded that the high-pressure carbon monoxide have the lowest environmental impact. Khanna and Bakshi [87] show that the use of polymer nano composites with lower CNF loading ratios can lead to a life cycle energy saving relative to steel, due to the fuel economy benefits. Nonetheless the authors alert to the need of analyzing other factors, such as the toxicity impact. Some authors have highlighted the importance of knowing the environmental hazards of nanoproducts. Babaizadeh and Hassan [88] conduct a LCA in order to evaluate the nano-size titanium dioxide as coating on windows glass. Zuin et al. [89] evaluated the environmental impacts (using the LCA methodology) of the layer-by-layer deposition of titanium dioxide nanoparticles on polymeric membranes and verified that it has an insignificant effect on all selected impact categories. Som et al. [90,91] outline the importance of conducting an LCA of nanoproducts and present the state of the art of the potential of nanomaterials but stresses the environmental and human health exposure. EPA [92] verified that a higher energy is needed to energy needed to produce the single-walled carbon nanotube (SWCNT) anodes for lithium-ion batteries for electric vehicles. They mention that the overall environmental profile of the technology has high potential to improve if the energy intensity of the manufacturing is reduced. Wang et al. [93] elaborate a LCA of a Li-ion battery including the end-of-life step. They conclude

that nickel, cobalt, manganese, and copper are the key contributors to overall eco-toxicity risk. However they use the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) to evaluate the eco-toxicity of materials contained in the batteries, and this federal law needs some determinations about whether and how to apply the regulatory programs. In addition the data on human health and eco-toxicity that form the basis for decisions are lacking [94]. Joshi [95] adds that a comprehensive, transparent, representative, and publicly available data is needed in order to carry out the requirements outlined in the ISO standards for LCA.

In addition to the small number of studies on nanomaterials LCA, the existing studies have several gaps. Most of them were based on the energy analysis. Others (such as [85,86,89]) assess the environmental impact of the production and use of nanomaterials, however they do not address the potential release of nanoparticles during these phases and their impacts on the environmental and human health. Since each stage of nanomaterials life can lead to the release of nanoparticles [35]. Neither study presents an analysis of the end-of-life of nanomaterials for hydrogen storage, so there is a big unknown about the impacts of nanowaste. There is no established methodology for risk assessment of nanomaterials, so its real impact of a full LCA remains ambiguous. Doak et al. [96] alert for the need to the strategic approach in order to answer the questions about genotoxicity of nanomaterials. They analyze the current *in vitro* OECD genotoxicity tests for nanomaterials and verified that the bacterial reverse mutation test (Ames test) does not appear to be suitable for nanomaterial assessment.

Köhlera et al. [97] performed two case studies in order to evaluate the possible sources of CNT-release during its life cycle. They choose two R&D hot topics for the CNT-release evaluation, namely the nanomaterials use in lithium-ion secondary batteries and synthetic textiles. Köhlera et al. [97] emphasize that the release of CNT can occur not only in the production phase, but also in the usage and disposal phases of nanotube applications. In addition they suggest) as well as Upadhyayula et al. [82] and Gajewicz et al. [83]) that an LCA methodology has to be created in order to overcome the uncertainties to quantify the CNTs toxicity. Choi et al. [98] analyze the impact of the nanomaterials toxicity costs. They conclude that the introduction of new nanomaterials will be influenced by the delay to analyze all current nanomaterials. Hischer et al. [99] and Fleischer et al. [100] indicate that long-term studies analyzing the effect of different nanoparticles on human and environment should be developed. To evaluate the nanoparticles toxicity, Arora et al. [101] show the importance of preliminary studies *in vitro* and then *in vivo* studies. Lindberg et al. [102] examined if inhalation of freshly generated nanosized titanium dioxide (TiO₂) could induce genotoxic effects in lungs of mice or systematically in peripheral blood polychromatic erythrocytes. They do not find genotoxic effects by the 5-day inhalation exposure to nanosized TiO₂ anatase. Nevertheless they highlight for the fact that the used exposure oral inhalation doses of TiO₂ were much lower than in previous studies. Sadiq et al. [103] evaluate the genotoxicity of 10 nm titanium dioxide anatase nanoparticles through an *In Vivo* study in the micronucleus and Pig-a (phosphatidylinositol glycan, class A gene) mutation assays of mice's. They

show that despite the titanium dioxide anatase nanoparticles can reach the mouse bone marrow and are capable of inducing cytotoxicity, the nanoparticles are not genotoxic when assessed with *in vivo* micronucleus and Pig-a gene mutation tests. Other well-known nanomaterial that it is used in several industrial and biomedical applications (such as cosmetics, food additives and drug delivery systems) is the amorphous silica nanoparticles, because it is considered to be non-toxic. So, Ubaldi et al. [104] investigated the effects of amorphous silica nanoparticles in mouse fibroblasts, focusing on cytotoxicity, cell transformation and genotoxicity. The results shown that it does not trigger any cytotoxic or genotoxic effect and do not induce morphological transformation. Schulz et al. [105] concluded that the micronucleus rate in bone marrow cells is not adversely affected by gold nanoparticles, after conducted an investigation of two genotoxic endpoints (alkaline Comet assay in lung tissue and micronucleation in polychromatic erythrocytes of the bone marrow) 72 h after a single instillation of 18 µg gold nanoparticles into the trachea of male adult Wistar rats.

An evaluation of silver nanoparticles genotoxicity was performed by Li et al. [106]. They conclude that despite the silver nanoparticles did not induce mutations, they are genotoxic in human lymphoblastoid TK6 cells. Chen et al. [107] showed that TiO₂ nanoparticles can induce genotoxic effects both *in vivo* and *in vitro* tests. With an *in vivo* study, Huertagarcía et al. [108] conclude that the exposure of brain cells to TiO₂ nanoparticles could cause brain injury. Sargent et al. [109] evaluate the mitotic spindle aberrations at concentrations anticipated in exposed workers to SWCNT and verified that it induce the multipolar mitotic spindles. The observed disruption is common in many solid tumors including lung cancer. In addition they refer that colony formation assays showed an increased proliferation seven days after exposure, therefore an alert is given in order to have a special caution in the handling and processing of carbon nanotubes. Pan et al. [110] using the *in vitro* screening arrays for assessing possible genotoxic reactivity of SWCNT, concluded that the SWCNT revealed a damaged DNA similar to a potent genotoxic agent. In other study, Pelka et al. [111] demonstrated that SWCNT have a genotoxic potential, after studying the cytotoxic and genotoxic properties in cells of the gastrointestinal tract and have verified an increase of kinetochore-negative micronuclei and phosphorylation of the tumor suppressor protein p53. Berlo et al. [112] verified that a short-term inhalation exposure to pure carbon nanoparticles can trigger dependent oxidative stress responses in the lungs of mice. However we still cannot extrapolate this result to humans [113].

Despite some studies have been elaborated in order to understand the toxicity effect of nanomaterials, there is no consensus among them, so it is necessary to develop a research strategy for nanomaterials impact analysis.

Research strategy

It is expected that the presence of nanotechnology increases in automobile industry with the emergence of new vehicles (electric vehicles and hydrogen fuel cell vehicles). However it becomes increasingly imperative to conduct an evaluation of

all the benefits and risks to health and environment from the production, use and end-of-life of this product.

It is very important to analyze the actual nanomaterials in all stages of their life cycle. The introduction of new nanomaterials will be influenced by the delay to analyze all current nanomaterials [98]. However nanomaterials in vehicles, is a recent technology, so the time between the launch of nanoproducts and the release of nanowaste to the environment has boosted a new paradigm about the possible toxicity of the nanoproducts use as well as the nanowaste. Therefore some authors warn to the collaboration between specialists, manufacturers, and economists in order to predict the amounts of nanowaste that will be disposed [114]. Nevertheless, prediction of the amount of nanowaste produced by particular nanomaterial is not the solution, as a methodology to assess their potential impacts on the environment and human health is needed. In a revision of the environmental impacts related to the application of nanocomposites in the automobile industry, Coelho et al. [78] alert for the use of risk assessment and LCA in nanomaterials analysis, in order to develop products and services without compromising the environment. There are still open questions regarding the effects of nanomaterials on human and ecological exposure. However, the use of LCA for nanotechnology applications has been primarily focused on their potential benefits. Nevertheless, as indicates Hirschler et al. [99], there is a gap in the information of the environmental and human health impacts of the exposure to nanomaterials (including H₂ storage applications).

Some initiatives in order to regulate the toxicity of some chemical substances were taken. The Project on Emerging Nanotechnologies of Woodrow Wilson International Center for Scholars issued a report (through Breggin and Pendergrass [94]) in order to show how nanowastes could be regulated under existing federal laws (Resource Conservation and Recovery Act (RCRA) and CERCLA). Some of the wastes from nanotechnology manufacturing are and will be conventional, but others will include nanomaterials in the waste stream, whether entering a landfill, incinerator or other end-of-life scenarios. Breggin and Pendergrass [94] highlight the end-of-life regulation of nanotechnologies and indicate that in many cases the data on human health and eco-toxicity that form the basis for decisions are lacking.

EPA uses the Toxics Substances Control Act (TSCA) in order to regulate new commercial chemicals before they enter the market [115]. In addition, Wardak et al. [116] propose a risk assessment methodology based on expert opinion and existing research and data.

However, there is a need for further toxicological studies of nanoproducts. Moreover, a state of the art review revealed that there is scant research on integrated approach of LCA and exposure analysis of developed nanocomposites for vehicle applications.

There should be a collaboration between the manufacturers of nanomaterials/vehicles, research centers and government agencies, where each have their role in order to avoid the crescent potential release of nanoparticles and their lack of toxicity information. The government agencies should establish protective regulatory actions that manufacturers of nanomaterials/vehicles would follow when developing a

product. An example of these regulatory actions is to prepare a report contains all the components (and their quantities) associated with the production of a product that containing nanomaterials. In the same document the expected lifetime of the product must be indicated. It is also the duty of government agencies to establish a symbol to characterize the products with nanomaterials. Manufacturers of nanomaterials/vehicles would be required to include the symbol in products that include nanotechnology, thus allowing an easier separation of nanoproducts in their end-of-life. These regulatory protection actions established by government agencies, and the data provided by the manufacturers of nanomaterials/vehicles about lifetime, components and quantities inherent to the production of a product will allow detailed studies of nanomaterials and their effects in the research centers. Some authors, such as Handy et al. [117] defend the need to create reference materials for ecotoxicology studies, due to the wide variety of nanomaterials and the lack of information about their real impacts on human health.

The role of research and development centers is to use the provided data by the manufacturers of nanomaterials/vehicles on the products currently produced in order to establish a chemical characterization of the materials. There is a need to create a methodology for toxicity analysis of nanomaterials, allowing to classify the various types of nanomaterials according to their potential impacts on human health and on the environment. This process is particularly important in the evaluation of end-of-life nanoproducts phase, which continues to be a great unknown in LCA. The existence of a methodology may enable an evaluation of nanoproducts before they are released to the market. This can be achieved not only by chemical analysis of nanoproducts and with nanomaterials impact analysis *in vitro* and *in vivo*, but also with the use of reference materials [117]. It is also the duty of the research centers, in cooperation with the above mentioned institutions, to assess the level of release of nanoparticles during the use and end-of-life of nanoproducts. The evaluation of the potential release of nanoparticles at the end-of-life of a product is important in order to establish the legislation for nanowaste storage.

Nevertheless, it is of utmost importance chemically classify and evaluate the toxicity of the existing nanomaterials. This is a difficult process because the new nanoproducts are constantly emerging. However it is a step that must be taken into account to select the best way forward the development of safe and “green” nanotechnology.

Conclusions

It is consensual that nanomaterials have a great technological impact in automotive industry, namely in the development of alternative propulsion types in vehicles (EV and FCV with H₂). Thus, they have been used in vehicles for different purposes. The applications in fuel cells, batteries, fuel storage and in vehicle structure in order to reduce the vehicle weight and consequently the fuel consumption are just simple examples of their applications.

Nevertheless these nanoproducts have been used without having full knowledge of their potential impacts in human

health and environment. The long time between the creation of nanoparticle and its end of life, including recycling and nanowaste disposal, has provided the launching of new nanomaterials without knowing the real impacts of the existing. Thus, there is a need to assess the risk of the existing nanoparticle, in order to enable technological and environmental evolution of new nanomaterials. LCA is a tool with great potential in this type of evaluation. However, governmental agencies should act in order to create a base methodology for the assessment of nanomaterials to be followed by manufactures. On the other hand, manufacturers should provide information of the life cycle of the developing nanoparticle.

Nevertheless, more studies on the toxicity of nanoparticle are needed, not only in the recycling and nanowaste disposal phases, but also during the production and use stages. As the literature review demonstrates, few *in vivo* and *in vitro* studies have been performed in order to evaluate the toxicity of nanomaterials. However, there is a need to develop not only more toxicity studies taking into account the several phases of nanoparticle life cycle (and for the different types of nanomaterials), but also in the development of integrated approaches of LCA and exposure analysis of developed nanocomposites for vehicle applications. It is of utmost importance chemically classify and evaluate the toxicity of the existing nanomaterials.

The technological potential of nanoparticle has been demonstrated and proven. Nevertheless, collaboration between several governmental, institutional and private institutions will be crucial for the sustainable development of nanomaterials and consequently the automotive industry.

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