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POSSIBLE APPROACHES TO LCA METHODOLOGY FOR NANOMATERIALS IN SUSTAINABLE ENERGY PRODUCTION

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Abstract: : Nano-engineered materials are playing an ever growing role in the rapidly developing field of sustainable energy production. Besides providing numerous opportuni-ties for innovations in this domain, utilisation of nanostructured materials raises numerous doubts regarding their impact on the environment and possible adverse effects on human health. Providing reliable methods for analysis, evaluation and dealing with the environ-mental and health effects of nanotechnology is therefore crucial. In this article we will try to give an outline of possible approaches to deployment of Life Cycle Assessment (LCA) tools to nanomaterials used in certain applications for sustainable energy production. Use of such methods should also provide the possibility of comparing these new, emerging, technologies with that of already existing conventional ones in terms of their environmental, health and safety impacts.

Keywords: nanomaterials, sustainable energy production, Life Cycle Assessment, LCA.

1. INTRODUCTION

The environmental threats have become nowadays one of the leading problems our society is struggling to diminish. Global warming, ozone depletion, air pollution and resource depletion are the phrases one can hear at almost every step – from daily press to scientific journals. It also became crystal clear that the main cause for this kind of issues is the actual energy production based on combustion of fossil fuels. Thus, huge efforts are constantly being made into the development of a more sustainable way for attaining energy, i.e. into the development of renewable energy sector. Energy production based on solar, wind, biomass, geothermal and other renewable energy resources represents a good replacement and environmental-friendly solution compared to energy obtained from combustion of fossil fuels. Nevertheless, these eco-friendly alternatives are still insufficiently used due to high costs of their establishment and use. A solution to this problem lies in the application of nanotechnology in renewable energy sector. Nanotechnology provides tools for development of new industries based on cost-effective and cost-efficient economies and seriously contributes to a sustainable economic growth. Nano-engineered materials are playing an ever growing role in rapidly developing field of sustainable energy production. Besides providing numerous opportunities for innovations in this domain, the utilisation of nanostructured materials raises numerous doubts regarding their impact on the environment and possible adverse effects on human health. Providing reliable methods for analysis, evaluation and dealing with the environmental and health effects of nanotechnology is therefore crucial. So far, many tools for assessing environmental burdens have been developed, such as: Strategic Environmental Assessment (SEA), Environmental Impact Assessment (EIA), Environmental Risk Assessment (ERA), Ecological Footprint and Life Cycle Assessment (LCA) [1]. Among all of these techniques, LCA becomes one of the leading and most used tools for environmental

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management in various research areas and thus represents the technique that we will discuss in this paper.

2. NANOMATERIALS IN RENEWABLE ENERGY SECTOR

As mentioned above, nanomaterials, i.e. manufactured nanomaterials or engineered nanomaterials (NM) are being more and more applied in systems that support renewable energy production. Since components based on nano-structured materials are usually much smaller than those traditionally used information-processing parts built in cell phones, computers, and other similar devices, less energy is required for their production [2]. According to most of the authors and published reports, the most promising application fields for the engineered nanomaterials are solar energy (mostly photovoltaic technology) and hydrogen production [3−5]. The inclusion of nanomaterials in photovoltaic cells, such as quantum dots or dye-sensitized solar cells, can prominently increase the efficiency/cost ratio due to their higher efficiency and lower costs compared to conventional silicon-based solar cells [3,6]. Also, feasible photocatalytic water splitting using TiO_2 for hydrogen production is being investigated. Different semiconductor nano-particulated catalyst systems based on CdS, SiC, $CuInSe_2$, or TiO_2 are produced for these purposes where TiO_2 has proved to be best candidate is. However, this technology is still in the research stage due to the cost associated with its low conversion efficiency, but it is predicted to play an important role in the hydrogen production and contribute much to the coming hydrogen economy in the nearest future [3,6,7].

In general, the application of nanotechnology in renewable energy based products brings the following recognized benefits:

- By application of carbon nano-tubes in solar and fuel cells, the energy conversion efficiency is increased, as well as the storage capacity of hydrogen [8].
- Manufacturing and electricity production costs can be remarkably lessened for PV systems.
- More efficient catalysts for water splitting, use of better nanostructured materials for higher hydrogen adsorption capacity and cheaper simpler fuel cells contributes to enhanced hydrogen production, storage and transformation into electricity in fuel cells [3] etc.
- The use of nanomaterials in lithium-ion batteries can bring advantages such as higher electron transfer rates, enhanced power capability, improved triggering of some of electrochemical reactions in bulk materials and increased specific capacity because of intensification of the presence of active sites for lithium storage due to the production of active materials with high surface to volume ratio [9].

3. LIFE CYCLE ASSESSMENT METHODOLOGY IN BRIEF

One of the biggest contributors for methodology development of LCA, the Society of Environmental Toxicology and Chemistry's (SETAC) defines LCA as „a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to effect environmental improvements" [10,11]. In other words, LCA follows the life cycle of a product, process or activity from extraction of raw materials, manufacturing, transport, use, re-use, maintenance and recycling, and lastly to final disposal of the used product. Compared with other methods such as Environmental Impact Assessment (EIA) or Environmental Audit (EA), LCA is not only focusing on the emissions and wastes generated by the plant or manufacturing site, but also includes wider system boundaries i.e. all burdens and impacts in the life cycle of a product or a process [10]. Several software solutions for practicing LCA such as SimaPro (developed by PRé Consultants), Umberto (developed by IFU Hamburg and IFEU Heidelberg), TEAM (developed by Ecobalance), GaBi (developed by Department of Life Cycle Engineering of the Chair of Building Physics at the University of Stuttgart and PE International GmbH), POLCAGE (developed by De La Salle University, Philippines, and University of Portsmouth, UK) and GEMIS (developed by Öko-Institut) are available for LCA practitioners. Probably the most used software for conducting the LCA studies is SimaPro [11].

The methodological framework for conducting LCA is defined both by SETAC and The International Organization for Standardization (ISO), which constituted four phases of LCA: Goal and Scope Definition, Life Cycle Inventory Analysis (LCI), Life Cycle Impact Assessment (LCIA), and Interpretation [12].

1. *Goal and Scope Definition,* includes the reasons for carrying out the study, the intended application, the intended audience [13,14] and defines boundaries of the analyzed system. Thus, there are several approaches in practicing LCA: "Cradle-to-grave", which is the most comprehensive study

that accounts all potential impacts of a chosen product from the raw materials acquisition till the product's end of life; „Cradle-to-gate" approach considers an assessment of a partial product life cycle from resource extraction (cradle) to the factory gate, i.e., before it is transported to the consumer. In this case, the use phase and disposal phase of the product are omitted [15−17]; „Cradle-to-cradle" approach which represents a specific kind of cradle-to-grave assessment, where the end-of-life disposal step is actually a recycling process, where new or practically the same product emerges from the used product [18−20]; „Well-to-wheel" is the specific LCA used for transportation fuels and vehicles [21−22].

2. *Inventory Analysis* (*LCI),* quantifies energy and raw material requirements, atmospheric emissions, waterborne emissions, solid wastes, and other releases in relation to the functional unit [23]. Different kind of sources can be used for the data collection – from literature review, generalized LCI databases, such as the ECOINVENT (developed by Swiss Center for Life Cycle Inventories), and of course, if available, specific data for the processes of the studied product. This phase is the most time consuming phase in LCA.

3. *Impact Assessment (LCIA),* assesses the potential effects of the energy, water, material usage and the environmental releases identified in the inventory analysis on human health and the environment. Many different Impact assessment (IA) methods (ReCiPe, Eco-indicator 99, IMPACT 2002+, TRACI, IPCC 2001 (climate change), Ecosystem damage potential – EDP, CML 2001, EDIP'97 and 2003 - Environmental Design of Industrial Products, etc.) which could facilitate and speed up the impact assessment process are available in software for LCA [24,25]. Depending on the LCIA method chosen, different impact categories can be assessed. The most investigated ones are Global Warming Potential, Ozone Depletion, Human toxicity, Respiratory inorganic, Ionizing radiation, Photeochemical ozone depletion (on ground level), Acidification (land and water), Eutrophication (land and water), Ecotoxicity, Land use, Resource depletion (minerals, fossil and renewable energy resources, water) [26].

4. *Interpretation* is the phase where the results from the previous phases are evaluated in relation to the goal and scope of the study, and conclusions and recommendations are suggested together with a clear understanding of the uncertainty and the assumptions used to generate the results [1,26].

The purpose of the LCA is to help decision-makers to select the product or process that has the least impact on the environment in combination with other factors such as cost and performance data. LCA is also a useful tool that avoids unwanted „shifting of burdens" in which the reduction of environmental burden at one point of life cycle leads to its increase at another [26].

This tool dates back to 1960, when it was mostly used for packaging sector. Since then the use of LCA has expanded to more different subjects and in the last two decades it achieved its methodological development [11]. The second decade of this century is predicted to be the decade of life cycle sustainability analysis [27].

4. LCA OF NANOMATERIALS

Life cycle assessment of nano-based technologies are essential to identify all potential environmental burdens, whether positive or negative, of nano-products and to prevent and treat all potential environmental risks of further technological developments. So far, a certain number of LCA studies dealing with the use of NM in sector of renewable energy have been conducted.

The most studied nanomaterials in the aspect of LCA methodology application are carbon nanotubes, i.e. single-walled carbon nanotubes (SWNT), which are applied in Li-ion batteries, nanophotovoltaic, such as quantum dots and dye-sensitized solar cells, nano-TiO_2 which are used in solar PV cells and for hydrogen generation. Of all environmental impacts occurring from nanomaterials life-cycle toxicity is the one that poses most concern.

4.1. Carbon nanotubes

Since Carbon nanotubes were among the earliest products of nanotechnology, they are the most analysed nano-products [28].When analyzing the synthesis of SWNT, the major contributor to the environmental burden comes from electricity consumption [29]. After analyses of the environmental impacts of three SWNT production processes, arc ablation (arc), chemical vapor deposition (CVD), and high-pressure carbon monoxide (HiPco) [30], it is concluded that the high-pressure carbon monoxide has the lowest environmental impact in the case of base yield conditions, while arc ablation has the lowest impact in the case of best yield conditions. When comparing impacts of the production of traditional, battery-grade graphite anode and the SWCNT anode [31], it is showed that energy requirements for the production of the SWCNT anode is significantly greater than the energy requirements for the production of battery-grade graphite anodes and that it would annul any potential benefits that would occur from the use phase. Nevertheless, it is indicated that if electricity consumption during SWCNT manufacture is reduced to 11 kWh per kWh capacity, all impacts on the human health and the environment would be comparable to the ones occurring from the graphite anode production, except the occupational non-cancer hazard impacts. The estimation of occupational non-cancer hazard impact is especially sensitive to the SWCNT-based anode because this kind of anode has a hazard value that is much higher than the geometric mean hazard of all chemical feedstocks in the impact category. In contrast, due to the emission of insignificant quantity of ozone depletion in the process of domestic electricity generation, ozone depletion potential is practically negligible. CNTs may be released throughout all phases of a Li-ion battery life cycle, depending on how they are incorporated into a particular material [32]. Another study found that 50% of CNTs from electronics and batteries are released into the environment, primarily during the end-of-life (EOL) stage [33].

The toxicology hazard value is subject to a high degree of uncertainty since it is extrapolated from multi-walled carbon nano-tube toxicity in rodents, due to the lack of SWCNT-specific data in the literature. In order to prevent exposure to potentially toxic materials during current battery recycling operations, factors that should be altered are melting point behavior and susceptibility to Brownian motion (i.e. random movement of particles) of nanomaterials [34]. Considering the LCA for end-of-life phase of Li-ion batteries [35], it can be concluded that some particles do contribute to overall eco-toxicity risk, such as nickel, cobalt, manganese and copper,(by using the Comprehensive Environmental Response Compensation and Liability Act (CERCLA)), while there are considerable environmental uncertainties and concerns which include the fate of nano-particles in landfills, in waste water, soil leaching, and disposal in general. Still, one can scrutinize these findings considering that this CERCLA federal law has a lot of uncertainties in its application [36].

4.2. Nano-photovoltaic

A very comprehensive „cradle-to-gate" LCA study for different types of nano-structured solar cells was conducted. In this study, a proposed type of nanophotovoltaic, quantum dot photovoltaic (QDPV) module, composed of CdSe was analyzed from raw materials acquisition, manufacturing to its use phase [27,28]. The analysis was carried out using the LCA software SimaPro, where for the LCI phase Ecoinvent database and information from the peer reviewed, patent literature and other online sources are used, due to the absence of case specific data. For this reason, one can say about this study that it is a more speculating than real situation study about impacts of a QDPV. Four environmental impacts over the life cycle of PV modules were investigated: CED, GWP, aquatic acidification potential, and heavy metal emissions, since those four indicators are the most commonly reported indicators in the reviewed literature. Toxicity, one of probably the most concerning impacts from use of nano-materials, is excluded from this study, due to the lack of relevant knowledge. The result showed that, compared with other types of PV modules and energy sources, such as Ribbon multicrystalline-silicon, Monocrystalline-silicon, Multicrystalline-silicon, Amorphous silicon, Compound semiconductor, Copper indium gallium diselenide, Copper indium diselenide (CIGS/CIS), Dye sensitized PV (DSPV),QDPV modules have shorter Energy PayBack Time (EPBT − except CdTe PV modules) (Figure 1), lower Global Warming Potential (GWP) (Figure 2), lower acidification potential (SOx and NOx emissions) (Figure 3) than other types of PV modules, but also higher heavy metal emissions (Figure 4). The results of the analysis were compared with other energy sources, both renewable and nonrenewable, (such as coal, oil, lignite, diesel, natural gas, nuclear, wind, and hydropower) and it was showed that QDPV modules were better in all impact categories assessed than carbon-based energy sources, but had higher GWP and longer EPBT than wind and hydropower (Figure 5). Since materials for quantum dots for solar cell application usually contain toxic elements, it is necessary to include the toxicity impact category into LCA of QDPV.

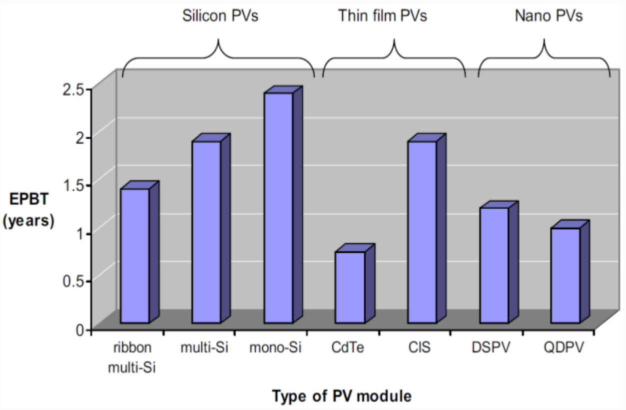

Figure 1. Comparison of EPBT of different types of PV modules [37]

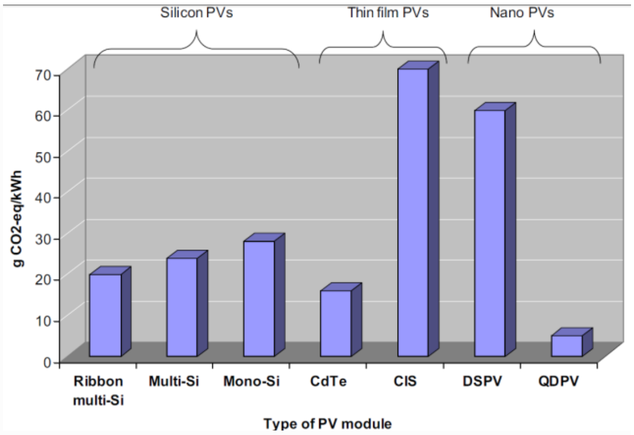

Figure 2. Comparison of GWP, expressed as CO_2 eq/kWh, of QDPV modules [37]

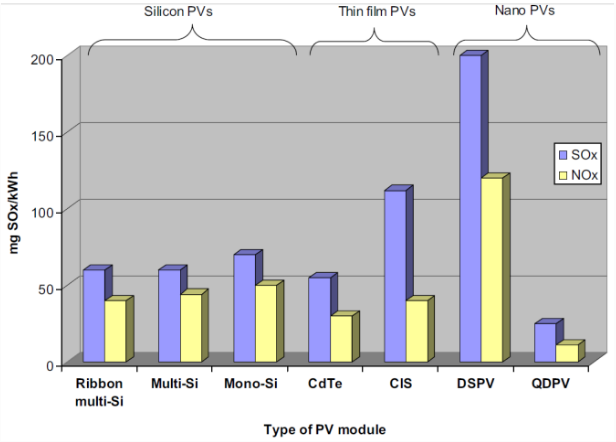

Figure 3. Comparison of Acidification potential i.e. emissions of sulphur oxides and nitrogen oxides for QDPV modules with different types of PV modules [37]

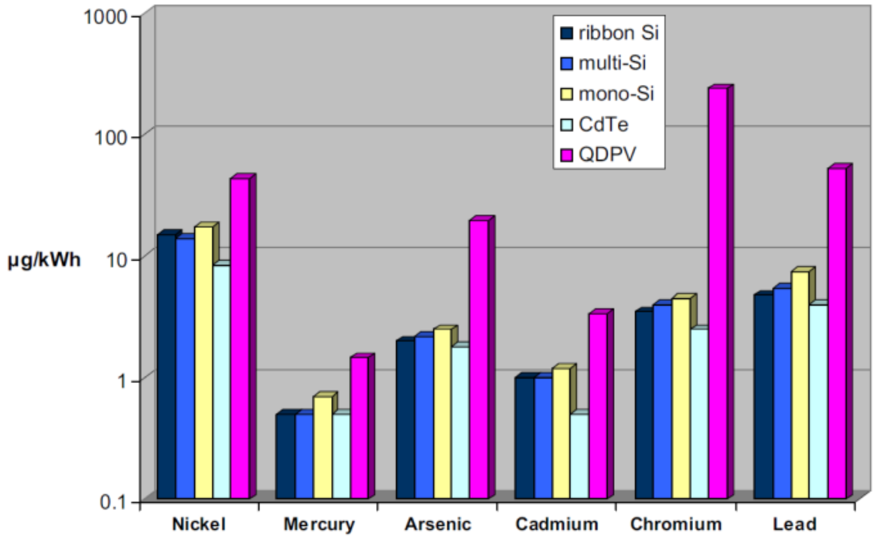

Figure 4. Comparison of heavy metal emissions, QDPV modules with silicon and CdTe PV modules [37]

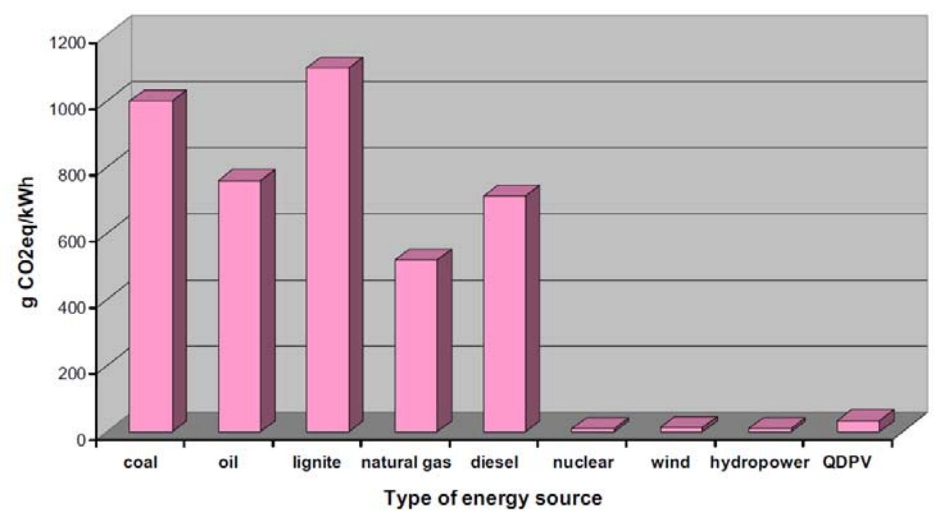

Figure 5. Comparison of GWP, expressed as CO_2eq/kWh, of QDPV modules with other energy sources, renewable and non-renewable energy sources [37]

The acquisition of raw materials for quantum dot synthesis is likely to be a major contributor to the environmental impacts. Considering conventional route of synthesis of CdSe quantum dots [39], it is showed that air emissions contribute the most to the cumulative emissions, followed by water and soil emissions. This, of course, could vary when considering the alternative route for CdSe quantum dots.

4.3. Impact of nanomaterials to human health and ecosystems

Considering the assessment of NM life cycle, one of the main concerns is if they exert any potentially negative impact on human health and ecosystems. Potential impacts of NPs may be immensely underestimated if genotoxicity is not considered. A lot of studies considering potential toxicity impact of NM have been published [40–45]. For this reason, toxicity, i.e. genotoxicity and ecotoxicity have been considered in more detail in this paper.

It is shown that the exposure to nanoparticles in plants induces reduced germination or growth, membrane damage, impaired photosynthesis, slowed or reduced reproductive development and mortality. The exposure to NPs in animals induces cytotoxicity by necrosis or apoptosis, tissue or organ-level damage, growth inhibition, impaired reproduction and/or development and mortality. For humans, molecular changes upon exposure can affect either somatic or germ cells and subsequent adverse birth outcomes and genetic diseases and carcinogenesis [40]. The mitotic spindle aberrations are anticipated in exposed workers to SWCNT. The observed disruption is common in many solid tumors including the lung cancer. Cytotoxic and genotoxic properties of SWCNT have been verified in cells of the human gastrointestinal tract [41]. Also, oxidative stress responses in the lungs of mice can be triggered by inhalation of pure CNT [42]. Some recent studies [46] found that CdSe-core QDs were indeed toxic under certain conditions and this toxicity can be modeled by processing parameters during synthesis, UV light exposure and surface coating and that it correlates with the liberation of Cadmium ions. In some studies it is shown that the penetration of quantum dots through abrasions in the skin is possible [47], and also that quantum dots can be transferred through a small food chain [48]. The minute concentrations of QDs could be sufficient to cause long lasting, even transgenerational, effects in exposed cells. Even though QDs can partially degrade in the environment or in biological systems over time, they can eventually cause small, but cumulative undesirable effects [49]. Regarding nano-TiO_2, there are a lot of uncertainties and discrepancies in the achieved results. The investigation of potential genotoxicity of TiO_2 nano-particles exposure showed contradictory results. After 5 days inhalation of mice, no genotoxic effects were observed [43] while, on the other hand, it is also showed that TiO_2 nanoparticles can induce genotoxic effects both *in vivo* and *in vitro* tests. *In vivo* tests showed that TiO_2 nanoparticles can enter directly into the brain through the olfactory bulb and can be deposited in the hippocampus region, damaging rat and human glial cells [44]. The investigation of the potential ecotoxicity impacts on algae, daphnia and fish as a result of direct release of Ag and TiO_2 nano-particles (mainly <200 nm in nominal diameter size) from various nano-materials products to the freshwater has been analyzed [45]. It was shown that nanomaterials, constituted from TiO_2 had lower ecotoxic impact than those made from Ag and there was a linear regression between Ag nanomaterials content in the considered products and the potential ecotoxicity impacts to the freshwater species, according to the release of total Ag during use (mainly washing). In general, if and how genotoxicity of NP can be induced in higher trophic level organisms through food chain remains undiscovered. The current understanding of ENP fate and transport in environmental and biological systems is poor and the current literature relies exclusively on nominal exposure [40].

The results of potential toxicity, i.e. genotoxicity of nanoparticles in the living organisms, like for nano-sized TiO_2, are taken from certain number of studies that deal with the estimation based on the results gathered from *in vitro* or *in vivo* studies [50,45,46] where no origin of these particles is taken into account, i.e. the pathways of these particles from their release till their ingestions by living beings remain unknown. In other words, the indications of genotoxicity considered in these studies are not strictly associated with the emissions of nano-TiO_2 from the structures supporting renewable energy provision and storage, such as nanostructured titania catalyst system and other similar structures, but represents undefined and more general situation. Due to the lack of exact data about behavior and impact on human health of these particles, it can only be predicted that they are causing the same effects on human and animal genome as TiO_2 nano particles studied in the aforementioned articles.

4.4 Release of nanomaterials

In order to more precisely analyze the impact of nanomaterials, i.e. nanoparticles, on human and ecosystem toxicity or even genotoxicity, it is important to assess the amount of nano-particles emitted in the environment during manufacture, transport, use, and waste disposal phases. Unfortunately, there is a big uncertainty about the releases of these particles through all of these phases.

In most of the studies dealing with the identification of possible impact from use of nanomaterials, releases are neglected. There is only one study reporting information about releases of NM from nanosilver [51]. Also, Life Cycle Impact Assessment (LCIA) publications and ecoinvent version v3.01 do not cover emissions of PM 0.1 category, which is the size category covering nanomaterials. For that reason, some authors tried to make a framework for LCI modeling of releases of NM along their life cycle [52]. They considered emissions of nanomaterials on the level of life cycle inventory (LCI) and tried to identify elements and properties that are supposed to be reported for an emission of a nanomaterial. A framework for adequate and comprehensive integration of NM releases into LCA studies has been given in a three-step method: the first step was characterization of nanomaterials, where the list of all properties for a comprehensive characterization of nanomaterials was completed according to a literature review. In the second step, this list is refined to contain only such properties that can be identified as being LCA relevant i.e., that can induce the impacts in the areas of human toxicity and ecotoxicity. The first priority properties identified are shape, size (distribution) and surface chemistry and properties of NM, whereby the second priority properties identified are composition and amount. The third and final step had an aim to translate all these NM properties into a language that LCA tools can understand. This will allow an adequate calculation of the related impacts in a subsequent impact assessment. Finally, it is outlined that a broad testing of this framework in various situations, by different case studies (covering different types of nanomaterials) is needed in order to show if the simplifications and reductions made characterization of NM releases specific enough.

5. SUMMARY AND CONCLUSION

In general, there are a lot of uncertainties considering LCA for nanomaterials. The majority of published studies analyze only the energy requirements during the production and use of nanomaterials, and if even assessing the environmental impact occurring in these phases, do not single out the potential release of nanoparticles. Effects of the exposure of humans and the environment to nanomaterials have not yet been entirely determined. It can be observed that basically all LCA studies for NM conducted so far, are not actually "cradle-to-grave" since they are focused on impacts during production and use phase, while the end-of life phase is generally omitted due to the lack of data. The potential impacts of nanowaste are still insufficiently investigated. The reason for this lies in a fairly long life cycle of nanoproducts - it takes a long time between the creation of nanoparticle till its end-of-life. New nanoproducts are emerging while there is no knowledge of all potential impacts from the existing ones. Also, no methodology for risk assessment of nanomaterials has been established, so the real impact remains vague. It is necessary to assess the risk of the existing nanoproducts, in order to enable technological and environmental evolution of new nanomaterials. Even though a lot of studies analyzing toxicity of nano-particles have been carried out, there is no consensus among them. This implies need for an integrated approach development. Due to long time of *in vivo* testing of NM, the introduction of new ones can be practically delayed. This imposes necessity for the development of less rigorous but reliable tolls for reduction of all possible negative impacts from the existing NM and to accelerate the assessment and development of the new ones [53].

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МОГУЋИ НАЧИНИ ПРИМЈЕНЕ ЛЦА МЕТОДОЛОГИЈЕ НА НАНО-МАТЕРИЈАЛЕ КОЈИ СЕ КОРИСТЕ У ОДРЖИВОЈ ПРОИЗВОДЊИ ЕНЕРГИЈЕ

Сажетак: Наноматеријали имају све већу улогу у брзо растућој области одрживе производње енергије. Поред доказаних предности коришћења наноматеријала за иновације у овом домену, њихов утицај на животну средину и здравље људи је још увек недовољно испитан. С тим у вези, налажење одговарајућих метода за анализу, процјену и третман потенцијалних ефеката примјене нанотехнологије на животну средину и здравље људи је више него неопходно. У овом раду покушаћемо да представимо кратак преглед могуће примјене процјене животног циклуса (LCA) на нанометеријале коришћене у одређеним апликцијама за одрживу производњу енергије. Коришћење ове методе би такође требало да пружи могућност за поређење нових технологија са већ постојећим конвенционалним технологијама у смислу њихових утицаја на животну средину, здравље и безбједност.

Кључне ријечи: наноматеријали, одржива производња енергије, LCA, процјена животног циклуса.

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