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Sustainable Nanotechnologies

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Methods to extrapolate and scale - up nanomanufacturing processes

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1 Description of Task

In the early stage of the development of new nanotechnological techniques major gaps in quantified material and energy flow data exist. Likewise, when comparing established or mature technologies with those still in development, one must recognize that a new technology is at the beginning of its “learning curve” and holds the potential for significant increases in practical knowledge. Against this background, methods are developed to extrapolate and scale-up nanomanufacturing processes from the laboratory scale to plant scale. The different influences of the inputs and outputs of the process are considered by appropriate conversion factors (e.g. change of yield, change of energy efficiency, change of efficiency of operating supplies).

The goal of the task 2.3 is the development of methods to extrapolate and scale-up nanomanufacturing processes to integrate the information in forecast LCA data.

2 Description of Work & Main Achievements

2.1 Introduction

In the early stage of the development of new nanotechnologies, a large degree of freedom exists to perform a more prospective environmental (or technological) assessment and a more preliminary assessment of nanotechnology.

Due to the interdisciplinary nature of nanotechnology, an enormous wealth of methods for the production of nano-scale products can be found in the literature. Products can for example be differentiated according to their basic nano-scale structure: particle-like structures (e.g. nanocrystals, nanoparticles, and molecules), linear structures (e.g. nanotubes, nanowires, and nanotrenches), layer structures (nanolayers), and other structures such as nanopores, etc. Materials can also be produced from the gas phase, the liquid phase, or from solids in such a way that they are nano-scalar in at least one dimension.

These techniques can be classified based on the type of approach as top-down or bottom-up. Top-down processes achieve nanoscale dimensions through carving or grinding methods (e.g., lithography, etching, and milling). Bottom-up methods assemble matter at the atomic scale through nucleation and/or growth from liquid, solid, or gas precursors by chemical reactions or physical processes (e.g. gas-phase deposition, flame-assisted deposition, sol-gel processes, precipitation, and self-organization techniques).

With the enormous variety of manufacturing processes of nanomaterials it would be naturally very desirable to know already as early as possible in the innovation process with which environmental impacts these various specific nanotechnological techniques are connected.

Life cycle assessment (LCA) is the most extensively developed and standardized methodology for assessing the environmental aspects and product-specific potential environmental impacts associated with the complete life cycle of a product or a process system.

The essential basis of analysis through LCA is the inventory data, such as type and amount of material and energy flows (raw material inputs, wastes, emissions, etc.). The LCA can be carried out at different stages of new nanomaterial and product development such as at laboratory level, pilot, small scale or large scale plant.

Especially in the context of the early stage of the process development specific questions arise:

- How can LCA data based on a laboratory experiment or based on a pilot plant be representative in comparison with LCA data of an industrial scale plant?
- How large are the differences of LCA data between each stage of process or product development?
- Are extrapolating estimations in different scenarios for the Scale-up and optimization of the different nanotechnologically-based manufacturing process possible?

The development of methods to extrapolate and scale-up nanomanufacturing processes to integrate the information in forecast LCA data is carried out in two steps

1. Evaluation of published LCAs of the manufacture of nanoparticles and nanocomponents
2. Description of principle method of LCA forecast of plant based on laboratory data

2.2 Evaluation of published LCAs of the manufacture of nanoparticles and nanocomponents

The largest groups of manufactured nanoparticles for industrial applications are inorganic nanoparticles (e.g. TiO_2, ZnO, SiO_2, Ag), carbon-based nanomaterials (carbon nanofiber, multi wall carbon nanotubes (MWCNT), single wall carbon nanotubes (SWCNT)), and quantum dots (semiconductor nanoparticles with a specific size (e.g. CdSe, CdS, GaN)). Beside qualitative environmental assessments of the different manufacturing methods (Steinfeldt et al. 2007; Sengül et al. 2008), unfortunately quantified material and energy flows data exist also within this range only for a very small number of manufacturing processes and/or for individual nanomaterials. A summary of published studies is shown in Table 1. Particularly remarkable is that the majority of the studies investigate the production of carbon-based nanomaterials.

Table 1: Overview of studies of published LCAs of the manufacture of nanoparticles and nanocomponents (based on Meyer et al (2009) and own data)

Nanoparticle and/or nanocomponent	Assessed impact(s)	References
Carbon nanotubes	Substance Flow Analysis (SFA)	(Lekas 2005)
Metal nanoparticle production (TiO_2, ZrO_2)	Cradle-to-gate energy assessment, global warming potential	(Osterwalder et al. 2006)
Nanoclay production	Cradle-to-gate assessment, energy use, global warming potential, ozone layer depletion, abiotic depletion, photo-chemical oxidant formation, acidification, eutrophication, cost	(Roes et al. 2007)
Several nanomaterial syntheses	E-factor Analysis	(Eckelman et al. 2008)
Carbon nanoparticle production	Cradle-to-gate energy assessment	(Kushnir and Sandén 2008)
Carbon nanotube production	Cradle-to-gate assessment with SimaPro software, energy use, global warming potential, …	(Singh et al. 2008)
Single-walled carbon nanotube (SWCNT) production	Cradle-to-gate assessment with SimaPro software, energy use, global warming potential, …	(Healy et al. 2008)
Carbon nanofiber production	Energy use, global warming potential, ozone layer depletion, radiation, ecotoxicity, acidification,	(Khanna et al. 2008)

	eutrophication, land use	
Nanoscale semiconductor	Cradle-to-gate assessment, energy use, global warming potential	(Krishnan et al. 2008)
Single-walled carbon nanotube (SWCNT) synthesis process	Stochastic multiattribute analysis	(Canis et al. 2010)
Nanoscaled polyanilin production	Cradle-to-gate assessment with Umberto software, energy use energy use, global warming potential, …	(Steinfeldt et al. 2010a)
Multi-walled carbon nanotube (MWCNT) production	Cradle-to-gate assessment with Umberto software, energy use, global warming potential, …	(Steinfeldt et al. 2010a)
Nanoscaled Titanium dioxide	Cradle-to-gate assessment, Ecoindicator 99 methodology, energy use, exergy	(Grubb and Bakshi 2010)
Fullerene (C60, C70)	Cradle-to-gate assessment with SimaPro, energy use, material intensity	(Anctil et al. 2011)
Silver nanoparticle production	Cradle to gate assessment with Umberto software and economic analysis, cost, energy use, global warming potential, …	(Kück et al. 2011)

Lekas evaluated in a substance flow analysis carbon nanotubes (CNT) throughout the economy from cradle to grave. The goal of the study was to gather production and use information of carbon nanotubes (current production, raw material inputs and quantities, end-use applications and destination of materials) from literature and nanotube company (Lekas 2005).

Osterwalder and coworkers performed cradle-to-gate assessments of titanium dioxide (TiO_2) and zirconia dioxide (ZrO_2) nanoparticle production (Osterwalder et al. 2006). The goal of the study was to compare energy requirements and greenhouse gas emissions for the classical milling process with that of a novel flame synthesis technique using organic precursors. The functional unit of the study was 1 kg of manufacturing materials.

Roes and co-workers evaluated the use of nanocomponents in packaging film, agricultural film, and automotive panels (Roes et al. 2007). The goal of the prospective assessment was to determine if the use of nanoclay additives in polymers (polypropylene, polyethylene, glass fibre-reinforced polypropylene) is more environmentally advantageous than conventional materials. Specific material and energy flows of the nanoclay production were collected. The manufacture of nanoclay includes several processes, e.g. raw clay (Ca-bentonite) extraction, separation, spray drying, organic modification, filtering, and heating.

Eckelman and co-workers have performed an E-factor analysis of several nanomaterial syntheses (Eckelman et al. 2008), as the E-factor is a measure of environmental impact and sustainability that has been commonly employed by chemists. The E-factor (or waste-to-product ratio) includes all chemicals involved in production. Energy and water inputs are generally not included in E-factor calculations, nor are products of combustion, such as water vapour or carbon dioxide. Unfortunately, the results are not comparable with the other studies.

Kushnir and Sanden modeled the requirements of future production systems of carbon nanoparticle and used also a cradle-to-gate perspective, including all energy flows up to the production and purification of carbon nanoparticles (Kushnir and Sanden 2008). All calculations are made for a functional unit of 1 kg of nanoparticles. Several production systems (fluidized bed chemical vapour deposition (CVD), floating catalyst CVD, HiPco, pyrolysis, electric arc, laser ablation, and solar furnace) are investigated and possible efficiency improvements are discussed. Carbon nanoparticles were found to be highly energy-intensive materials, in the order of 2 to 100 times more energy intensive than aluminium, given a thermal to electric conversion efficiency of 0.35.

Singh and co-workers performed environmental impact assessments for two potential continuous processes for the production of carbon nanotubes (CNT) (Singh et al. 2008). The high–pressure carbon monoxide disproportionation in a plug-flow reactor (CNT-PFR) and the cobalt-molybdenum fluidized bed catalytic reactor (CNT-FBR) were selected for the conceptual design. The CNT-PFR reactor has catalytic particles formed in situ by thermal decomposition of iron carbonyl. The CNT-FBR process employs the synergistic effect between the cobalt and molybdenum giving high selectivity to carbon nanotubes from CO disproportionation.

Healy and co-workers have performed life cycle assessment of the three more established SWNT manufacturing processes: arc ablation (arc), chemical vapour deposition (CVD), and high pressure carbon monoxide (HiPco) (Healy et al. 2008). Each method consists of process steps that include catalyst preparation, synthesis, purification, inspection, and packaging. In any case, the inspection and packaging steps contribute minimally to the overall environmental loads of the processes. Although the technical attributes of the SWNT products generated via each process may not always be fully comparable, the study provides a baseline for the environmental footprint of each process. All calculations are made with a functional unit of 1 g of SWNT.

Khanna and co-workers (Khanna et al. 2008) have performed a cradle-to-gate assessment of carbon nanofiber (CNF) production. The goal of the assessment was to determine the non-renewable energy requirements and environmental impacts associated with the production of 1 kg of CNFs. Life cycle energy requirements for CNFs from a range of feedstock materials are found to be 13 to 50 times higher than primary aluminium on an equal mass basis.

Krishnan and co-workers have presented a cradle-to-gate assessment and a developed a library of materials and energy requirements, and global warming potential of nanoscale semiconductor manufacturing (Krishnan et al. 2008). The goal of the study was to identify potential process improvements. The functional unit selected was 1 silicon wafer with a 300-mm diameter that can be used to produce 442 processor chips. The total energy required for the process is 14,100 MJ/wafer including 2,500 MJ/wafer that accounts for the manufacture of fabrication equipment. The greenhouse potential is 13 kg CO_2 eq/wafer.

Canis and co-workers (Canis et al. 2010) relate to a product development problem of selecting the most advantageous technology for manufacturing single-walled carbon nanotubes (SWCNT). Four different synthesis processes were investigated: High Pressure Carbon Monoxide (HiPCO), arc discharge (Arc), chemical vapor deposition (CVD), and laser vaporization (Laser). The case study is an example of a stochastic multicriteria decision analysis (MCDA)-based method for situations where knowledge of the weights is lacking and uncertainty about criteria scores is significant. Unfortunately, the results are not comparable with the other studies.

Steinfeldt and co-workers have performed several in-depth life cycle assessments of processes and products, including cradle-to-gate assessments of the production of nanoscaled polyaniline and of the production of multi-walled carbon nanotube (MWCNT) (Steinfeldt et al. 2010a). With the cooperation of producers, it was possible to produce detailed models of the manufacturing processes for nanoscaled polyaniline and MWCNT, and to generate specific life cycle assessment data.

Grubb and Bakshi (2010) have investigated the life cycle assessment of the hydrochloride nanomanufacturing process for producing TiO_2 nanoparticles in comparison with conventional titanium dioxide. The functional unit of the study was 1 kg of manufacturing materials. This work also includes an exergy analysis to account for material resource consumption in the process.

Anctil and co-workers (Anctil et al. 2011) have performed a cradle-to-gate energy assessment of manufacturing of fullerenes and modified derivatives. The inventory is based on the functional unit of 1 kg of product (either C60 or C70), and four synthesis methods were investigated. The embodied energy of 1 kg C60 after synthesis and separation is very different (pyrolysis with tetralin 12.7 GJ/kg C60; pyrolysis with toluene 17.0 GJ/kg C60; plasma Arc 88.6 GJ/kg C60, and plasma radio frequency (RF) 106.9 GJ/kg C60).

Kück and co-workers (Kück et al. 2011) have investigated green silver nanoparticle production using a micro reactor technology method in comparison with water-based batch synthesis. The aim of the study was to reveal the potential and constraints of this approach and to show how economic and environmental costs vary depending on process conditions. Because of the lower energy consumption and lower demand of cleaning agents, the micro reactor is the best ecological choice.

The data above can provide some insights regarding the potential burdens that must be addressed if the large-scale use of these types of nanoparticles and nanocomponents is to continue. For this purpose, the data from the studies is expressed in a common mass-based unit. Accordingly, energy demand is presented in MJ-Equivalents/kg material and global warming potential is expressed as kg CO_2-Equivalent/kg product. Energy consumption during the product life cycle is very important because it relates to the consumption of fossil fuels and the generation of greenhouse gases. Therefore, it is desirable to design manufacturing processes that minimize the use of energy. The data for energy consumption of the materials discussed above is shown in Figure 1 and 2. Additionally the comparison data of conventional materials is included.

The represented cumulative energy requirements for various carbon nanoparticle manufacturing processes differ very strongly from each other. The various processes for the production of SWCNT (excluding equipment fabrication) are by far the most energy intensive processes as compared with the production of other carbon nanoparticles. A cause for the very large differences between the examined studies lies in the different process conditions (temperature, pressure) of the manufacturing processes. Furthermore large differences are found in the assumptions of reaction and purification yields. The relatively small reference value appears remarkable for the mass production of carbon black by means of flame synthesis and also for the pilot plant production of MWCNT based on catalyst CVD.

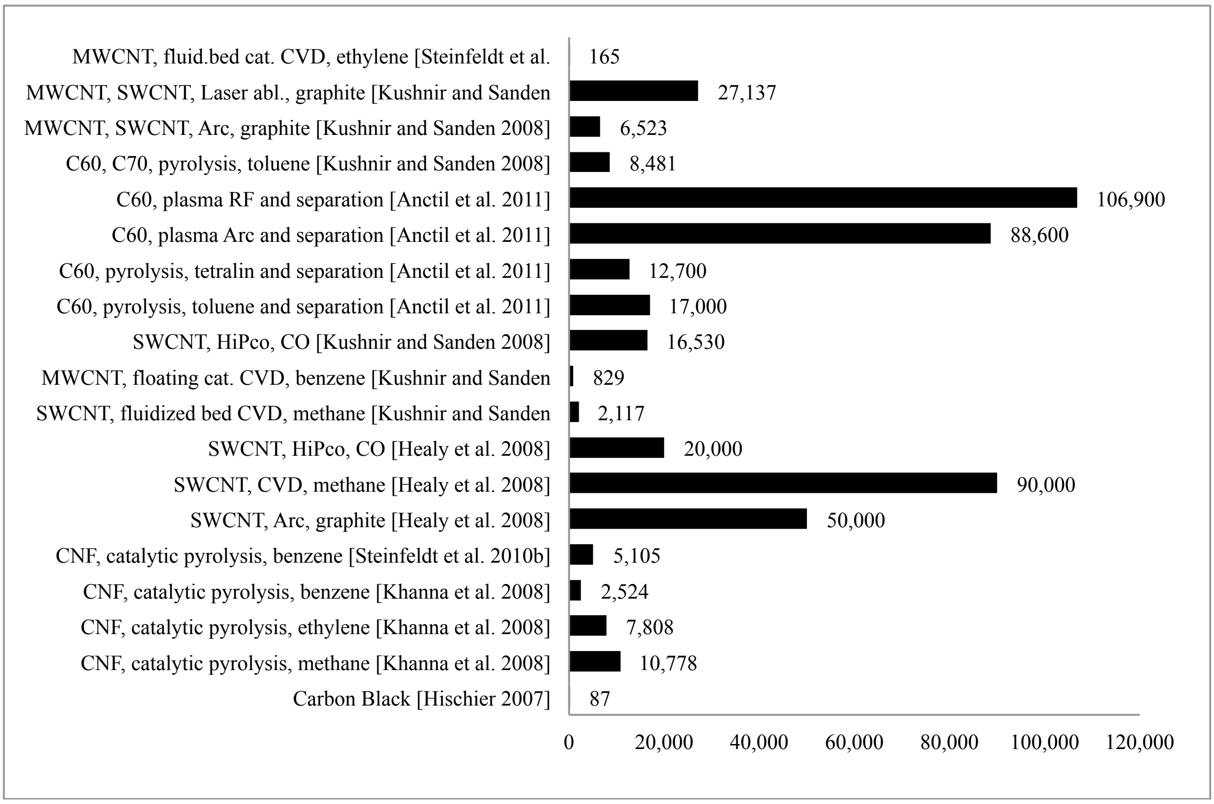

Figure 1. Comparison of the cumulative energy requirements for various carbon nanoparticle manufacturing processes [MJ-Equivalent/kg material]

The comparison of the cumulative energy requirements for the production of other conventional and nanoscaled materials and components make clear that the production of nanosemiconductors is also a very energy intensive process. Only the extraction of the precious metal platinum as an example is still more complex. The production of nanoscaled polyaniline is likewise very energy-intensive.

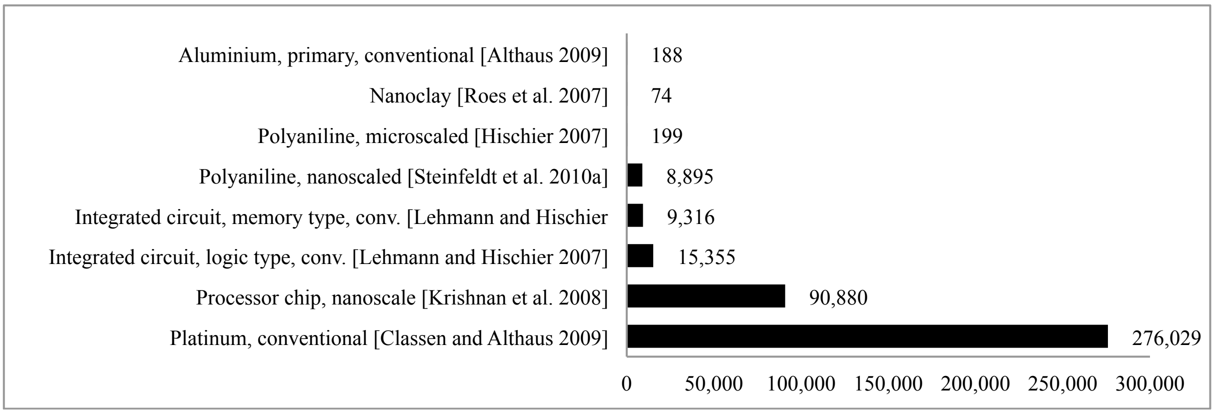

Figure 2. Comparison of the cumulative energy requirements for the production of various conventional and nanoscaled materials and components [MJ-Equivalent/kg product] (in parts own calculation)

A comparison of the global warming potential for the production of various conventional and nanoscaled materials is shown in Figure 3. The production of silver nanoparticles has the largest impact when compared to the other materials. However, the production of carbon nanofiber and nanoscaled polyaniline demonstrates also a high global warming potential. The reason for the larger global warming potentials for silver nanoparticle, CNF and polyaniline manufacturing is the much larger energy requirements when compared to other nanoparticle production. Also the cleaning agents in the manufacturing processes have a large influence on the global warming potentials. The production of MWCNT based on fluidized bed catalyst CVD is notable also here with a small global warming potential.

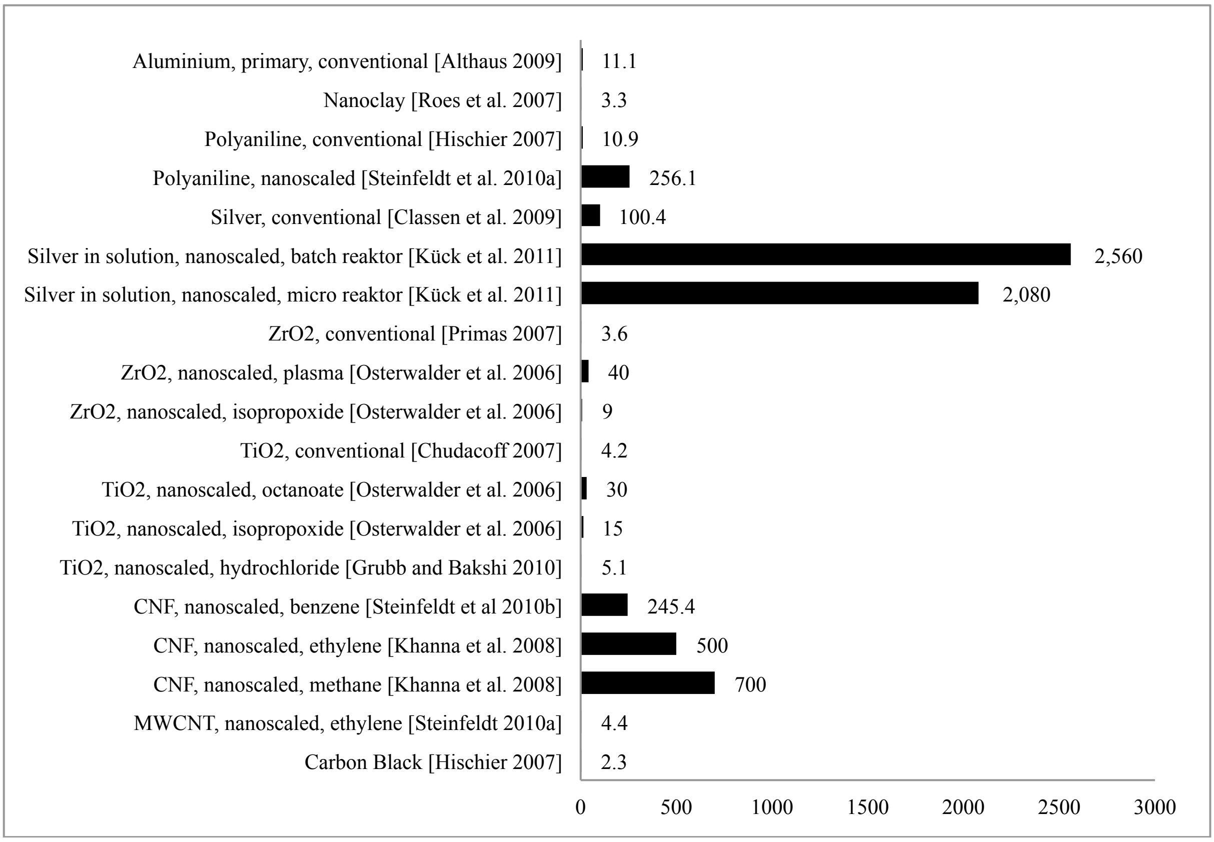

Figure 3: Comparison of the global warming potential for the production of various conventional and nanoscaled materials [CO2-Equivalent/kg product] (in parts own calculation)

The represented data are characterized by a wide range. They are derived from different LCA studies. The models of the LCA studies depict partly model data, partly laboratory data, partly data from pilot plants and large scale plant data, so that an evaluation of the results is very difficult. The comparability of the analyzed data is not actually given.

The data presented are results of 'Cradle-to-gate' Life Cycle Assessments of the production of different nanomaterials. The data do offer useful insight when considering the environmental impact of various nanotechnology-based applications with 'Cradle-to-grave' Life Cycle Assessments. Cradle-to-grave is the full Life Cycle Assessment from (pre)manufacture to use phase and disposal / recycling phase of applications. It is commonly pointed out that the nanocomponent is only a fraction of the total product (often only 1, 2 or 3 percent) implying that only a small fraction of the environmental impact of a nanoproduct can be attributed to the nanocomponent and its manufacture. The high specific energy demand for the production of the nanoparticle is reflected itself then in nanoproduct.

2.3 Description of principle method of LCA forecast of plant based on laboratory data

In the new approach of LCA forecasts are modeled on the laboratory experiments and mini plants level. On this basis extrapolating estimations in different scenarios for the Scale-up and optimization of the manufacturing process are investigated (see figure 4).

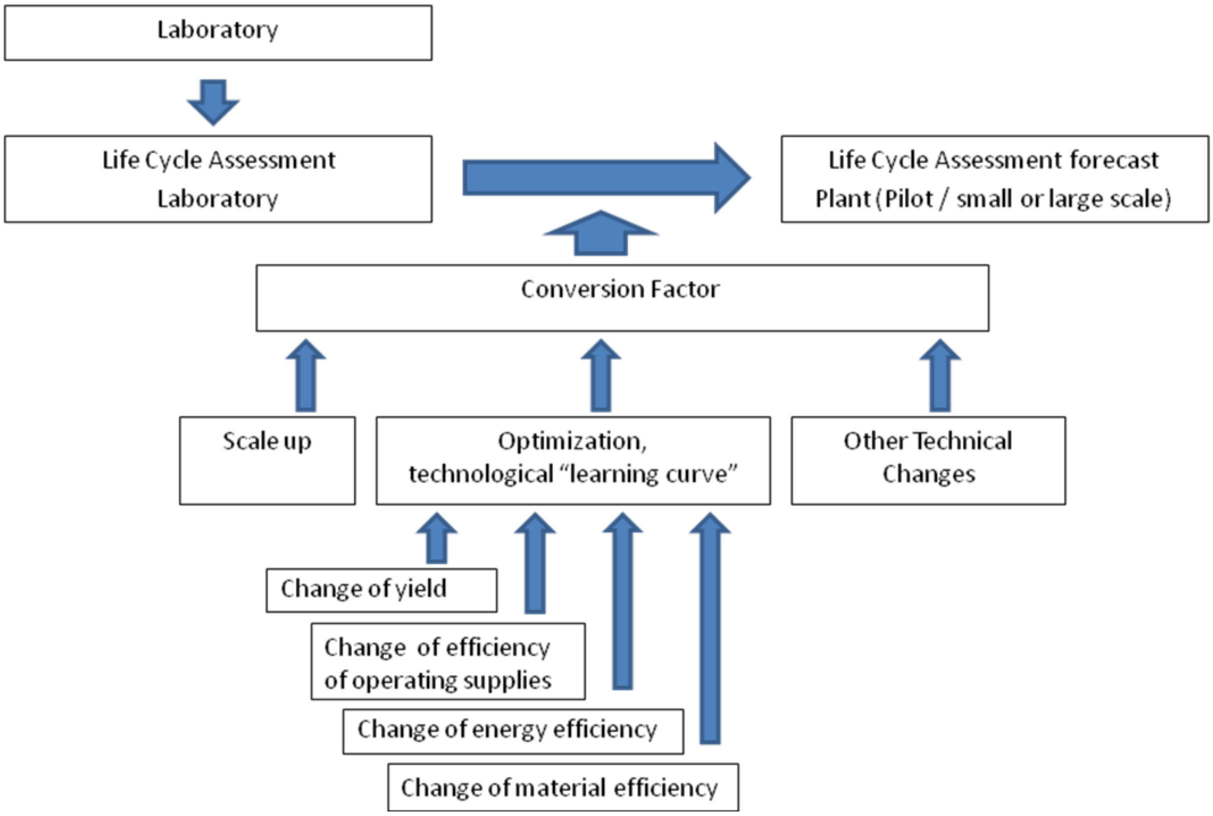

Figure 4: Principle method of LCA forecast of plant based on laboratory data (following Shibasaki 2007 and 2009)

The different influences of the inputs and outputs of the manufacturing process are considered by appropriate conversion factors.

Influence and Conversion factor by Scale up

The development of new nanotechnology based process passes through several theoretical and experimental development phases from calculation models, laboratory scale, mini plant, pilot plant to the industrial (small or large) scale. LCA analyses the manufacturing processes from a technical point of view. For reaching a specific scale up estimation, it is necessary to examine the technical process for scalability. Many chemical processes can be scaled up using dimension analysis. Also several nanological manufacturing processes (e.g. chemical vapor deposition) can be scaled up in this form.

Influence and Conversion factor by Optimization

The production scale process is an optimized process with high efficiency. During the process development at the laboratory stage the technological 'learning curve' is in the beginning. That means that the yield of synthesis, the energy efficiency, the efficiency of operating supplies, and the material efficiency are still not very optimized. With the passage of time, the enterprises gain practical knowledge in handling new technology, enabling them to reduce the material and energy inputs per unit. E.g. the yield of the new chemical process is in the beginning at the laboratory scale only 50 - 60 percent. A successful industrial process or a chemical synthesis should ensure a degree of efficiency of 80-90 percent.

A yield change can be expressed in relevant LCA data by change of required materials per functional unit, energy requirements per functional unit, emissions per functional unit etc.

Influence and Conversion factor by other Technical changes

A scale up from the laboratory scale to a production plant is often accompanied by technical changes and changes in plant design. Batch processes are mostly carried out in the laboratory scale. Continuous processes are more favorable for the cost effective production with higher output of products. The effect of the change from batch to continuous manufacturing process is taken into account in the conversion factor 'Other technical changes'.

After the investigation of all these possible influences it is possible to estimate different conversion factors. These possible conversion factors affect the change of specific material flows, of specific operating supplies flows, and of specific energy flows of the forecast plant processes in comparison to the analyzed laboratory processes.

So it is possible to perform cradle-to-gate Life Cycle Inventory data of nanotechnological techniques for the production of nanoparticles and nanocomponents in scale-up plant (see figure 4).

3 Deviations from the Workplan

The planned two steps of the task

1. Evaluation of published LCAs of the manufacture of nanoparticles and nanocomponents
2. Description of principle method of LCA forecast of plant based on laboratory data are on schedule.

During the work on this task, it became clear that, in addition and expansion to the proposal, a further step should be added. We are planning the following third step: Plausibility check, testing and derivation of appropriate conversion factors on basis of the SUN case studies.
This step can be performed only in the further phase of the project parallel to the case studies and will be reported after the month 24 as an annex of D2.2.

4 Performance of the Partners

All partners performed in satisfactory time and quality.

5 Conclusions

The goal of the task 2.3 is the development of methods to extrapolate and scale-up nanomanufacturing processes to integrate the information in forecast LCA data.

Currently, a large number of data gaps exist when considering the application of LCA to nanoproducts. Specifically, only minimal data detailing the material and energy inputs and environmental releases related to the manufacture, release, transport, and ultimate fate of nanocomponents and nanoproducts exist. The presented new approach of prospective technological assessment of nanotechnological processes throughout their life cycle based on prospective scenarios and scaling-up models can help to close the existing data gaps.

The development of methods to extrapolate and scale-up nanomanufacturing processes to integrate the information in forecast LCA data is carried out in two steps

1. Evaluation of published LCAs of the manufacture of nanoparticles and nanocomponents

2. Description of principle method of LCA forecast of plant based on laboratory data

These planned steps of the task are completed. During the work on this task, it became clear that, in addition and as an expansion to the proposal, a further step should be added.

Quantification of the conversion factors will be determined as far as possible in the context of further work on the case studies. The practical knowledge of the project enterprises in upscaling processes should be obtained. In addition, the manageability of the conversion factors as well as pooling the different flows (main materials, energies, operating supplies) should be checked.

The results of this third step 'Plausibility check, testing and derivation of appropriate conversion factors on basis of the SUN case studies' will be reported after the month 24 as an annex of D2.2.

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