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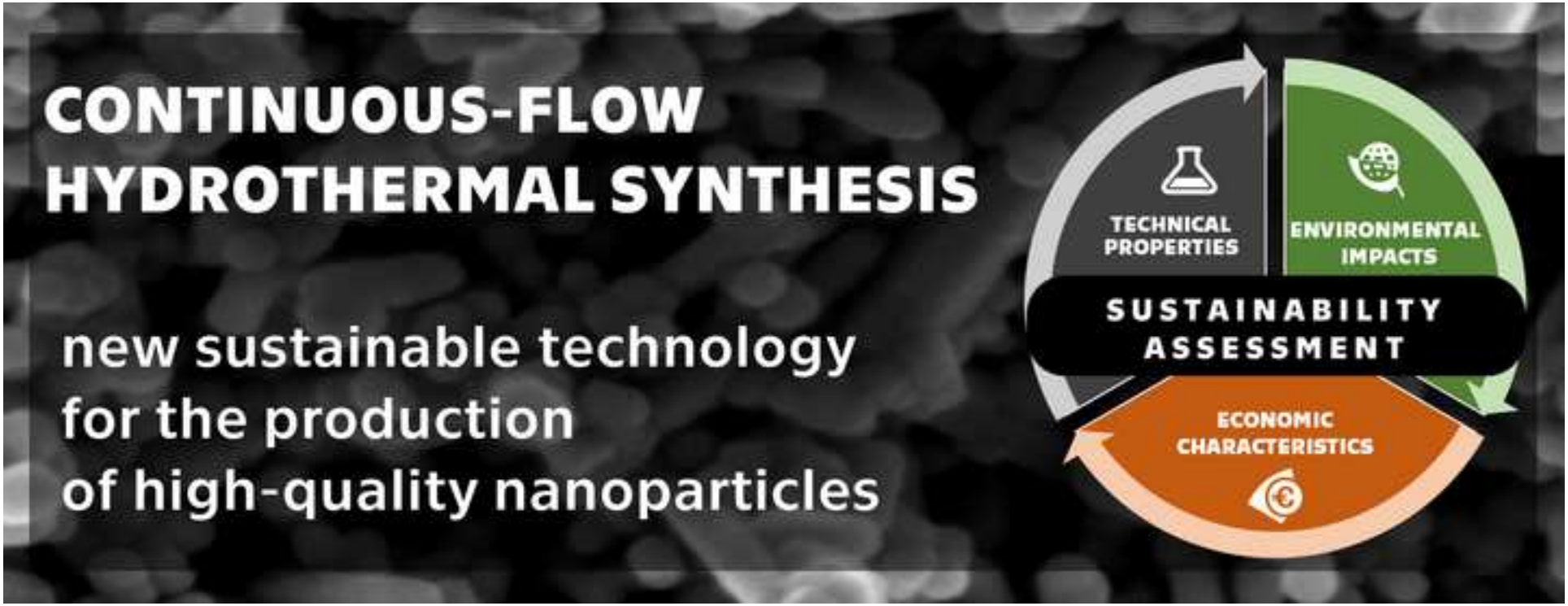
Abstract: In this paper, we provide a comprehensive techno-economic and life cycle environmental evaluation of the continuous-flow hydrothermal synthesis (CFHS) of nanoparticles in the context of current production technologies. This method is compared with a set of competitor technologies: Plasma syntheses; Flame pyrolysis; Sol-gel synthesis; Batch Solvo/Hydrothermal syntheses; and Altair hydrochloride process. Technical criteria such as scale and variability of production and material properties are accounted for in the environmental and economic analyses. Case study nanomaterials are investigated with a range of potential applications: titanium dioxide (smart coatings, electronics, and water purification); zinc oxide (smart coatings, cosmetics); zirconium dioxide (nanocomposites, electronics); and lithium phosphate (lithium ion battery cathode material).
Results show that CFHS can be ranked among the most productive methods capable of producing up to 100-250 kg/h of different types of high quality NPs dispersed in water. In terms of the environmental impacts, this newly developed technology does not use any toxic solvents, there are no emissions into the environment and the risk of leakage of NPs into environment is negligible. Comparison of values of selected environmental impact categories Cumulative Energy Demand (CED) and Global Warming Potential (GWP) shows that CFHS can compete with industrial technologies with low production variability and limited product quality (e.g. sulfate and chloride processes) and achieves much better results in comparison with technologies with similar variability (e.g. HT plasma or sol-gel) and product quality (sol gel). The same conclusion can be made in the case of an economic assessment. The combination of large scale and variability of production and quality of produced NPs can be considered as the major source of competitive potential of CFHS.

**Graphical Abstract**



## Highlights

- We present a comprehensive comparison of nanoparticles production methods
- Comprehensive comparison covers technical, environmental and economic aspects
- Four nanoparticle types are included in the comparison: $TiO_2$, ZnO, $ZrO_2$, $LiFePO_4$
- LCA was used as a key method for assessment of environmental impacts
- Detailed cost structure of produced nanoparticles is revealed in this study

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March 02, 2018, Prague

**Cover letter to support the publication of "Sustainability Assessment of Continuous-flow Hydrothermal Synthesis of Nanomaterials (CFHS) in the Context of Other Production Technologies"**

In this collaborative paper, we present a comprehensive sustainability assessment of newly developed technology CFHS for production of high quality nanoparticles that is compared with existing production technologies.

This article represents an output of the teamwork of researchers from Czech Technical University in Prague and University of Nottingham who was cooperating within the "Sustainable Hydrothermal Manufacturing of Nanomaterials" project (SHYMAN FP7-NMP4-LA-2012-280983), under the EU's Seventh Framework Programme. The main focus of the project has been the scaling up of existing pilot scale technologies for nanoparticle synthesis towards full scale plant. In this project the target was set for a 1000 ton plant and this plant is now completed.

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Scale up of the continuous supercritical hydrothermal synthesis technology realized within the SHYMAN project opens possibilities for full commercial use of nanoparticles produced in large quantities. The potential for massive use of this innovative technology increases the need for a proper assessment of its sustainability.

The main innovative and unique ideas and approaches presented in this paper are:

- assessment of entirely new technology producing large quantities of high-quality nanoparticles suitable for commercial use;
- wide spectrum of aspects covered by the sustainability assessment – technical, environmental, economic, safety;
- wide spectrum of assessed technologies;
- sustainability assessment and technology comparison for three types of nanoparticles – $TiO_2$, ZnO, $LiFePO_4$.

We believe that this paper studying the issue of nanoparticles' production from a broad perspective and covering different points of view on sustainability supplements detailed studies in this field and perfectly corresponds with the focus of the Journal of Cleaner Production.

We would like to thank you for considering the manuscript for publication.

Sincerely,

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# Sustainability Assessment of Continuous-flow Hydrothermal Synthesis of Nanomaterials in the Context of Other Production Technologies

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**Figure 1 - CFHS process flow-chart**
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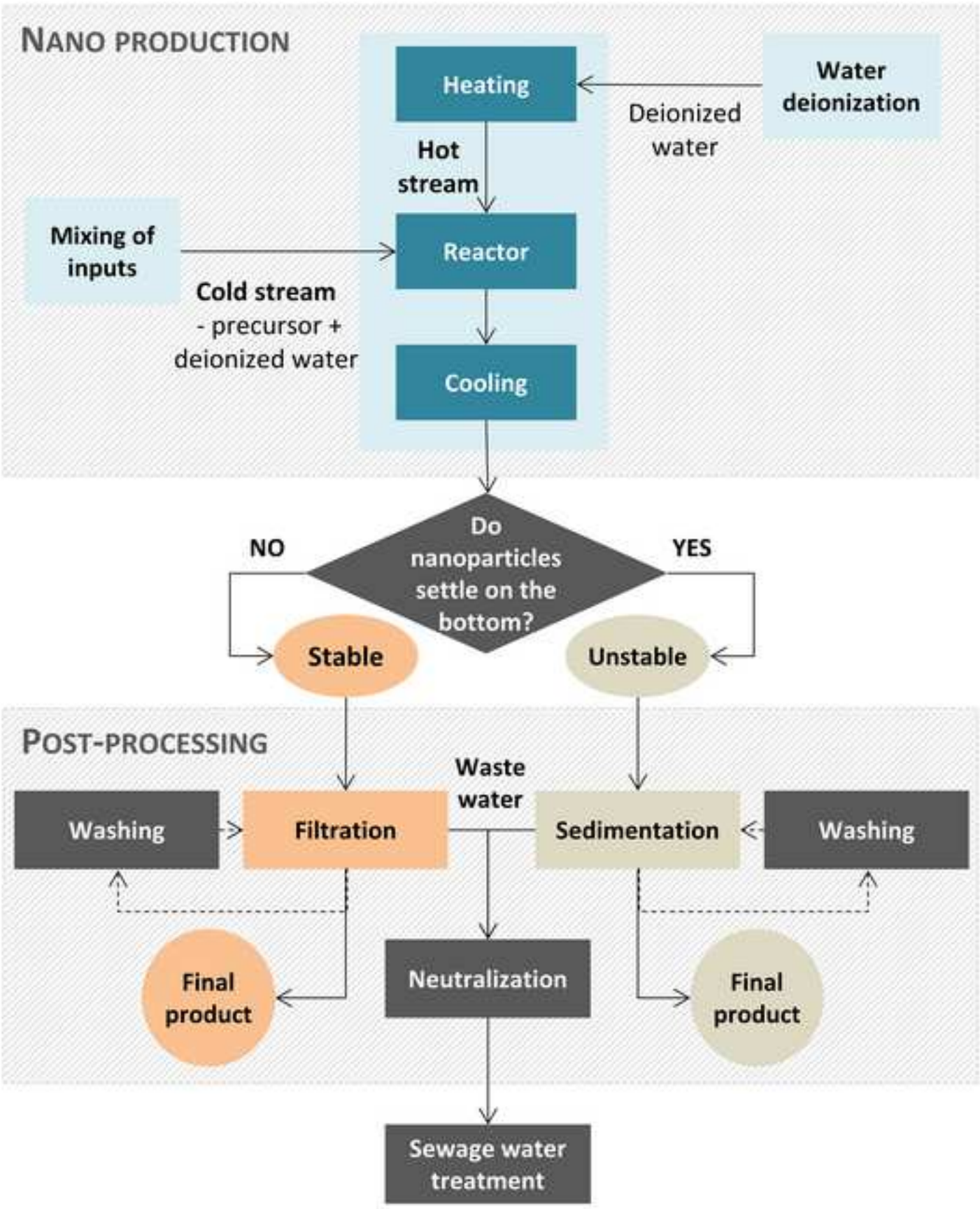

**Figure 2 - CEDs (a) and GWPs (b) of different NPs**
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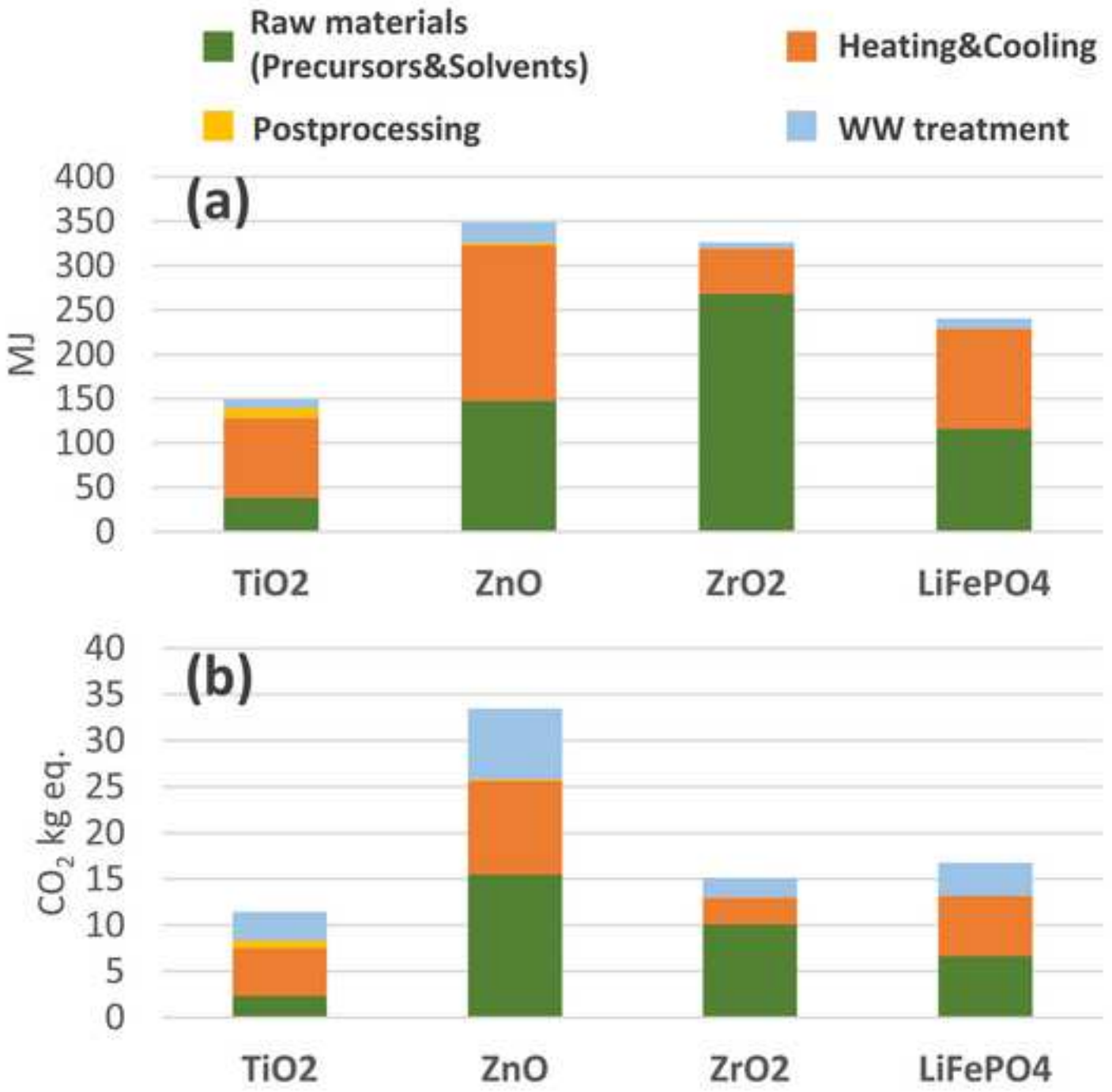

**Figure 3 - Total unit costs of CFHS for individual NPs**
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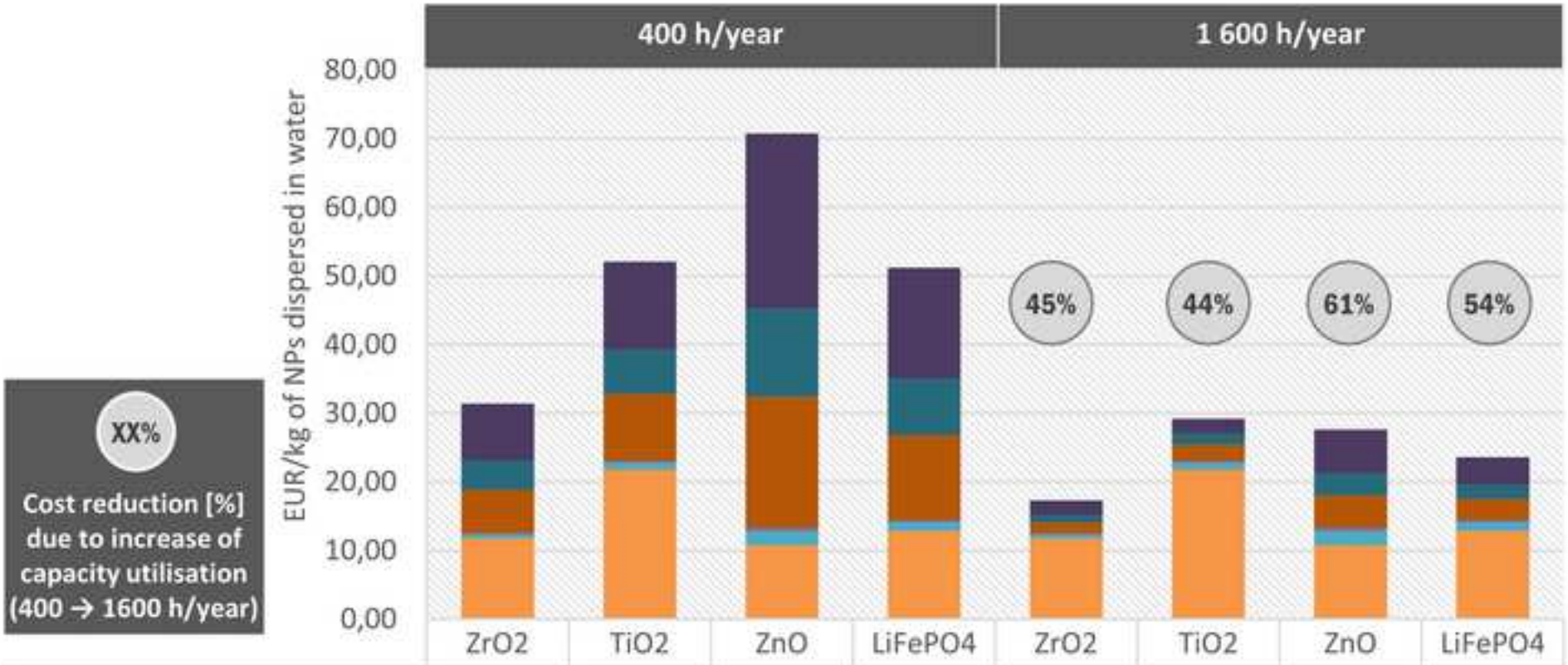


| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **TOTAL UC [EUR/kg]** | **31,42** | **52,06** | **70,77** | **51,19** | **17,30** | **29,20** | **27,63** | **23,63** |
| Costs of equipment | 8,37 | 12,76 | 25,57 | 16,15 | 2,16 | 2,11 | 6,39 | 4,04 |
| **SUBTOTAL II [EUR/kg]** | **23,06** | **39,30** | **45,20** | **35,04** | **15,14** | **27,09** | **21,24** | **19,59** |
| Other costs | 4,23 | 6,52 | 12,79 | 8,25 | 1,06 | 1,63 | 3,20 | 2,06 |
| Personal costs | 6,33 | 9,76 | 19,15 | 12,35 | 1,58 | 2,44 | 4,79 | 3,09 |
| Electricity | 0,14 | 0,21 | 0,41 | 0,27 | 0,14 | 0,21 | 0,41 | 0,27 |
| Natural Gas | 0,59 | 1,04 | 2,04 | 1,32 | 0,59 | 1,04 | 2,04 | 1,32 |
| Costs of chemicals and water | 11,78 | 21,77 | 10,80 | 12,86 | 11,78 | 21,77 | 10,80 | 12,86 |

**Figure 4 - Comparison matrix**
**Click here to download high resolution image**

| Technology/ Criterion | Production rate | Quality | Variability | Cost of inputs | Cost of equipment | Energy Consumption process | Energy Consumption embodied | CO2 emissions | Important sources |
|---|---|---|---|---|---|---|---|---|---|
| CFHS | High | Very good | Very high | Different | Medium | Low | Different | Low | |
| VAFS | Very high | Good | Low | Low | Very High | Low | Low | Low | Stark and Pratsinis, 2002<br>Teoh et al., 2010 |
| Sulfate process | High | Good | Low | Low | High | Low | Low | Low | Procházka, pers. communication |
| Altair | High | Good | Medium | Low | Medium | Low | Low | Low | Grubb and Bakshi, 2010<br>Verhulst et al., 2003 |
| HT plasma | High/medium | Good | High | Different | Medium | Very high | Different | High | Osterwalder et al., 2006<br>Vollath, 2007<br>Jurewicz et al., 2011<br>www.tekna.com |
| FSP | Medium | Good | High | High | Medium | Low | High | Medium | Pratsinis, mail<br>Teoh et al., 2010<br>Wegner et al., 2011<br>Mueller et al., 2004 |
| LT plasma | Low | Very good | Medium | Different | Medium | N/A | Different | N/A | Vollath, 2007 |
| CS solution | Low | Very good | High | High | Low | N/A | High | N/A | Aruna and Mukasyan, 2008<br>Chung and Wang, 2012 |
| Sol-gel | Low | Very good | Very high | Different | Low | High | Different | High | Pini et al., 2014<br>Bahnajady, mail<br>Bahnajady et al., 2011<br>Gupta and Tripathi, 2012 |
| Solvothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | Gupta and Tripathi, 2012 |
| Hydrothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | Gupta and Tripathi, 2012 |
| Precipitation | Low | Very good | Very high | Different | Low | High | High | High | Gupta and Tripathi, 2012<br>Manda et al., 2012 |

Wordcount: 7684 words

# Sustainability Assessment of Continuous-flow Hydrothermal Synthesis of Nanomaterials in the Context of Other Production Technologies


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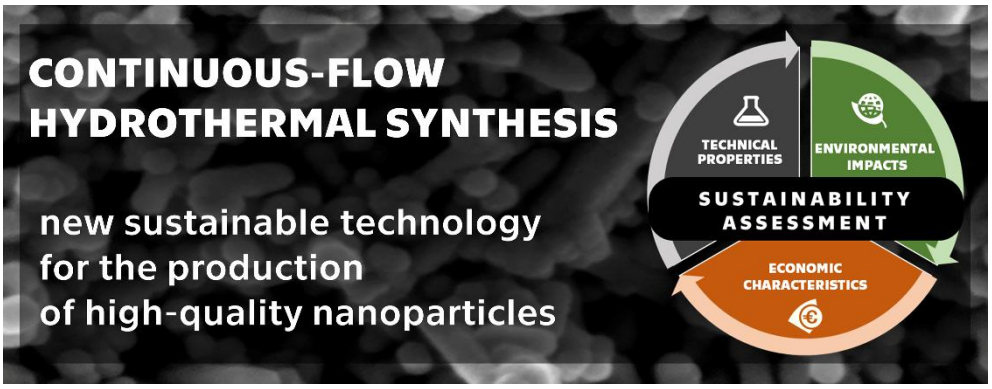
## Abstract

In this paper, we provide a comprehensive techno-economic and life cycle environmental evaluation of the continuous-flow hydrothermal synthesis (CFHS) of nanoparticles in the context of current production technologies. This method is compared with a set of competitor technologies: Plasma syntheses; Flame pyrolysis; Sol-gel synthesis; Batch Solvo/Hydrothermal syntheses; and Altair hydrochloride process. Technical criteria such as scale and variability of production and material properties are accounted for in the environmental and economic analyses. Case study nanomaterials are investigated with a range of potential applications: titanium dioxide (smart coatings, electronics, and water purification); zinc oxide (smart coatings, cosmetics); zirconium dioxide (nanocomposites, electronics); and lithium phosphate (lithium ion battery cathode material).

Results show that CFHS can be ranked among the most productive methods capable of producing up to 100-250 kg/h of different types of high quality NPs dispersed in water. In terms of the environmental impacts, this newly developed technology does not use any toxic solvents, there are no emissions into the environment and the risk of leakage of NPs into environment is negligible. Comparison of values of selected environmental impact categories Cumulative Energy Demand (CED) and Global Warming Potential (GWP) shows that CFHS can compete with industrial technologies with low production variability and limited product quality (e.g. sulfate and chloride processes) and achieves much better results in comparison with technologies with similar variability (e.g. HT plasma or sol-gel) and product quality (sol gel). The same conclusion can be made in the case of an economic assessment. The combination of large scale and variability of production and quality of produced NPs can be considered as the major source of competitive potential of CFHS.


## Graphical abstract



## Highlights

- We present a comprehensive comparison of nanoparticles production methods.
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- Four nanoparticle types are included in the comparison: $TiO_2$, ZnO, $ZrO_2$, $LiFePO_4$.
- LCA was used as a key method for assessment of environmental impacts.
- Detailed cost structure of produced nanoparticles is revealed in this study.

***Keywords:*** *Nanoparticles, nanoparticles production, hydrothermal syntheses, sustainability, life cycle assessment, production costs*

# 1. Introduction

## 1.1 Purpose and characteristics of the study

Nowadays, there is a rapid development in the field of nanoparticle production technologies and intense increase of application of nanomaterials, the number of registered nanoproducts has been augmented from 54 in 2005 to 1865 in 2013 (www.nanotechproject.org). Many studies predict a massive development in various application areas, such as the smart nano-coatings (Grand view research, 2014). Environmental impact assessments, alongside economic benefits evaluation, are currently growing in importance as nanomaterials transfer from laboratories into everyday life. Therefore, the evaluation of environmental impacts and economic benefits was an integral part of the FP7 project Sustainable Hydrothermal Synthesis of Nanomaterials (SHYMAN), which was focused on development of large-scale continuous-flow NPs production technology based on hydrothermal synthesis.

In order to assess whether the newly developed technology is a source of economic or environmental benefits compared to the current state of the art, a comprehensive study has been developed to characterize both the new technology and the existing production technologies. This comparative analysis covers:

- basic technical characteristics - product characteristics, production scale and variability, basic operation conditions – temperatures, pressures,
- environmental characteristics – impact categories: Cumulative Energy Demand (CED), Global Warming Potential (GWP); assessment of risk of release of NP during production; necessary safety measures,

- economic characteristics – total production costs or selling price of nanoparticles (NPs), investment costs and cost of variable inputs.

As a main NP for comparison, we chose $TiO_2$ because of its wide applicability (smart coatings, electronics, and water purification) and availability of data. We also collected characterization data for other widely used NPs: $ZrO_2$ (nanocomposites, electronics), ZnO (smart coatings, cosmetics), $LiFePO_4$ (active material in Li-ion batteries) but information for comparison was only available for a very limited number of technologies.

### 1.2 Data overview and limitation

This study is based on a large variety of information sources, especially existing LCA studies oriented on nanoparticle production and other literature sources focused on the production of the nanoparticles by different technologies. More information was obtained via email communication with authors of different articles (Prof. Pratsinis, Bahnajady), personal discussion with experts (such as dr. Procházka from Advanced Materials and HE3DA Company, dr. Ieva from SOLVAY Company), and form SimaPro software connected to Ecoinvent databases. The overview of the key studies is given in the Tab. 1.

Tab. 1 Overview of important studies focused on the presentation of environmental and economic data of individual NPs production technologies.

| **Study** | **Technology** | **Scale of production** | **NPs** | **Application** | **Environmental data** | **NPs release** | **Economic data** |
|---|---|---|---|---|---|---|---|
| Osterwalder et al., 2006 | Traditional and new methods (e.g. plasma syntheses) | | $TiO_2$, $ZrO_2$ (nano and micro ) | Only production of NPs | Energy consumption<br>$CO_2$ emissions | No | No |
| Grubb and Bakshi 2011, Grubb, 2010 | Altair hydrochloride process | Pilot plant | $TiO_2$<br>Anatase, 40 nm | Only production of NPs | Fossil fuel use<br>Eco-indicator 99 method<br>(Beside LCA also exergy analysis) | No | No |
| Zackrisson et al., 2010 | Solid-sate | Laboratory condition | $LiFePO_4$ | Batteries | Publication details the GWP. The energy requirements per kg of $LiFePO_4$ was roughly estimated (3 kJ/g $LiFePO_4$) | No | No |
| Wegner et al., 2011 | Flame spray pyrolysis (FSP) | Pilot scale | $Bi_2O_3$, $ZrO_2$ | Only production of NPs | No | - | Yes, detailed cost study |
| Majeau-Bettez et al., 2011 | Batch hydrothermal process | Industrial modelling from a laboratory | $LiFePO_4$ | Batteries | Publication of input data – CED and GWP was calculated using | No | No |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | condition | | | SimaPro software | | |
| Manda et al., 2013 | Precipitation process | Laboratory condition | $TiO_2$ | Paper industry | NREU<br>GHG emission | No | No |
| Nanosustain project, 2013 | NA | NA | $TiO_2$, ZnO, $ZrO_2$ | NA | CED, GWP | NA | No |
| Pini et al., 2014 | Sol-gel process | Large production( Colorobbia S.p.A. Italy) | $TiO_2$<br>30 nm | Self-clean coating | NREU, GWP<br>Impact 2002+ method | Yes, two impact cath.: Nano $TiO_2$ ecotoxicity in freshwater, Nano $TiO_2$ carcinogens in freshwater | Yes, basic information – only total costs are published |
| Yu et al., 2014 | Solid-state | Laboratory condition | $LiFePO_4$ | Batteries | Publication of input data – CED and GWP was calculated using SimaPro software | No | No |
| Middlemas et al., 2015 | Alkaline roasting of titania slag (ARTS) | Virtual ARTS processing plant | Only Micro $TiO_2$, | Only production of $TiO_2$ in a bulk form | CED, GWP | - | No |
| Liang et.al., 2017 | Solid-state | Laboratory condition | $LiFePO_4$ | Batteries | Publication only details the GWP for the raw materials. | No | No |

NREU – Non-renewable energy use, CED – cumulative energy demand, GWP – global warming potential

Although we used a broad spectrum of information sources, we were not able to collect data for all evaluated technologies and all evaluating criteria. It is particularly difficult to find published economic data for commercial reasons, and only the Wegner et al. (2011) study presents, in detail, cost structures of the FSP method for a pilot plant. From the summary of key studies it is evident that there is no such a complex study that would evaluate NPs production technologies from the different perspectives and which would combine technical, environmental and economic characteristics. Moreover, the quality of environmental data of individual studies is limited: they are modelled based on laboratory conditions (Majeau-Bettez et al.) could be overestimated (as it is described in Manda et al., 2013) or underestimated as Zackrisson et al. (2010) with energy requirements of only 3 kJ/g $LiFePO_4$ or Majeau-Bettez et al. study excluding the energy to dry the NPs and some material inputs. The data are often incomplete for example: process energy requirements of $LiFePO_4$ solid-state production is not included in Liang et al. study or the use of argon, necessary in the sintering/calcination stage is omitted in the LCA calculation.

## 2. Methods

### 2.1 Continuous-flow hydrothermal synthesis

The process of NP creation by continuous-flow hydrothermal syntheses (CFHS) in a specially designed reactor was detailed in Lester et al. (2006). Within the SHYMAN project, the reactor was completely re-evaluated to enable large-scale production. Alongside with the reactor the whole large scale production process was designed and built. Simplified flowchart of the production process is depicted in the Fig. 1.

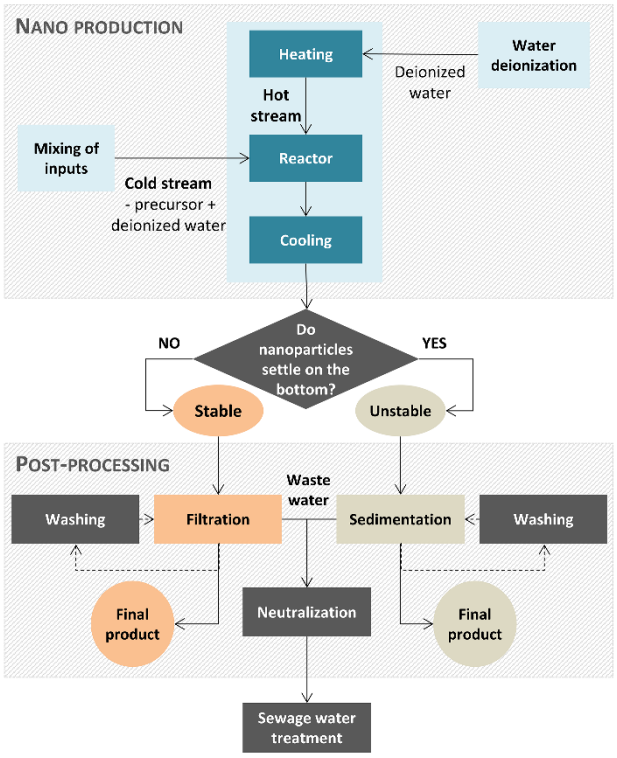



Fig. 1 CFHS process flow-chart

The hot stream (deionized water) and cold stream (precursor mixed with deionized water) meet in the reactor to form NPs. The temperature of the downstream flow of deionized water into the reactor where the NPs are created ranges typically from 250°C to 400°C. The NP production process is followed by post-processing, which aims to increase the NP concentration (from 0.5% wt up to more than 10% wt.) in the water suspension and dispose unwanted materials. Post-processing varies depending upon the character of NP processed.

If the NPs do not tend to settle out (i.e. stable NPs), the concentration increase is achieved through a set of filters. The dispersion is forced through tubes of porous polymer, during which process the NPs, due to their size, do not escape through the pores, whereas the water molecules are forced out of the tube. In this manner a dispersion concentration exceeding 10% wt. can typically be achieved in real time during production.

The concentration of nanoparticles that settle over time (unstable NPs) is increased by their sedimentation at the bottom. The concentrate is then released from the sedimentation tank from the bottom. Wastewater remains in the upper part of the tank to be further processed. Unwanted materials and impurities are removed through a washing of NPs - the concentrated solution is diluted with deionized water and post-processing is repeated. The production and post-processing of NPs is followed by the water treatment process, where the pH of the waste water (WW) is adjusted to meet requirements set by the WW treatment plant.

Comparison of production conditions for production of NPs that are thoroughly investigated in the following chapters is displayed in the Tab. 2.

Tab. 2 Production condition of individual NPs produced by CFHS

| | **$TiO_2$** | **ZnO** | **$ZrO_2$** | **$LiFePO_4$** |
|---|---|---|---|---|
| **Precursors used for the synthesis of nanoparticles – Input flow rate** | • Titanium oxysulfate (TiOS) – 799.65 kg/h (15%wt) | • Zinc nitrate ($Zn(NO_3)_2$) – 72.64 kg/h<br>• Pottassium hydroxide (KOH) – 22.44 kg/h (90%wt) | • Zirconium acetate (Zr(AC)) – 515.7 kg/h (22%) | • Iron sulphate ($FeSO_4$) – 57.54 kg/h<br>• Ascorbic acid – 33.02 kg/h<br>• Lithium hydroxide (LiOH) – 26.94 kg/h<br>• Phosphoric acid ($H_3PO_4$) – 43.24 kg/h (85% wt) |
| **Post processing** | Sedimentation | Sedimentation | Filtration | Sedimentation |
| **Temperature** | 400°C | 400°C | 400°C | 400°C |
| **Output flow rate (kg/h)** | 59.9 | 30.53 | 92.41 | 47.33 |
| **Concentration** | 8% | 3.4% | 11.4% | 3.6% |

### 2.2 Life Cycle Assessment methodology

To assess the environmental impacts of production of individual NPs – $TiO_2$, ZnO, $ZrO_2$, $LiFePO_4$ by CFHS technology, Life Cycle Assessment (LCA) models were developed in accordance with ISO standards (Guinée et al. 2002, ISO 14040:2006, ISO 14044:2006). For the evaluation of environmental impact of individual NPs a cradle to gate analysis is undertaken, excluding ultimate use of the NPs, and 1 kg of NPs dispersed in water is set as a declared unit. Fig. 1 displays the system boundaries for the analysis. Following inputs and unit processes are included in the system:

- Precursors (theirs hourly flow rates are specified in the Tab. 2)
- Deionization of water - tap water is deionized for further use (HCl, NaCl, electricity use)
- Mixing of inputs - inflows are mixed at the desired concentration (electricity use)
- Heating and cooling stages as described above (natural gas and electricity use)

- Postprocessing steps – sedimentation or filtration (electricity use), washing (electricity use), neutralisation (NaOH 32%, water and electricity use)
- WW treatment as it is modelled in SimaPro database
- Packaging and transportation of all materials

Information based on the current plant built in Nottingham, prior nanoparticles production and work experience is used to determine electrical consumption of equipment, natural gas of the boiler, typical flow rates and volume used during the manufacturing of NPs.

LCI data were taken from the SimaPro version 8.1.1.166 connected to Ecoinvent 3 databases. Because no LCI data about some inputs are present in the SimaPro databases: as a proxy for ascorbic acid an average of three substances was used: methane, formaldehyde and acetic acid (Krewer, 2005); zirconium acetate production was modelled based on US 3076831 and zinc nitrate production based on US 3206281.

CED and GWP were chosen because of their wide publication and general understanding as characterisation impact categories for the environmental assessment of individual NPs.

### 2.3 Economic assessment methodology

Economic assessment of the CFHS technology has been conducted by using the full costs model elaborated within SHYMAN project, which allows allocation of all production costs. Production conditions of individual NPs considered for economic assessment are shown in Tab 2. The cost model takes into account variable and fixed costs.

The key variable costs represent:

- costs of precursors;
- costs of other chemicals used for NPs precipitation, cleaning of the rig and WW neutralization;
- costs of deionizing of tap water and cost of WW treatment in plant;
- costs of electricity powering pumps, cooling unit, mixers and control system;
- costs of natural gas used in the heater.

The same approach, methods and data sources as for LCA were used for determination of precursors, other chemicals and water flow-rates, for gas and electricity consumption. Purchasing prices especially for chemical

substances can vary depending on the volume of the order and specific contract conditions. For this cost calculation prices based upon pre-negotiated business offers and internet sources were used.

Fixed costs represent the following cost groups:

- **cost of equipment**– depreciation period is conservatively chosen for 3 years;
- **personnel costs** – we assume 4 full time equivalents working in 1 operating shift
- **other costs** represent mainly costs of space, maintenance costs, services (e.g. legal, marketing), small assets, HW, SW, insurance, etc.

Individual fixed costs were allocated by using hourly cost tariff (HCT) method. HCT [EUR or USD per hour] is calculated by dividing fixed costs [EUR, USD per year] by effective production capacity of the facility [hours per year]. Allocation to the allocation unit is done by multiplication of HCT by the process time needed to produce 1 kg of NPs dispersed in water.

We calculated total fixed costs for two potential scenarios:

- 400 hours/year of effective capacity (approx. 20% of capacity utilization in 1 shift) – characterizing initial years of the full-scale plant operation when there is not enough business orders and the most of the production is used for testing runs;
- 1600 hours/year (approx. 80% of capacity utilization in 1 shift) – characterizing following period when the capacity is effectively utilized to cover business orders.

## 3. Results and discussion

In this paper, we present detailed results for individual groups of characterization criteria. Each section starts with the characterization of CFHS, characterization of other competing technologies follows. The comprehensive results of the comparison are summed up in a matrix at the end of this part (Fig.4).

### 3.1. Basic criteria

Basic criteria characterise scale and variability of production and quality of produced NPs.

#### 3.1.1. Basic criteria - CFHS

CFHS technology has demonstrated a significant flexibility enabeling the use of different precursors, solvents, operational conditions and production configurations using the counter-current reactor. This fact has led the

production of a wide variety of NPs (Dunne et al., 2015) (from simple oxides and sulphides, to complex compounds like $LiFePO_4$ or Metal Organic Frameworks (MOFs)) with high production rates. Production rates vary with the type of NP, the concentration of the input precursor and defined synthesis conditions (Tab. 2.). They ranges typically in tens of kilograms per hour and can reach up to 100 kg/hour (and up to 250 kg/hr in specific cases, such as MOFs). CFHS attains a high quality of dispersed and formulated product. For example $TiO_2$ characteristics – fine grain 9 ± 1.9 nm, BET specific surface area (SSA) 159 $m^2/g$, crystallinity 80%, 100% anatase phase. $ZrO_2$ characteristics – very stable suspension, very high SSA of dry powder - above 200 $m^2/g$, 6 nm grain size, high crystallinity already in suspension, there is no need for further processing.

### 3.1.2. Basic criteria in comparison with literature data

Methods with the **highest production rates** include vapour assisted flame pyrolysis (VAFP), a chloride process with production rate for fine metal powders of up to 25 000 kg/h (Stark and Pratsinis, 2002), sulfate process and Altair hydrochloride process for which there is a pilot plant with production rate of 100 kg/hour as described in Grubb (2010). These methods are not particularly versatile – VAFP is applicable for $TiO_2$, $SiO_2$ and other simple oxides; the sulfate process is applicable only for $TiO_2$. A high production rate, significantly lower than that for VAFP, is attained by high temperature plasma (HT plasma); the highest production rate for HT plasma can be estimated at up to 60kg/hour at 400 kW. The production rate of the typical HT plasma plant is less than 10 kg/hour (Volath, 2007). CFHS with typical production rate of tens kilograms per hour is one of highly productive methods capable to produce large volumes of NPs demanded by commercial applications. **Lower production rates** are achieved by FSP; Prof. Pratsinis of ETH Zurich and his team have attained up to 5 kg/h (Pratsinis, email communication). Wet production methods such as the sol-gel, batch solvo/hydrothermal methods achieve low production rates. The main reason is the long production time and batch character of production especially for the hydrothermal and solvothermal methods, which use special autoclaves. Another low productivity method is the low temperature plasma method, which can be effectively applied for production of small quantities of highly specialized materials and synthesis of coated particles (Vollath, 2007).

**The quality of NPs** characterized by particle size, particle size distribution, BET surface, agglomeration, and the distinctive properties of the NP – depends on a great range of factors and the capability of the production methods to control these factors. Wet methods generally perform better in terms of quality and the NPs are better suited for specialized applications than those produced by dry methods. For example, batch hydrothermal and solvothermal methods produce NPs suitable for use in the electrical industry as semiconductor materials (QD –

CdSe, ZnO). The particle size of $TiO_2$ produced by wet technologies varies from 10 to 20 nm, with a high percentage of anatase phase material. (e.g.: Bahnajady et al., 2011). CFHS is a wet method, which is capable to produce NPs of highest quality. Very small and non-agglomerated NPs are also produced by combustion synthesis (e.g.: Chung and Wang, 2012) while LT plasma is used for production of NPs for highly specialized products. The Altair hydrochloride process produces anatase $TiO_2$ NPs with the average diameter of 40 nm (Grubb et Bakshi, 2011). Standard quality is represented by commercially produced nano $TiO_2$ AEROXIDE® TiO2 P 25 with 80% of the anatase phase, average particle size 21nm, BET SSA ($m^2/g$): 45.63. P 25 is produced by VAFP in high productivity flame reactors (Roth, 2007). VAFP is geared mainly towards the production of NPs for commodity applications, such as $TiO_2$ with a diameter of 200 nm for use in pigments. The size of NPs produced by HT plasma ranges from 50 to 100 nm; with quenching a narrower size distribution can be achieved (www. tecna.com). FSP also achieves a small NP size, such as $ZrO_2$ measuring 30 nm (Mueller et al., 2004). In general, there is a broader size distribution in the case of dry synthesis than with wet methods because of the greater difficulties in controlling the production process.

As it can be seen from this comparison of characteristics of individual methods, CFHS ranks among the methods with high production rates and at the same time is able to produce wide variety of high quality products. The aggregated comparison within basic criteria is shown in Fig. 4.

### 3.2. Environmental comparison

Firstly, detailed charts of both impact category results for NPs produced by CFHS ($TiO_2$, ZnO, $ZrO_2$ and $LiFePO_4$) are presented on Fig. 2. Results of CED and GWP of various NPs should not be directly compared due to their different functional applications but they clearly show different energy demands and global warming potentials of individual NPs and contributions of individual components and processes. CED and GWP values of different types of NPs produced by CFHS are then compared with other production technologies – Tab. 3 and Tab 4. In addition to this comparison, we prepared an evaluation of other emissions and NPs release risks.

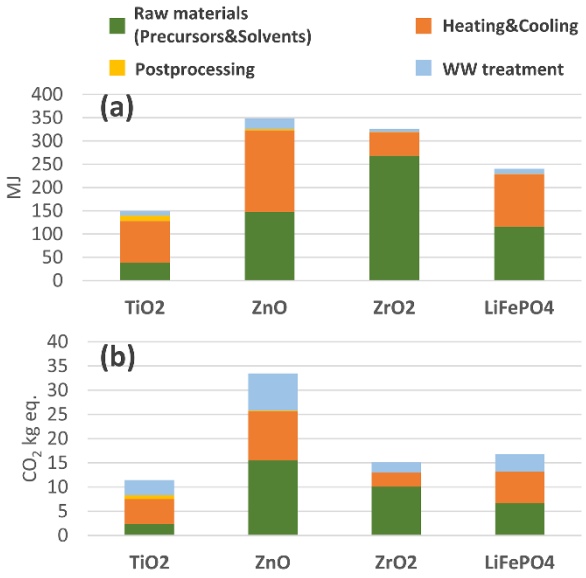



Fig. 2 CEDs (a) and GWPs (b) of different NPs

### 3.2.1. Cumulative energy demand and Global warming potential of CFHS

From the Fig. 2 it is apparent that embodied energy in the precursor and the heating and cooling stages has the most significant impact on total CED. It is possible to observe a clear positive effect of higher output flow-rate on the impact of heating and cooling stages of different NPs - similar amount of process energy is divided into a larger volume of production (e.g. $ZrO_2$ NPs with the greatest output flow rate of 92 kg/hour have the lowest impact on heating and cooling stages). The lowest CED values are returned by $TiO_2$ due to the use of the simple precursor Titanium(IV) oxysulfate (TiOS) with low embodied energy. The use of more complex precursors and organic solvents as inputs for $TiO_2$ production is associated with much higher environmental impacts as it is shown in the recent LCA study published by Caramazana-Gonzalez (2017). GWP results for individual NPs produced by CFHS technology show that the output flow rate has similar influence on the contribution of the heating and cooling stages as for CED - the higher the output flow rate, the lower the impact. Compared to the CED category, the wastewater treatment process has a greater contribution in the total GWP category.

### 3.2.2. CED and GWP of $TiO_2$ nanoparticles in comparison with literature data

Table 3 presents a comparison of CEDs and GWPs for the production of 1 kg of $TiO_2$ NPs using different production methods. For the production of $TiO_2$ NPs (8% dispersion) from TiOS precursor, the comparison of data implies that CFHS ranks among the methods with low energy consumption as measured by CED. It should be pointed out that low variable technologies (e.g. sulfate and Altair hydrochloride processes) have a slightly lower CED than the CFHS but in comparison with technologies with similar variability (e.g. HT plasma or sol-

gel) and product quality (sol gel) CFHS performs very well in terms of CED. The energy consumption of the CFHS production process depends on the type of NPs (as it is mentioned above). CFHS performs well also in the case of GWP impact category.

For product application requiring powder form of NPs, drying of the water dispersion should be also included in the evaluation. In this case, it is necessary to add an energy of about 29.79 MJ for 1 kg of $TiO_2$ NPs. It corresponds to the CED value of 90.7 MJ and GWP of 5.1 $CO_2$ kg.eq/kg.

Tab. 3 Energy consumption and CO2 kg eq. emissions for the production of 1 kg of TiO2 (*NREU – Non-renewable energy use)

| **Technology** | **Production scale** | **Form of NPs** | **Characteristics of NPs** | **CED (MJ/kg)** | **GWP ($CO_2$ kg.eq/kg)** |
|---|---|---|---|---|---|
| **CFHS** | Industrial | 8% dispersion | 9 nm, anatase | 149 (+90.7for drying) | 11.42 (+5.1 for drying) |
| Solgel Process (Pini et al., 2014) | Industrial | 6% dispersion | 30 nm | 1049* | 58 |
| Precipitation process (Manda et al. 2013) | Laboratory | Powder | - | 540* | 30 |
| Altair hydrochloride process (Grubb and Bakshi, 2011) | Pilot scale | Powder | 40nm, anatase, | 140* | 6 |
| Sulfate process (Procházka, flow chart in Tichá et al. (2016)) | - | Powder | 30 nm, anatase | 88.9 | 7.39 |
| Unspecified process (Nanosustain, 2013) | - | Powder | - | 81.4 | 4.26 |
| Combustion of Ti – isopropox. (FSP) (Osterwalder et al., 2006) | - | Powder | - | - | 15 |

To complete the CED comparison of $TiO_2$ production methods we should also mention the recent LCA study conducted by Middlemas et al. (2015), which focused on the alkaline roasting of titania slag (ARTS) – method for the production of $TiO_2$ pigments (micro-size). The CED of ARTS (90 MJ/kg) (Middlemas et al., 2015) is lower than the majority of early published results of CED for production of $TiO_2$ pigments (micro size) by traditional production methods. Middlemas (2015) concludes that $CO_2$ emissions are also low.

### 3.2.3. CED and GWP comparison of other NPs ($ZrO_2$, ZnO, $LifePO_4$) with literature data

The CED and GWP values of other NPs are summarized in table 4. The CED of the production of $ZrO_2$ NPs by CFHS (325 MJ/kg) is very low compared to HT plasma syntheses, which has a very high energy consumption. 520 MJ is needed just for the dispersion of the Zr metal and the heating of the gas to process temperature (Osterwalder et al., 2006). Above-mentioned 520 MJ of electricity, medium voltage at grid, UK corresponds to CED of 1500 MJ and GWP of 88 kg $CO_2$ eq. (SimaPro).

Tab. 4 Comparison of CEDs and GWPs of $ZrO_2$, ZnO and of $LiFePO_4$ NP production (CEDs and GWPs of production referenced in Yu et al. and in Majeau-Bettez et al. was calculated in SimaPro with published primary data. *The use of argon, necessary in the sintering/calcination stage, is not include in the LCI.)

| | **Technology** | **Scale of production** | **Form of NPs** | **Characteristics** | **CED (MJ/kg)** | **GWP ($CO_2$ kg.eq/kg)** |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| **$ZrO_2$** | **CFHS** | Industrial | 11.36 % dispersion | 200$m^2$/g(SSA), 6 nm | 325 (+61.3for drying) | 16.16 (+3.41 for drying) |
| | HT plasma NP (Osterwalder et al. 2006) | - | Powder | - | | 40 |
| | Combustion of Zr-isopropoxide (Osterwalder et al. 2006) | - | Powder | - | | 9 |
| | Nano-milling (Osterwalder et al. 2006) | - | Powder | - | | 35 |
| **ZnO** | CFHS | Industrial | 3.4 % dispersion | 36 $m^2$/g (SSA) 44.5 ± 21 nm | 347 (+224 for drying) | 33.45 (+12.5 for drying) |
| | Unspecified process (Nanosustain, 2013) | | | - | 474,27 | 21 |
| **$LiFePO_4$** | CFHS | Industrial | 3.6 % dispersion | | 240 (+211 for drying) | 16.77 (+11.8 for drying) |
| | Batch hydrothermal synthesis - 5h in reactor then 5h drying (Majeau-Bettez et al., 2011) * | Simulation | Powder | | 104 | 5.44 |
| | Solid-state process (Yu et al., 2014) | Laboratory | Powder | | 390 | 20.2 |

**ZnO** NPs (3.4 % dispersion) produced by CFHS achieves lower CED than NPs referenced in the NanoSustain project (Tab. 4) but GWP potential is higher. Because of lack of detailed information about production methods used within the NanoSustain project, it is hard to identify the main cause. Possibly the wastewater treatment process included in the CFHS evaluated system can be the reason of higher impacts.

Water dispersion with **$LiFePO_4$** NPs produced by CFHS has lower CED than the solid-state process (Yu et al., 2014), but higher than hydrothermal syntheses reported by Majeau-Bettez et al., 2011. The inclusion of the drying process will further increase the impacts of the CFHS. However, LCI data for study published by Majeau Bettez were quantified based on theoretical assumptions not real measurements and especially process energy is underestimated. Majeau-Bettez et al. (2011) used a batch hydrothermal technique (Chen and Whittingham, 2006) with the addition of multi-wall carbon nanotubes to enhance the electronic conductivity of $LiFePO_4$. The use of carbon nanotubes as a nano-product require higher demand of energy that is not included in the CED, as well as the ascorbic acid and the energy of drying NPs are omitted. Comparison of GWP impact category shows worse results for CFHS then for other technologies but the quality and completeness of the data of the studies mentioned above remains a question.

### 3.2.4. Nanoparticle release

The risk of NPs exposure depends on the work procedure and applied risk management measures (EPA, 2010). There is a difference in exposure for dry and wet methods. Dry methods rank among those with a high risk of NP release to the air (Gottschalk and Nowack, 2011) so there is a need for strenuous measures to protect the working

environment and beyond. Such measures are described in Jurewicz et al. (2011) for HT plasma synthesis and in Wegner et al. (2011) for FSP. They include working in a fully enclosed room, personal protection, particle counters, HEPA filters, etc. In the case of dry NP production methods, water is used for cleaning and maintenance: the resulting slurry containing NPs is recovered and disposed of as hazardous waste (Wegner et al., 2011). In general, however, as noted in EPA report (2010), actual industrial practices employed by individual manufacturers are uncertain. For wet production methods, there is a risk of leakage of NP mainly to the water. Prof. Bahnajady (via email) claimed for the sol-gel process that the value of NP release is very low with a negligible ppm level. Pini et al. (2014) have assumed for cleaning operations (bottom-up hydrolytic sol-gel syntheses) that 1% of the $TiO_2$ nanoparticle suspension (6% $TiO_2$ NPs in suspension) remains on the reactor walls. For sulfate production of nano $TiO_2$ Hichier et al. (2015) state that water emissions of nano $TiO_2$ NPs in a realistic case scenario are per Buchmüller (2012) 0.03%, emissions to air are presumed to be 0%, as the process is a precipitation process. Some recently published studies, have made an attempt to consider the environmental effects of $TiO_2$ NP release: Pini et al. (2014), Hichier et al. (2015).

CFHS is a wet synthesis method with low risk of planned and unplanned emissions of NPs. The whole production process is a closed system. The precursors are completely dissolved in water and the reaction occurs in a closed reactor. Sedimentation of nanoparticles does not produce any emissions to the air (closed sedimentation tanks). Currently, the emissions into the air are negligible due to the lack of dry NPs. The emissions into the wastewater are low and probably similar to Pini et al. (2014) or Hichier et al. (2015). The risk of unplanned NP emission of CFHS can be classified as very low: there is a wide range of safety measures preventing any leakages of NPs and other hazardous substances. In case of sudden increases in pressure, there are pressure relief valves and a back pressure relief valve system. To prevent overflow in the storage tanks, there are the level indicators, the tanks that operate with hazards components and nanoparticle suspension are connected to a “line out of tank”. Leakages and spillage are prevented by bund tanks.

#### 3.2.5. Other emissions

Both liquid phase and gas phase processes generate pollutants. For dry processes, there is a large amount of gas generated and released during reaction as stated in Chung and Wang (2012) for combustion solution synthesis. Emissions into the environment depend on the efficiency of each separator. For example when using nitrate precursors the DeNOx treatment unit must be applied (Wegner et al., 2011). For the Altair hydrochloride process

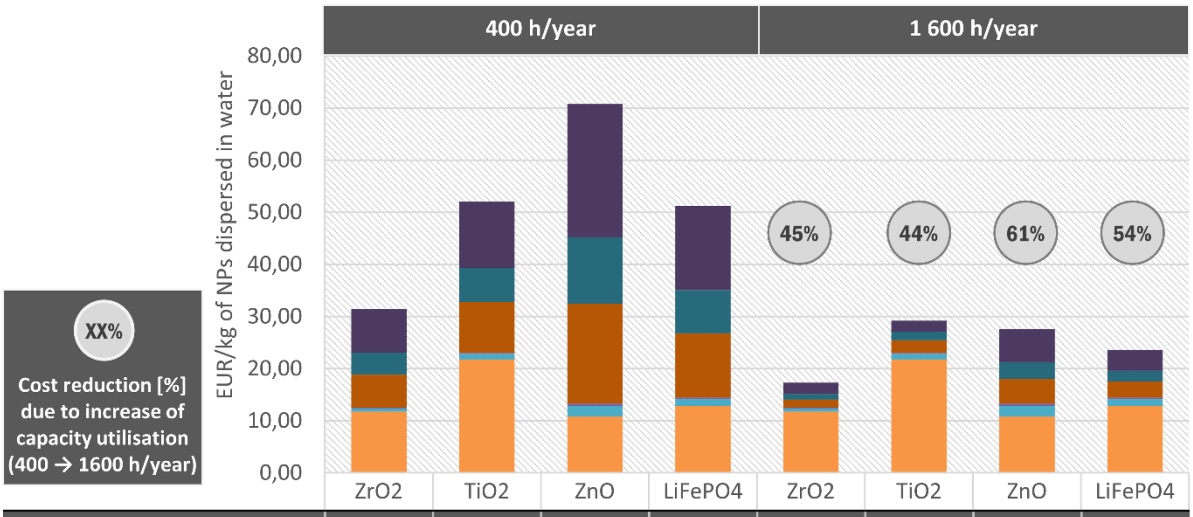
fugitive emissions of HCl in the early stages of the process and fugitive emissions of methane during a hydrolysis stage and have been estimated to have the highest impact on human toxicity potential and global warming potential (Grubb, 2010). A conservative estimate of 1% fugitive emission rate was assumed for volatile organics. Pini et al. (2014) state that during the production and purification steps, the release of $HNO_3$ into the air occurs. One percent of the total amount of material has been assumed to be emitted. For the sol-gel process, Bahnajady states that if the production process is carried out in a highly controlled way, there will be no emissions to the environment. For hydrothermal synthesis there is no use of organic solvents as for solvothermal synthesis and there is no risk of producing harmful emissions – for example products of incomplete combustion (NOx and CO) as have been proved for the glycine nitrate process (Pine et al., 2007).

### 3.3. Economic comparison

There is a lack of the published economic data characterising NPs production in the literature. The only study showing the whole cost structure was published by Wegner et al. (2011) for $ZrO_2$ NPs. In other cases we had to compare production costs with unstructured total values – Pini et al. (2014) for solgel technology ($TiO_2$ NPs), or with benchmark prices based on consultations with dr. Procházka from Advanced Materials and HE3DA company, dr. Ieva from SOLVAY company and internet pricelists. Firstly, detailed CFHS cost structure for studied NPs is presented.

#### 3.3.1. CFHS total costs

A comparison of the absolute values of overall costs per 1 kg for each NP type for different capacity utilization is illustrated in **Error! Reference source not found.**. Equipment costs have been calculated at approx. 900 000 €. Personnel costs were set for 4 workers per full-time (1 shift).




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **TOTAL UC [EUR/kg]** | **31,42** | **52,06** | **70,77** | **51,19** | **17,30** | **29,20** | **27,63** | **23,63** |
| Costs of equipment | 8,37 | 12,76 | 25,57 | 16,15 | 2,16 | 2,11 | 6,39 | 4,04 |
| **SUBTOTAL II [EUR/kg]** | **23,06** | **39,30** | **45,20** | **35,04** | **15,14** | **27,09** | **21,24** | **19,59** |
| Other costs | 4,23 | 6,52 | 12,79 | 8,25 | 1,06 | 1,63 | 3,20 | 2,06 |
| Personal costs | 6,33 | 9,76 | 19,15 | 12,35 | 1,58 | 2,44 | 4,79 | 3,09 |
| Electricity | 0,14 | 0,21 | 0,41 | 0,27 | 0,14 | 0,21 | 0,41 | 0,27 |
| Natural Gas | 0,59 | 1,04 | 2,04 | 1,32 | 0,59 | 1,04 | 2,04 | 1,32 |
| Costs of chemicals and water | 11,78 | 21,77 | 10,80 | 12,86 | 11,78 | 21,77 | 10,80 | 12,86 |

Fig. 3 Total unit costs of CFHS for individual NPs

Values in grey circles (Fig. 3) show the percentage of costs savings achieved by a production capacity utilization change from 400 h/year to 1 600 h/year (application of Economies of Scale). Considering lower capacity utilization, $ZrO_2$ NPs which are produced with the highest output flow rate of 92 kg /hr, have the lowest costs. The nanoparticles with the highest cost are, on the contrary, nanoparticles of ZnO, which are produced with the output flow rate of only 30 kg /hour. Raising capacity utilization causes reduction of unit costs of NPs, due to the decrease in fixed costs (equipment, personnel and other costs) per kg of NPs. As the unit variable costs are not changing as capacity utilization increases, their share in total costs is also increasing. Further increase of capacity utilization thus does not have such an influence on total production cost.

### 3.3.2. Comparison of CFHS costs with costs and prices of other technologies

Limited information on the cost of nanoparticle production is available publicly. We compare CFHS costs with available data for $ZrO_2$, $TiO_2$, and $LiFePO_4$. In comparison to FSP synthesis (Wegner at al., 2011), costs for the CFHS technology for $ZrO_2$ NPs in low capacity operations are roughly one-third (100 EUR/kg as opposed to 30 EUR/kg). The difference can be credited to the use of a less costly precursor Zr(Ac) and unit fixed costs due to the economy of scale. The unit costs of CFHS would be even lower when considering 10 years instead of 3 years

depreciation period of investments and unrealistic four-shift operation as for FSP instead of 3 years. In light of the fact that the current commercial benchmark price based on personal consultation with dr. Ieva from Solvay company – producer of NP containing products, was set at 35 EUR/kg, production of nano $ZrO_2$ by the CFHS method is profitable, even at low levels of utilization. This price, however, represents conventional commercially available nanoparticles with worse qualitative parameters. Costs per 1 kg of nano $TiO_2$ produced using CFHS technology are approximately 51 EUR/kg for a presumed 20% capacity utilization (Fig. 3). The greatest share of the total costs are the costs of precursors; these costs are higher than for $ZrO_2$ NPs. Increasing capacity utilisation means a decrease in investment, personnel and other costs per unit up to 28 EUR/kg. It corresponds to market price of nano-sized $TiO_2$ AEROXIDE® P 25 and the profit would be in this case negligible. However, the product produced by CFHS technology achieves much better qualitative parameters (pure anatase phase, smaller average particle size, narrow particle size distribution, higher BET SSA) and because of this higher value especially for special applications much higher sales price is presumed. For example: $TiO_2$ dispersion with similar parameters is offered by US Research Nanomaterials (http://www.us-nano.com/inc/sdetail/630) at a retail price of 165 USD for 1 000 ml 15 wt% dispersion. That is a cost of 1 100 USD/kg for $TiO_2$ NPs. For the sol gel process (Pini et al., 2014), the costs of 1 kg of the 6 % wt. $TiO_2$ NPs suspension was calculated to be 30.4 EUR, so the cost is 507 EUR/kg of $TiO_2$ NPs.

Costs per 1 kg of $LiFePO_4$ using CFHS (23.63 EUR/kg) are comparable with benchmark price of roughly 25 EUR/kg (based on personal correspondence with dr. Procházka and from the study by Fabrice Renard (2014)), but these costs would be even slightly higher as it is necessary to dry NPs for battery application. The most promising way to increase the profit from these NPs is through the increase of output flow rate.

The possibility of using simple precursors is an important competitive advantage of the CFHS unlike methods where more expensive organic precursors are needed as for FSP, solvothermal and for solution combustion synthesis. There is also no need for expensive organic solvents as is the case for solvothermal or FSP. From an input costs perspective, the strategic location of the plant is also important as it provides opportunities to share inputs and outputs (e.g. Cabot's plant with Evonik's fumed silica plant described in Pratsinis, (2011). In terms of energy costs CFHS ranks among low energy consumption methods with low energy costs per kg of NPs (electricity + natural gas costs represent less than 5% of total production costs).

## 4. Conclusion

Information from previous parts were aggregated and transformed into a comparison matrix (Fig 4.), which in a very compact form provides characterization and comparison of individual production technologies.

| Technology/ Criterion | Production rate | Quality | Variability | Cost of inputs | Cost of equipment | Energy Consumption process | Energy Consumption embodied | CO2 emissions | Important sources |
|---|---|---|---|---|---|---|---|---|---|
| CFHS | High | Very good | Very high | Different | Medium | Low | Different | Low | |
| VAFS | Very high | Good | Low | Low | Very High | Low | Low | Low | Stark and Pratsinis, 2002<br>Teoh et al., 2010 |
| Sulfate process | High | Good | Low | Low | High | Low | Low | Low | Procházka, pers. communication |
| Altair | High | Good | Medium | Low | Medium | Low | Low | Low | Grubb and Bakshi, 2010<br>Verhulst et al., 2003 |
| HT plasma | High/medium | Good | High | Different | Medium | Very high | Different | High | Osterwalder et al., 2006<br>Vollath, 2007<br>Jurewicz et al., 2011<br>www.tekna.com |
| FSP | Medium | Good | High | High | Medium | Low | High | Medium | Pratsinis, mail<br>Teoh et al., 2010<br>Wegner et al., 2011<br>Mueller et al., 2004 |
| LT plasma | Low | Very good | Medium | Different | Medium | N/A | Different | N/A | Vollath, 2007 |
| CS solution | Low | Very good | High | High | Low | N/A | High | N/A | Aruna and Mukasyan, 2008<br>Chung and Wang, 2012 |
| Sol-gel | Low | Very good | Very high | Different | Low | High | Different | High | Pini et al., 2014<br>Bahnajady, mail<br>Bahnajady et al., 2011<br>Gupta and Tripathi, 2012 |
| Solvothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | Gupta and Tripathi, 2012 |
| Hydrothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | Gupta and Tripathi, 2012 |
| Precipitation | Low | Very good | Very high | Different | Low | High | High | High | Gupta and Tripathi, 2012<br>Manda et al., 2012 |

Fig. 4 Comparison matrix

The results of "cradle to gate" assessment show that CFHS can compete with high-productive technologies (e.g. VAFS, Altair process, sulfate process) in terms of production rates, costs and environmental impacts but offers considerably higher variability, process controllability and product quality of NPs. Technologies like precipitation, sol-gel, and batch solvo/hydrothermal syntheses that can provide similar range of NPs with comparable quality parameters are associated with significantly higher environmental impacts and production costs and cannot offer sufficient productivity that would enable full industrial application in the end products.

For this reason, the combination of productivity, variability and quality can be considered as the major source of competitive potential of CFHS. The biggest challenge will be finding proper commercial product applications that fully utilize the high value of NPs produced by this new technology.

The following environmental benefits of the CFHS should also be highlighted:

- no use of organic solvents as in the case of solvothermal method and no risk of producing harmful emissions – product of incomplete combustion (NOx and CO);
- possibility for avoiding the use of expensive organic precursors with high environmental impacts as is the case for solvothermal method or FSP, no need for different gases – e.g. Ar, $H_2$, $O_2$, $CH_4$, $N_2$ as is the case of other methods;

- low risk of NP release: NP emission into the air are negligible because the product is in suspension form not dry powder; emissions into the WW are also very low as shown through the NanoMile project (http://nanomile.eu-vri.eu/).

Our main goal in this paper was to assess sustainability of newly developed technology based on the widest possible range of factors, compare it with existing production technologies and identify its major benefits, risks, strengths and weaknesses. For nanotechnology selection, we recommend to continue with a stochastic multi-criteria decision analysis as applied in e.g. Canis, L. et al. (2010) or Linkov, I., et al. (2011), where the uncertainties in performance assessment and in stakeholders' preferences are treated. For such an analysis additional parameters as demanded production volumes, requirements for production variability and quality, etc. has to be known. This analysis, however, is beyond the scope of this article.

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**References**


1. Aruna, S.T., Mukasyan, A. S., 2008. Combustion synthesis and nanomaterials. Current Opinion in Solid State and Materials Science 12, 44–50.
2. Behnajady, M.A., Eskandarloo, H., Modirshahla, N., Shokri, M., 2011. Investigation of the effect of sol–gel synthesis variables on structural and photocatalytic properties of $TiO_2$ NPs. Desalination. 278, 10–17.
3. Brugger, W. 1963. US Pat., 3076831 A.
4. Buchmüller, O., Diplomarbeit, Universität Augsburg, 2012.
5. Canis, L., Linkov, I., Seager, T.P., 2010. Application of stochastic multiattribute analysis to assessment of single walled carbon nanotube synthesis processes. Environmental Science and Technology, 44, 8704-8711.
6. Caramazana-González, P., Dunne, P. W., Gimeno-Fabra, M., Zilka, M. Ticha, M, Stieberova, B., Freiberg, F., McKechnie, J., Lester, E. H., 2017. Assessing the life cycle environmental impacts of titania nanoparticle production by continuous flow solvo/hydrothermal syntheses, Green Chem. 19, 1536-1547.
7. Dunne, P.W., Munn, A.S., Starkey, C.L., Huddle, T.A. and Lester, E.H., 2015. Continuous-flow hydrothermal synthesis for the production of inorganic nanomaterials. Phil. Trans. R. Soc. A, 373(2057), p.20150015.
8. Gottschalk, F., Nowack, B., 2011. The release of engineered nanomaterials to the environment. Journal of Environmental Monitoring. 13, 1145–1155.
9. Grubb, G. F., 2010. Improving the environmental performance of manufacturing systems via exergy, techno-ecological synergy, and optimisation. Ph.D. thesis. The Ohio State University.
10. Grubb, G.F., Bakshi, B.R., 2011. Life cycle of Titanium Dioxide Nanoparticle production, Impact of emissions and use of Resources. Journal of industrial technology, 15. 81–95.
11. Guinée, J.B., Gorrée, M., Heijungs, R., Huppes, G., Kleijn, R., de Koning, A., van Oers, L., Wegener Sleeswijk, A., Suh, S., Udo de Haes, H.A., de Bruijn, H., van Duin, R., Huijbregts, M.A.J.,2002. Handbook on life cycle assessment, Kluwer Academic Publishers, Dordrecht, Netherlands.
12. Gupta S. M., Tripathi, M., 2012. A review on the synthesis of $TiO_2$ nanoparticles by solution route. Central European Journal of Chemistry. 10(2), 279-294.
13. Hischier, R, Nowack, B., Gottschalk, F., Hincapié, I., Steinfeldt, M., Som, C., 2015. Life cycle assessment of facade coating Systems containing manufactured nanomaterials. Journal of Nanoparticle Research. 17,68-81.
14. Chen, J., Whittingham, M.S., 2006. Hydrothermal synthesis of lithium iron phosphate. Electrochemistry Communications. 8(5), 855-858.
15. Chung, S. L., Wang, Ch. M., 2012. Solution combustion synthesis of $_{TiO2}$ and its use for fabrication of photoelectrode for dye-sensitized solar cell. J. Mater. Sci. Technol. 28(8), 713–722.
16. International Organization for Standardization ISO 14044:2006, Geneva, Switzerland, 2006.
17. International Organization for Standardization, ISO 14040:2006, Geneva, Switzerland, 2006.
18. Jurewicz J. W., Boulos M. I., Brochu L., Crête J. P., Dignard,N., D. Héraud, D., Hudon, F., Ostiguy, C., 2011. Can induction plasma technology be nano-safe, "green" and energy efficient? Journal of Physics: Conf. Ser. 304, 012072.
19. Krewer C., 2005. Environmental LCA of utilizing red cabbage trimmings as novel products. Master of Science Thesis. Chalmers University of Technology. Göteborg, 2005.
20. Lester, E., Blood, P., Denyer, J. D., Giddings, D., Azzopardi, B., Poliakoff, M., 2006. Reaction engineering: The supercritical water hydrothermal synthesis of nano-particles. J Supercrit Fluids. 37, 209-214.
21. Liang, Y., Su, J., Xi, B., Yu, Y., Ji, D., Sun, Y., Cui, C. Zhu, J., 2017. Life cycle assessment of lithium-ion batteries for greenhouse gas emissions. Resources, Conservation and Recycling. 117, 285-293.
22. Linkov, I., Bates, M.E., Canis, L.J., Seager, T.P., Keisler, J.M., 2011. A decision-directed approach for prioritizing research into the impact of nanomaterials on the environment and human health. Nature Nanotechnology, 6, 784–787.
23. Majeau-Bettez, G., Hawkins, T. R., Strømman, A.H., 2011. Life cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. Environmental Science & Technology. 45 (10), 4548–4554.

24. Manda, B. M. K., Blok, K., Patel, M. K., 2012. Innovations in papermaking: An LCA of printing and writing paper from conventional and high yield pulp. Science of the Total Environment. 439, 307–320.
25. Middlemas, S., Fang, Z.Z., Fan, P., 2015. Life cycle assessment comparison of emerging and traditional titanium dioxide manufacturing processes. Journal of Cleaner Production 89: 137-147.
26. Moeller, A. 1965. US Pat., 3206281.
27. Mueller, R., Jossen, R., Pratsinis, S. E., Watson, M.A., Kamal, M., 2004. Zirconia nanoparticles made in spray flames at high production rates, Journal of the American Ceramic Society. 87 (2): 197-202.
28. Osterwalder, N., Capello, C., K. Hungerbuhler, K., Stark W.J., 2006. Energy consumption during nanoparticle production: How economic is dry synthesis? Journal of Nanoparticle Research. 8, 1–9.
29. Pine, T., Lu, X., Mumm, D.R., Samuelsen, G.S., Brouwer, J., 2007. Emission of pollutants from glycine–nitrate combustion synthesis processes. Journal of the American Ceramic Society. 90 [12], 3735–3740.
30. Pini, M., Rosa, R., Neri, P., Bondioli, F., Ferrari, A.M., 2014. Environmental assessment of a bottom-up hydrolytic synthesis of $TiO_2$ nanoparticles. Green Chem. 17, 518-531.
31. Pratsinis, S.E., 2011. History of manufacture of fine particles in high-temperature aerosol reactors. Ensor, D.S. (Eds.), Aerosol Science and Technology: History and Reviews. RTI Press, Research Triangle Park, NC, pp. 475-508.
32. PRé Consultants, SimaPro 8.0.4 (Ecoinvent inventory database v.3.), Amersfoort, Netherlands, 2013.
33. Roth, P., 2007. Particle synthesis in flames. Proceedings of the Combustion Institute. 31, 1773–1788.
34. Stark, W. J., Pratsinis, S. E., 2002. Aerosol flame reactors for manufacture of nanoparticles. Powder Technology 126: 103–108.
35. Teoh, W. Y., Amal, R., Madler, L., 2010. Flame spray pyrolysis: An enabling technology for nanoparticles design and fabrication. Nanoscale. 2, 1324–1347.
36. Tichá, M., Žilka, M., Stieberová, B, Freiberg, F., 2016. Life cycle assessment comparison of photocatalytic coating and air purifier. Integr Environ Assess Manag. 12(3), 478-85.
37. Vollath, D., 2007. Plasma Synthesis of Nanoparticles. KONA Powder and Particle Journal. 25.
38. Wegner, K., Schimmoeller, B., Thiebaut, B., Fernandez, C., RAO, T.N., 2011. Pilot plants for industrial nanoparticle production by flame spray pyrolysis. KONA Powder and Particle Journal. 29, 251-265.
39. Yu, Y., Wang, D., Huang, K., Wang, X., Liang, Y., Sun, W., Chen, B., Chen, S., 2014. Assessment of cathode active materials from the perspective of integrating environmental impact with electrochemical performance. Journal of Cleaner Production. 82, 213–220.
40. Zackrisson, M., Avellán, L., Orlenius J., 2010. Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles - Critical issues. Journal of Cleaner Production. 18, 1519-1529.

**Web references**

41. Nanocoatings market analysis by product by application and segment forecasts to 2020. http://www.grandviewresearch.com/industry-analysis/nanocoatings-market (accessed april 2016).
42. NanoMile project. http://nanomile.eu-vri.eu/.
43. Nanopowders production. http://www.tekna.com/technology/nanopowder-synthesis (accessed November 2013).
44. Nanosustain project. (http://www.tecdesign.uni-bremen.de/typo3/forschung/abgeschlossene-forschungsprojekte/nanosustain.html (accessed 5 June 2015).
45. Project on Emerging Nanotechnologies. www.nanotechproject.org (accessed June 2014).
46. Renard, F., 2015. 2020 cathode materials cost competition for large scale applications and promising LFP best-in-class performer in term of price per kWh. https://www.eiseverywhere.com/ehome/oreba1.0/204235/login.php (accessed 22 September 2015).
47. U.S. EPA, 2010. State of the science literature review: Nano titanium dioxide environmental matters. https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=498019 (accessed 16 november 2013).
48. Verhulst, D., Sabacky, B., Spitler, T., Prochazka, J., 2003. New developments in the altair hydrochloride $TiO_2$ pigment process. http://www.b2i.cc/Document/546/AltairHydro2003.pdf (accessed 8 october 2013).

**Figure Captions:**

Fig.1 CFHS process flow-chart

Fig.2 CEDs (a) and GWPs (b) of different NPs

Fig.3 Total unit costs of CFHS for individual NPs

Fig.4 Comparison matrix

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# Sustainability Assessment of Continuous-flow Hydrothermal Synthesis of Nanomaterials in the Context of Other Production Technologies

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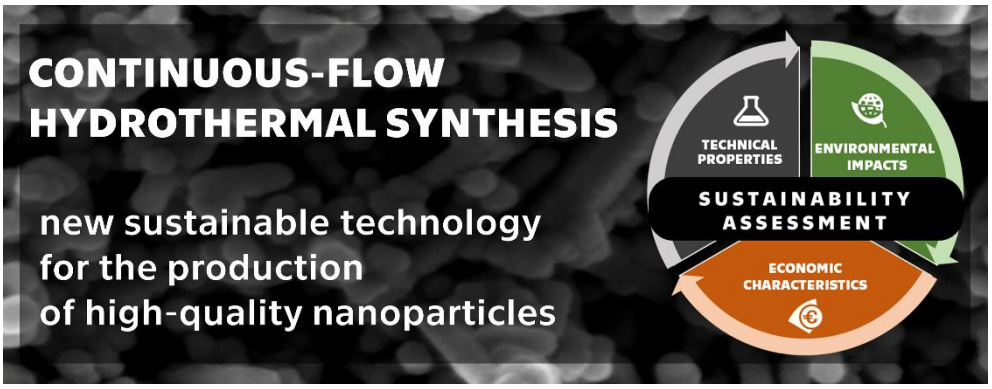
## Abstract

In this paper, we provide a comprehensive techno-economic and life cycle environmental evaluation of the continuous-flow hydrothermal synthesis (CFHS) of nanoparticles in the context of current production technologies. This method is compared with a set of competitor technologies: Plasma syntheses; Flame pyrolysis; Sol-gel synthesis; Batch Solvo/Hydrothermal syntheses; and Altair hydrochloride process. Technical criteria such as scale and variability of production and material properties are accounted for in the environmental and economic analyses. Case study nanomaterials are investigated with a range of potential applications: titanium dioxide (smart coatings, electronics, and water purification); zinc oxide (smart coatings, cosmetics); zirconium dioxide (nanocomposites, electronics); and lithium phosphate (lithium ion battery cathode material).

Results show that CFHS can be ranked among the most productive methods capable of producing up to 100-250 kg/h of different types of high quality NPs dispersed in water. In terms of the environmental impacts, this newly developed technology does not use any toxic solvents, there are no emissions into the environment and the risk of leakage of NPs into environment is negligible. Comparison of values of selected environmental impact categories Cumulative Energy Demand (CED) and Global Warming Potential (GWP) shows that CFHS can compete with industrial technologies with low production variability and limited product quality (e.g. sulfate and chloride processes) and achieves much better results in comparison with technologies with similar variability (e.g. HT plasma or sol-gel) and product quality (sol gel). The same conclusion can be made in the case of an economic assessment. The combination of large scale and variability of production and quality of produced NPs can be considered as the major source of competitive potential of CFHS.


## Graphical abstract



## Highlights

- We present a comprehensive comparison of nanoparticles production methods.
- Comprehensive comparison covers technical, environmental and economic aspects.
- Four nanoparticle types are included in the comparison: $TiO_2$, ZnO, $ZrO_2$, $LiFePO_4$.
- LCA was used as a key method for assessment of environmental impacts.
- Detailed cost structure of produced nanoparticles is revealed in this study.

***Keywords:*** *Nanoparticles, nanoparticles production, hydrothermal syntheses, sustainability, life cycle assessment, production costs*

## 1. Introduction

### 1.1 Purpose and characteristics of the study

Nowadays, there is a rapid development in the field of nanoparticle production technologies and intense increase of application of nanomaterials, the number of registered nanoproducts has been augmented from 54 in 2005 to 1865 in 2013 (www.nanotechproject.org). Many studies predict a massive development in various application areas, such as the smart nano-coatings (Grand view research, 2014). Environmental impact assessments, alongside economic benefits evaluation, are currently growing in importance as nanomaterials transfer from laboratories into everyday life. Therefore, the evaluation of environmental impacts and economic benefits was an integral part of the FP7 project Sustainable Hydrothermal Synthesis of Nanomaterials (SHYMAN), which was focused on development of large-scale continuous-flow NPs production technology based on hydrothermal synthesis.

In order to assess whether the newly developed technology is a source of economic or environmental benefits compared to the current state of the art, a comprehensive study has been developed to characterize both the new technology and the existing production technologies. This comparative analysis covers:

- basic technical characteristics - product characteristics, production scale and variability, basic operation conditions – temperatures, pressures,
- environmental characteristics – impact categories: Cumulative Energy Demand (CED), Global Warming Potential (GWP); assessment of risk of release of NP during production; necessary safety measures,

- economic characteristics – total production costs or selling price of nanoparticles (NPs), investment costs and cost of variable inputs.

As a main NP for comparison, we chose $TiO_2$ because of its wide applicability (smart coatings, electronics, and water purification) and availability of data. We also collected characterization data for other widely used NPs: $ZrO_2$ (nanocomposites, electronics), ZnO (smart coatings, cosmetics), $LiFePO_4$ (active material in Li-ion batteries) but information for comparison was only available for a very limited number of technologies.

### 1.2 Data overview and limitation

This study is based on a large variety of information sources, especially existing LCA studies oriented on nanoparticle production and other literature sources focused on the production of the nanoparticles by different technologies. More information was obtained via email communication with authors of different articles (Prof. Pratsinis, Bahnajady), personal discussion with experts (such as dr. Procházka from Advanced Materials and HE3DA Company, dr. Ieva from SOLVAY Company), and form SimaPro software connected to Ecoinvent databases. The overview of the key studies is given in the Tab. 1.

Tab. 1 Overview of important studies focused on the presentation of environmental and economic data of individual NPs production technologies.

| **Study** | **Technology** | **Scale of production** | **NPs** | **Application** | **Environmental data** | **NPs release** | **Economic data** |
|---|---|---|---|---|---|---|---|
| Osterwalder et al., 2006 | Traditional and new methods (e.g. plasma syntheses) | | $TiO_2$, $ZrO_2$ (nano and micro ) | Only production of NPs | Energy consumption<br>$CO_2$ emissions | No | No |
| Grubb and Bakshi 2011, Grubb, 2010 | Altair hydrochloride process | Pilot plant | $TiO_2$<br>Anatase, 40 nm | Only production of NPs | Fossil fuel use<br>Eco-indicator 99 method<br>(Beside LCA also exergy analysis) | No | No |
| Zackrisson et al., 2010 | Solid-sate | Laboratory condition | $LiFePO_4$ | Batteries | Publication details the GWP. The energy requirements per kg of $LiFePO_4$ was roughly estimated (3 kJ/g $LiFePO_4$) | No | No |
| Wegner et al., 2011 | Flame spray pyrolysis (FSP) | Pilot scale | $Bi_2O_3$, $ZrO_2$ | Only production of NPs | No | - | Yes, detailed cost study |
| Majeau-Bettez et al., 2011 | Batch hydrothermal process | Industrial modelling from a laboratory | $LiFePO_4$ | Batteries | Publication of input data – CED and GWP was calculated using | No | No |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | condition | | | SimaPro software | | |
| Manda et al., 2013 | Precipitation process | Laboratory condition | $TiO_2$ | Paper industry | NREU<br>GHG emission | No | No |
| Nanosustain project, 2013 | NA | NA | $TiO_2$, ZnO, $ZrO_2$ | NA | CED, GWP | NA | No |
| Pini et al., 2014 | Sol-gel process | Large production( Colorobbia S.p.A. Italy) | $TiO_2$<br>30 nm | Self-clean coating | NREU, GWP<br>Impact 2002+ method | Yes, two impact cath.: Nano $TiO_2$ ecotoxicity in freshwater, Nano $TiO_2$ carcinogens in freshwater | Yes, basic information – only total costs are published |
| Yu et al., 2014 | Solid-state | Laboratory condition | $LiFePO_4$ | Batteries | Publication of input data – CED and GWP was calculated using SimaPro software | No | No |
| Middlemas et al., 2015 | Alkaline roasting of titania slag (ARTS) | Virtual ARTS processing plant | Only Micro $TiO_2$, | Only production of $TiO_2$ in a bulk form | CED, GWP | - | No |
| Liang et.al., 2017 | Solid-state | Laboratory condition | $LiFePO_4$ | Batteries | Publication only details the GWP for the raw materials. | No | No |

NREU – Non-renewable energy use, CED – cumulative energy demand, GWP – global warming potential

Although we used a broad spectrum of information sources, we were not able to collect data for all evaluated technologies and all evaluating criteria. It is particularly difficult to find published economic data for commercial reasons, and only the Wegner et al. (2011) study presents, in detail, cost structures of the FSP method for a pilot plant. From the summary of key studies it is evident that there is no such a complex study that would evaluate NPs production technologies from the different perspectives and which would combine technical, environmental and economic characteristics. Moreover, the quality of environmental data of individual studies is limited: they are modelled based on laboratory conditions (Majeau-Bettez et al.) could be overestimated (as it is described in Manda et al., 2013) or underestimated as Zackrisson et al. (2010) with energy requirements of only 3 kJ/g $LiFePO_4$ or Majeau-Bettez et al. study excluding the energy to dry the NPs and some material inputs. The data are often incomplete for example: process energy requirements of $LiFePO_4$ solid-state production is not included in Liang et al. study or the use of argon, necessary in the sintering/calcination stage is omitted in the LCA calculation.

## 2. Methods

### 2.1 Continuous-flow hydrothermal synthesis

The process of NP creation by continuous-flow hydrothermal syntheses (CFHS) in a specially designed reactor was detailed in Lester et al. (2006). Within the SHYMAN project, the reactor was completely re-evaluated to enable large-scale production. Alongside with the reactor the whole large scale production process was designed and built. Simplified flowchart of the production process is depicted in the Fig. 1.

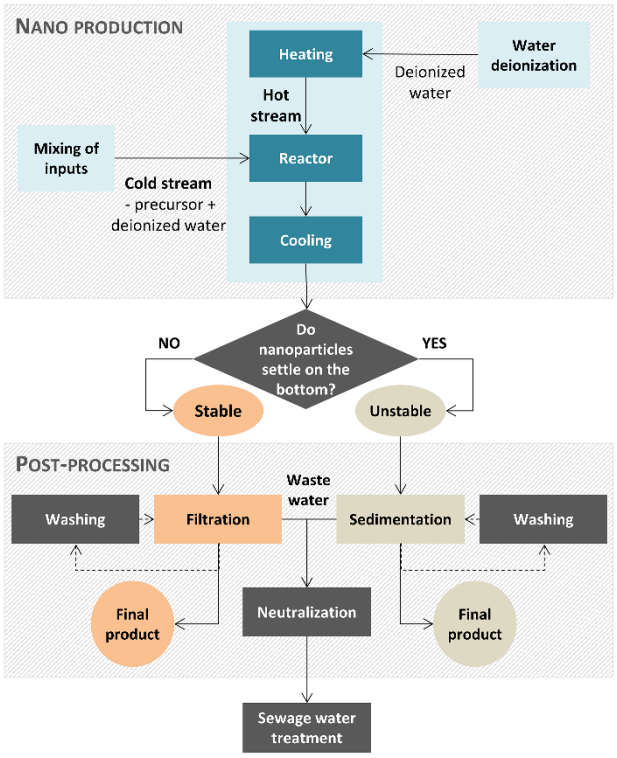



Fig. 1 CFHS process flow-chart

The hot stream (deionized water) and cold stream (precursor mixed with deionized water) meet in the reactor to form NPs. The temperature of the downstream flow of deionized water into the reactor where the NPs are created ranges typically from 250°C to 400°C. The NP production process is followed by post-processing, which aims to increase the NP concentration (from 0.5% wt up to more than 10% wt.) in the water suspension and dispose unwanted materials. Post-processing varies depending upon the character of NP processed.

If the NPs do not tend to settle out (i.e. stable NPs), the concentration increase is achieved through a set of filters. The dispersion is forced through tubes of porous polymer, during which process the NPs, due to their size, do not escape through the pores, whereas the water molecules are forced out of the tube. In this manner a dispersion concentration exceeding 10% wt. can typically be achieved in real time during production.

The concentration of nanoparticles that settle over time (unstable NPs) is increased by their sedimentation at the bottom. The concentrate is then released from the sedimentation tank from the bottom. Wastewater remains in the upper part of the tank to be further processed. Unwanted materials and impurities are removed through a washing of NPs - the concentrated solution is diluted with deionized water and post-processing is repeated. The production and post-processing of NPs is followed by the water treatment process, where the pH of the waste water (WW) is adjusted to meet requirements set by the WW treatment plant.

Comparison of production conditions for production of NPs that are thoroughly investigated in the following chapters is displayed in the Tab. 2.

Tab. 2 Production condition of individual NPs produced by CFHS

| | **$TiO_2$** | **ZnO** | **$ZrO_2$** | **$LiFePO_4$** |
|---|---|---|---|---|
| **Precursors used for the synthesis of nanoparticles – Input flow rate** | • Titanium oxysulfate (TiOS) – 799.65 kg/h (15%wt) | • Zinc nitrate ($Zn(NO_3)_2$) – 72.64 kg/h<br>• Pottassium hydroxide (KOH) – 22.44 kg/h (90%wt) | • Zirconium acetate (Zr(AC)) – 515.7 kg/h (22%) | • Iron sulphate ($FeSO_4$) – 57.54 kg/h<br>• Ascorbic acid – 33.02 kg/h<br>• Lithium hydroxide (LiOH) – 26.94 kg/h<br>• Phosphoric acid ($H_3PO_4$) – 43.24 kg/h (85% wt) |
| **Post processing** | Sedimentation | Sedimentation | Filtration | Sedimentation |
| **Temperature** | 400°C | 400°C | 400°C | 400°C |
| **Output flow rate (kg/h)** | 59.9 | 30.53 | 92.41 | 47.33 |
| **Concentration** | 8% | 3.4% | 11.4% | 3.6% |

### 2.2 Life Cycle Assessment methodology

To assess the environmental impacts of production of individual NPs – $TiO_2$, ZnO, $ZrO_2$, $LiFePO_4$ by CFHS technology, Life Cycle Assessment (LCA) models were developed in accordance with ISO standards (Guinée et al. 2002, ISO 14040:2006, ISO 14044:2006). For the evaluation of environmental impact of individual NPs a cradle to gate analysis is undertaken, excluding ultimate use of the NPs, and 1 kg of NPs dispersed in water is set as a declared unit. Fig. 1 displays the system boundaries for the analysis. Following inputs and unit processes are included in the system:

- Precursors (theirs hourly flow rates are specified in the Tab. 2)
- Deionization of water - tap water is deionized for further use (HCl, NaCl, electricity use)
- Mixing of inputs - inflows are mixed at the desired concentration (electricity use)
- Heating and cooling stages as described above (natural gas and electricity use)

- Postprocessing steps – sedimentation or filtration (electricity use), washing (electricity use), neutralisation (NaOH 32%, water and electricity use)
- WW treatment as it is modelled in SimaPro database
- Packaging and transportation of all materials

Information based on the current plant built in Nottingham, prior nanoparticles production and work experience is used to determine electrical consumption of equipment, natural gas of the boiler, typical flow rates and volume used during the manufacturing of NPs.

LCI data were taken from the SimaPro version 8.1.1.166 connected to Ecoinvent 3 databases. Because no LCI data about some inputs are present in the SimaPro databases: as a proxy for ascorbic acid an average of three substances was used: methane, formaldehyde and acetic acid (Krewer, 2005); zirconium acetate production was modelled based on US 3076831 and zinc nitrate production based on US 3206281.

CED and GWP were chosen because of their wide publication and general understanding as characterisation impact categories for the environmental assessment of individual NPs.

### 2.3 Economic assessment methodology

Economic assessment of the CFHS technology has been conducted by using the full costs model elaborated within SHYMAN project, which allows allocation of all production costs. Production conditions of individual NPs considered for economic assessment are shown in Tab 2. The cost model takes into account variable and fixed costs.

The key variable costs represent:

- costs of precursors;
- costs of other chemicals used for NPs precipitation, cleaning of the rig and WW neutralization;
- costs of deionizing of tap water and cost of WW treatment in plant;
- costs of electricity powering pumps, cooling unit, mixers and control system;
- costs of natural gas used in the heater.

The same approach, methods and data sources as for LCA were used for determination of precursors, other chemicals and water flow-rates, for gas and electricity consumption. Purchasing prices especially for chemical

substances can vary depending on the volume of the order and specific contract conditions. For this cost calculation prices based upon pre-negotiated business offers and internet sources were used.

Fixed costs represent the following cost groups:

- **cost of equipment**– depreciation period is conservatively chosen for 3 years;
- **personnel costs** – we assume 4 full time equivalents working in 1 operating shift
- **other costs** represent mainly costs of space, maintenance costs, services (e.g. legal, marketing), small assets, HW, SW, insurance, etc.

Individual fixed costs were allocated by using hourly cost tariff (HCT) method. HCT [EUR or USD per hour] is calculated by dividing fixed costs [EUR, USD per year] by effective production capacity of the facility [hours per year]. Allocation to the allocation unit is done by multiplication of HCT by the process time needed to produce 1 kg of NPs dispersed in water.

We calculated total fixed costs for two potential scenarios:

- 400 hours/year of effective capacity (approx. 20% of capacity utilization in 1 shift) – characterizing initial years of the full-scale plant operation when there is not enough business orders and the most of the production is used for testing runs;
- 1600 hours/year (approx. 80% of capacity utilization in 1 shift) – characterizing following period when the capacity is effectively utilized to cover business orders.

## 3. Results and discussion

In this paper, we present detailed results for individual groups of characterization criteria. Each section starts with the characterization of CFHS, characterization of other competing technologies follows. The comprehensive results of the comparison are summed up in a matrix at the end of this part (Fig.4).

### 3.1. Basic criteria

Basic criteria characterise scale and variability of production and quality of produced NPs.

#### 3.1.1. Basic criteria - CFHS

CFHS technology has demonstrated a significant flexibility enabeling the use of different precursors, solvents, operational conditions and production configurations using the counter-current reactor. This fact has led the

production of a wide variety of NPs (Dunne et al., 2015) (from simple oxides and sulphides, to complex compounds like $LiFePO_4$ or Metal Organic Frameworks (MOFs)) with high production rates. Production rates vary with the type of NP, the concentration of the input precursor and defined synthesis conditions (Tab. 2.). They ranges typically in tens of kilograms per hour and can reach up to 100 kg/hour (and up to 250 kg/hr in specific cases, such as MOFs). CFHS attains a high quality of dispersed and formulated product. For example $TiO_2$ characteristics – fine grain 9 ± 1.9 nm, BET specific surface area (SSA) 159 $m^2/g$, crystallinity 80%, 100% anatase phase. $ZrO_2$ characteristics – very stable suspension, very high SSA of dry powder - above 200 $m^2/g$, 6 nm grain size, high crystallinity already in suspension, there is no need for further processing.

### 3.1.2. Basic criteria in comparison with literature data

Methods with the **highest production rates** include vapour assisted flame pyrolysis (VAFP), a chloride process with production rate for fine metal powders of up to 25 000 kg/h (Stark and Pratsinis, 2002), sulfate process and Altair hydrochloride process for which there is a pilot plant with production rate of 100 kg/hour as described in Grubb (2010). These methods are not particularly versatile – VAFP is applicable for $TiO_2$, $SiO_2$ and other simple oxides; the sulfate process is applicable only for $TiO_2$. A high production rate, significantly lower than that for VAFP, is attained by high temperature plasma (HT plasma); the highest production rate for HT plasma can be estimated at up to 60kg/hour at 400 kW. The production rate of the typical HT plasma plant is less than 10 kg/hour (Volath, 2007). CFHS with typical production rate of tens kilograms per hour is one of highly productive methods capable to produce large volumes of NPs demanded by commercial applications. **Lower production rates** are achieved by FSP; Prof. Pratsinis of ETH Zurich and his team have attained up to 5 kg/h (Pratsinis, email communication). Wet production methods such as the sol-gel, batch solvo/hydrothermal methods achieve low production rates. The main reason is the long production time and batch character of production especially for the hydrothermal and solvothermal methods, which use special autoclaves. Another low productivity method is the low temperature plasma method, which can be effectively applied for production of small quantities of highly specialized materials and synthesis of coated particles (Vollath, 2007).

**The quality of NPs** characterized by particle size, particle size distribution, BET surface, agglomeration, and the distinctive properties of the NP – depends on a great range of factors and the capability of the production methods to control these factors. Wet methods generally perform better in terms of quality and the NPs are better suited for specialized applications than those produced by dry methods. For example, batch hydrothermal and solvothermal methods produce NPs suitable for use in the electrical industry as semiconductor materials (QD –

CdSe, ZnO). The particle size of $TiO_2$ produced by wet technologies varies from 10 to 20 nm, with a high percentage of anatase phase material. (e.g.: Bahnajady et al., 2011). CFHS is a wet method, which is capable to produce NPs of highest quality. Very small and non-agglomerated NPs are also produced by combustion synthesis (e.g.: Chung and Wang, 2012) while LT plasma is used for production of NPs for highly specialized products. The Altair hydrochloride process produces anatase $TiO_2$ NPs with the average diameter of 40 nm (Grubb et Bakshi, 2011). Standard quality is represented by commercially produced nano $TiO_2$ AEROXIDE® TiO2 P 25 with 80% of the anatase phase, average particle size 21nm, BET SSA ($m^2/g$): 45.63. P 25 is produced by VAFP in high productivity flame reactors (Roth, 2007). VAFP is geared mainly towards the production of NPs for commodity applications, such as $TiO_2$ with a diameter of 200 nm for use in pigments. The size of NPs produced by HT plasma ranges from 50 to 100 nm; with quenching a narrower size distribution can be achieved (www. tecna.com). FSP also achieves a small NP size, such as $ZrO_2$ measuring 30 nm (Mueller et al., 2004). In general, there is a broader size distribution in the case of dry synthesis than with wet methods because of the greater difficulties in controlling the production process.

As it can be seen from this comparison of characteristics of individual methods, CFHS ranks among the methods with high production rates and at the same time is able to produce wide variety of high quality products. The aggregated comparison within basic criteria is shown in Fig. 4.

### 3.2. Environmental comparison

Firstly, detailed charts of both impact category results for NPs produced by CFHS ($TiO_2$, ZnO, $ZrO_2$ and $LiFePO_4$) are presented on Fig. 2. Results of CED and GWP of various NPs should not be directly compared due to their different functional applications but they clearly show different energy demands and global warming potentials of individual NPs and contributions of individual components and processes. CED and GWP values of different types of NPs produced by CFHS are then compared with other production technologies – Tab. 3 and Tab 4. In addition to this comparison, we prepared an evaluation of other emissions and NPs release risks.

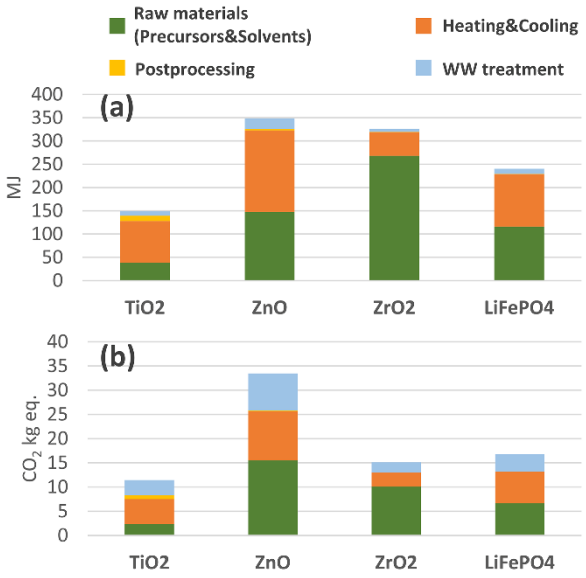



Fig. 2 CEDs (a) and GWPs (b) of different NPs

### 3.2.1. Cumulative energy demand and Global warming potential of CFHS

From the Fig. 2 it is apparent that embodied energy in the precursor and the heating and cooling stages has the most significant impact on total CED. It is possible to observe a clear positive effect of higher output flow-rate on the impact of heating and cooling stages of different NPs - similar amount of process energy is divided into a larger volume of production (e.g. $ZrO_2$ NPs with the greatest output flow rate of 92 kg/hour have the lowest impact on heating and cooling stages). The lowest CED values are returned by $TiO_2$ due to the use of the simple precursor Titanium(IV) oxysulfate (TiOS) with low embodied energy. The use of more complex precursors and organic solvents as inputs for $TiO_2$ production is associated with much higher environmental impacts as it is shown in the recent LCA study published by Caramazana-Gonzalez (2017). GWP results for individual NPs produced by CFHS technology show that the output flow rate has similar influence on the contribution of the heating and cooling stages as for CED - the higher the output flow rate, the lower the impact. Compared to the CED category, the wastewater treatment process has a greater contribution in the total GWP category.

### 3.2.2. CED and GWP of $TiO_2$ nanoparticles in comparison with literature data

Table 3 presents a comparison of CEDs and GWPs for the production of 1 kg of $TiO_2$ NPs using different production methods. For the production of $TiO_2$ NPs (8% dispersion) from TiOS precursor, the comparison of data implies that CFHS ranks among the methods with low energy consumption as measured by CED. It should be pointed out that low variable technologies (e.g. sulfate and Altair hydrochloride processes) have a slightly lower CED than the CFHS but in comparison with technologies with similar variability (e.g. HT plasma or sol-

gel) and product quality (sol gel) CFHS performs very well in terms of CED. The energy consumption of the CFHS production process depends on the type of NPs (as it is mentioned above). CFHS performs well also in the case of GWP impact category.

For product application requiring powder form of NPs, drying of the water dispersion should be also included in the evaluation. In this case, it is necessary to add an energy of about 29.79 MJ for 1 kg of $TiO_2$ NPs. It corresponds to the CED value of 90.7 MJ and GWP of 5.1 $CO_2$ kg.eq/kg.

Tab. 3 Energy consumption and CO2 kg eq. emissions for the production of 1 kg of TiO2 (*NREU – Non-renewable energy use)

| **Technology** | **Production scale** | **Form of NPs** | **Characteristics of NPs** | **CED (MJ/kg)** | **GWP ($CO_2$ kg.eq/kg)** |
|---|---|---|---|---|---|
| **CFHS** | Industrial | 8% dispersion | 9 nm, anatase | 149 (+90.7for drying) | 11.42 (+5.1 for drying) |
| Solgel Process (Pini et al., 2014) | Industrial | 6% dispersion | 30 nm | 1049* | 58 |
| Precipitation process (Manda et al. 2013) | Laboratory | Powder | - | 540* | 30 |
| Altair hydrochloride process (Grubb and Bakshi, 2011) | Pilot scale | Powder | 40nm, anatase, | 140* | 6 |
| Sulfate process (Procházka, flow chart in Tichá et al. (2016)) | - | Powder | 30 nm, anatase | 88.9 | 7.39 |
| Unspecified process (Nanosustain, 2013) | - | Powder | - | 81.4 | 4.26 |
| Combustion of Ti – isopropox. (FSP) (Osterwalder et al., 2006) | - | Powder | - | - | 15 |

To complete the CED comparison of $TiO_2$ production methods we should also mention the recent LCA study conducted by Middlemas et al. (2015), which focused on the alkaline roasting of titania slag (ARTS) – method for the production of $TiO_2$ pigments (micro-size). The CED of ARTS (90 MJ/kg) (Middlemas et al., 2015) is lower than the majority of early published results of CED for production of $TiO_2$ pigments (micro size) by traditional production methods. Middlemas (2015) concludes that $CO_2$ emissions are also low.

### 3.2.3. CED and GWP comparison of other NPs ($ZrO_2$, ZnO, $LifePO_4$) with literature data

The CED and GWP values of other NPs are summarized in table 4. The CED of the production of $ZrO_2$ NPs by CFHS (325 MJ/kg) is very low compared to HT plasma syntheses, which has a very high energy consumption. 520 MJ is needed just for the dispersion of the Zr metal and the heating of the gas to process temperature (Osterwalder et al., 2006). Above-mentioned 520 MJ of electricity, medium voltage at grid, UK corresponds to CED of 1500 MJ and GWP of 88 kg $CO_2$ eq. (SimaPro).

Tab. 4 Comparison of CEDs and GWPs of $ZrO_2$, ZnO and of $LiFePO_4$ NP production (CEDs and GWPs of production referenced in Yu et al. and in Majeau-Bettez et al. was calculated in SimaPro with published primary data. *The use of argon, necessary in the sintering/calcination stage, is not include in the LCI.)

| | **Technology** | **Scale of production** | **Form of NPs** | **Characteristics** | **CED (MJ/kg)** | **GWP ($CO_2$ kg.eq/kg)** |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| $ZrO_2$ | **CFHS** | Industrial | 11.36 % dispersion | 200$m^2$/g(SSA), 6 nm | 325 (+61.3for drying) | 16.16 (+3.41 for drying) |
| | HT plasma NP (Osterwalder et al. 2006) | - | Powder | - | | 40 |
| | Combustion of Zr-isopropoxide (Osterwalder et al. 2006) | - | Powder | - | | 9 |
| | Nano-milling (Osterwalder et al. 2006) | - | Powder | - | | 35 |
| ZnO | CFHS | Industrial | 3.4 % dispersion | 36 $m^2$/g (SSA) 44.5 ± 21 nm | 347 (+224 for drying) | 33.45 (+12.5 for drying) |
| | Unspecified process (Nanosustain, 2013) | | | - | 474,27 | 21 |
| $LiFePO_4$ | CFHS | Industrial | 3.6 % dispersion | | 240 (+211 for drying) | 16.77 (+11.8 for drying) |
| | Batch hydrothermal synthesis - 5h in reactor then 5h drying (Majeau-Bettez et al., 2011) * | Simulation | Powder | | 104 | 5.44 |
| | Solid-state process (Yu et al., 2014) | Laboratory | Powder | | 390 | 20.2 |

**ZnO** NPs (3.4 % dispersion) produced by CFHS achieves lower CED than NPs referenced in the NanoSustain project (Tab. 4) but GWP potential is higher. Because of lack of detailed information about production methods used within the NanoSustain project, it is hard to identify the main cause. Possibly the wastewater treatment process included in the CFHS evaluated system can be the reason of higher impacts.

Water dispersion with **$LiFePO_4$** NPs produced by CFHS has lower CED than the solid-state process (Yu et al., 2014), but higher than hydrothermal syntheses reported by Majeau-Bettez et al., 2011. The inclusion of the drying process will further increase the impacts of the CFHS. However, LCI data for study published by Majeau Bettez were quantified based on theoretical assumptions not real measurements and especially process energy is underestimated. Majeau-Bettez et al. (2011) used a batch hydrothermal technique (Chen and Whittingham, 2006) with the addition of multi-wall carbon nanotubes to enhance the electronic conductivity of $LiFePO_4$. The use of carbon nanotubes as a nano-product require higher demand of energy that is not included in the CED, as well as the ascorbic acid and the energy of drying NPs are omitted. Comparison of GWP impact category shows worse results for CFHS then for other technologies but the quality and completeness of the data of the studies mentioned above remains a question.

### 3.2.4. Nanoparticle release

The risk of NPs exposure depends on the work procedure and applied risk management measures (EPA, 2010). There is a difference in exposure for dry and wet methods. Dry methods rank among those with a high risk of NP release to the air (Gottschalk and Nowack, 2011) so there is a need for strenuous measures to protect the working

environment and beyond. Such measures are described in Jurewicz et al. (2011) for HT plasma synthesis and in Wegner et al. (2011) for FSP. They include working in a fully enclosed room, personal protection, particle counters, HEPA filters, etc. In the case of dry NP production methods, water is used for cleaning and maintenance: the resulting slurry containing NPs is recovered and disposed of as hazardous waste (Wegner et al., 2011). In general, however, as noted in EPA report (2010), actual industrial practices employed by individual manufacturers are uncertain. For wet production methods, there is a risk of leakage of NP mainly to the water. Prof. Bahnajady (via email) claimed for the sol-gel process that the value of NP release is very low with a negligible ppm level. Pini et al. (2014) have assumed for cleaning operations (bottom-up hydrolytic sol-gel syntheses) that 1% of the $TiO_2$ nanoparticle suspension (6% $TiO_2$ NPs in suspension) remains on the reactor walls. For sulfate production of nano $TiO_2$ Hichier et al. (2015) state that water emissions of nano $TiO_2$ NPs in a realistic case scenario are per Buchmüller (2012) 0.03%, emissions to air are presumed to be 0%, as the process is a precipitation process. Some recently published studies, have made an attempt to consider the environmental effects of $TiO_2$ NP release: Pini et al. (2014), Hichier et al. (2015).

CFHS is a wet synthesis method with low risk of planned and unplanned emissions of NPs. The whole production process is a closed system. The precursors are completely dissolved in water and the reaction occurs in a closed reactor. Sedimentation of nanoparticles does not produce any emissions to the air (closed sedimentation tanks). Currently, the emissions into the air are negligible due to the lack of dry NPs. The emissions into the wastewater are low and probably similar to Pini et al. (2014) or Hichier et al. (2015). The risk of unplanned NP emission of CFHS can be classified as very low: there is a wide range of safety measures preventing any leakages of NPs and other hazardous substances. In case of sudden increases in pressure, there are pressure relief valves and a back pressure relief valve system. To prevent overflow in the storage tanks, there are the level indicators, the tanks that operate with hazards components and nanoparticle suspension are connected to a “line out of tank”. Leakages and spillage are prevented by bund tanks.

#### 3.2.5. Other emissions

Both liquid phase and gas phase processes generate pollutants. For dry processes, there is a large amount of gas generated and released during reaction as stated in Chung and Wang (2012) for combustion solution synthesis. Emissions into the environment depend on the efficiency of each separator. For example when using nitrate precursors the DeNOx treatment unit must be applied (Wegner et al., 2011). For the Altair hydrochloride process

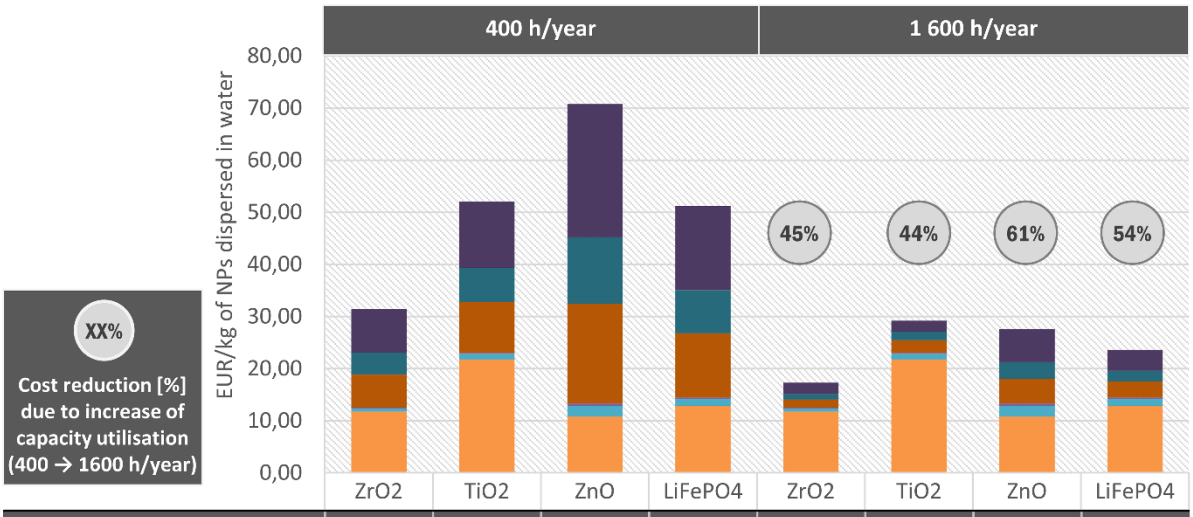
fugitive emissions of HCl in the early stages of the process and fugitive emissions of methane during a hydrolysis stage and have been estimated to have the highest impact on human toxicity potential and global warming potential (Grubb, 2010). A conservative estimate of 1% fugitive emission rate was assumed for volatile organics. Pini et al. (2014) state that during the production and purification steps, the release of $HNO_3$ into the air occurs. One percent of the total amount of material has been assumed to be emitted. For the sol-gel process, Bahnajady states that if the production process is carried out in a highly controlled way, there will be no emissions to the environment. For hydrothermal synthesis there is no use of organic solvents as for solvothermal synthesis and there is no risk of producing harmful emissions – for example products of incomplete combustion (NOx and CO) as have been proved for the glycine nitrate process (Pine et al., 2007).

### 3.3. Economic comparison

There is a lack of the published economic data characterising NPs production in the literature. The only study showing the whole cost structure was published by Wegner et al. (2011) for $ZrO_2$ NPs. In other cases we had to compare production costs with unstructured total values – Pini et al. (2014) for solgel technology ($TiO_2$ NPs), or with benchmark prices based on consultations with dr. Procházka from Advanced Materials and HE3DA company, dr. Ieva from SOLVAY company and internet pricelists. Firstly, detailed CFHS cost structure for studied NPs is presented.

#### 3.3.1. CFHS total costs

A comparison of the absolute values of overall costs per 1 kg for each NP type for different capacity utilization is illustrated in **Error! Reference source not found.**. Equipment costs have been calculated at approx. 900 000 €. Personnel costs were set for 4 workers per full-time (1 shift).




| TOTAL UC [EUR/kg] | 31,42 | 52,06 | 70,77 | 51,19 | 17,30 | 29,20 | 27,63 | 23,63 |
|---|---|---|---|---|---|---|---|---|
| Costs of equipment | 8,37 | 12,76 | 25,57 | 16,15 | 2,16 | 2,11 | 6,39 | 4,04 |
| **SUBTOTAL II [EUR/kg]** | **23,06** | **39,30** | **45,20** | **35,04** | **15,14** | **27,09** | **21,24** | **19,59** |
| Other costs | 4,23 | 6,52 | 12,79 | 8,25 | 1,06 | 1,63 | 3,20 | 2,06 |
| Personal costs | 6,33 | 9,76 | 19,15 | 12,35 | 1,58 | 2,44 | 4,79 | 3,09 |
| Electricity | 0,14 | 0,21 | 0,41 | 0,27 | 0,14 | 0,21 | 0,41 | 0,27 |
| Natural Gas | 0,59 | 1,04 | 2,04 | 1,32 | 0,59 | 1,04 | 2,04 | 1,32 |
| Costs of chemicals and water | 11,78 | 21,77 | 10,80 | 12,86 | 11,78 | 21,77 | 10,80 | 12,86 |

Fig. 3 Total unit costs of CFHS for individual NPs

Values in grey circles (Fig. 3) show the percentage of costs savings achieved by a production capacity utilization change from 400 h/year to 1 600 h/year (application of Economies of Scale). Considering lower capacity utilization, $ZrO_2$ NPs which are produced with the highest output flow rate of 92 kg /hr, have the lowest costs. The nanoparticles with the highest cost are, on the contrary, nanoparticles of ZnO, which are produced with the output flow rate of only 30 kg /hour. Raising capacity utilization causes reduction of unit costs of NPs, due to the decrease in fixed costs (equipment, personnel and other costs) per kg of NPs. As the unit variable costs are not changing as capacity utilization increases, their share in total costs is also increasing. Further increase of capacity utilization thus does not have such an influence on total production cost.

### 3.3.2. Comparison of CFHS costs with costs and prices of other technologies

Limited information on the cost of nanoparticle production is available publicly. We compare CFHS costs with available data for $ZrO_2$, $TiO_2$, and $LiFePO_4$. In comparison to FSP synthesis (Wegner at al., 2011), costs for the CFHS technology for $ZrO_2$ NPs in low capacity operations are roughly one-third (100 EUR/kg as opposed to 30 EUR/kg). The difference can be credited to the use of a less costly precursor Zr(Ac) and unit fixed costs due to the economy of scale. The unit costs of CFHS would be even lower when considering 10 years instead of 3 years

depreciation period of investments and unrealistic four-shift operation as for FSP instead of 3 years. In light of the fact that the current commercial benchmark price based on personal consultation with dr. Ieva from Solvay company – producer of NP containing products, was set at 35 EUR/kg, production of nano $ZrO_2$ by the CFHS method is profitable, even at low levels of utilization. This price, however, represents conventional commercially available nanoparticles with worse qualitative parameters. Costs per 1 kg of nano $TiO_2$ produced using CFHS technology are approximately 51 EUR/kg for a presumed 20% capacity utilization (Fig. 3). The greatest share of the total costs are the costs of precursors; these costs are higher than for $ZrO_2$ NPs. Increasing capacity utilisation means a decrease in investment, personnel and other costs per unit up to 28 EUR/kg. It corresponds to market price of nano-sized $TiO_2$ AEROXIDE® P 25 and the profit would be in this case negligible. However, the product produced by CFHS technology achieves much better qualitative parameters (pure anatase phase, smaller average particle size, narrow particle size distribution, higher BET SSA) and because of this higher value especially for special applications much higher sales price is presumed. For example: $TiO_2$ dispersion with similar parameters is offered by US Research Nanomaterials (http://www.us-nano.com/inc/sdetail/630) at a retail price of 165 USD for 1 000 ml 15 wt% dispersion. That is a cost of 1 100 USD/kg for $TiO_2$ NPs. For the sol gel process (Pini et al., 2014), the costs of 1 kg of the 6 % wt. $TiO_2$ NPs suspension was calculated to be 30.4 EUR, so the cost is 507 EUR/kg of $TiO_2$ NPs.

Costs per 1 kg of $LiFePO_4$ using CFHS (23.63 EUR/kg) are comparable with benchmark price of roughly 25 EUR/kg (based on personal correspondence with dr. Procházka and from the study by Fabrice Renard (2014)), but these costs would be even slightly higher as it is necessary to dry NPs for battery application. The most promising way to increase the profit from these NPs is through the increase of output flow rate.

The possibility of using simple precursors is an important competitive advantage of the CFHS unlike methods where more expensive organic precursors are needed as for FSP, solvothermal and for solution combustion synthesis. There is also no need for expensive organic solvents as is the case for solvothermal or FSP. From an input costs perspective, the strategic location of the plant is also important as it provides opportunities to share inputs and outputs (e.g. Cabot's plant with Evonik's fumed silica plant described in Pratsinis, (2011). In terms of energy costs CFHS ranks among low energy consumption methods with low energy costs per kg of NPs (electricity + natural gas costs represent less than 5% of total production costs).

## 4. Conclusion

Information from previous parts were aggregated and transformed into a comparison matrix (Fig 4.), which in a very compact form provides characterization and comparison of individual production technologies.

| Technology/ Criterion | Production rate | Quality | Variability | Cost of inputs | Cost of equipment | Energy Consumption process | Energy Consumption embodied | CO2 emissions | Important sources |
|---|---|---|---|---|---|---|---|---|---|
| CFHS | High | Very good | Very high | Different | Medium | Low | Different | Low | |
| VAFS | Very high | Good | Low | Low | Very High | Low | Low | Low | Stark and Pratsinis, 2002<br>Teoh et al., 2010 |
| Sulfate process | High | Good | Low | Low | High | Low | Low | Low | Procházka, pers. communication |
| Altair | High | Good | Medium | Low | Medium | Low | Low | Low | Grubb and Bakshi, 2010<br>Verhulst et al., 2003 |
| HT plasma | High/medium | Good | High | Different | Medium | Very high | Different | High | Osterwalder et al., 2006<br>Vollath, 2007<br>Jurewicz et al., 2011<br>www.tekna.com |
| FSP | Medium | Good | High | High | Medium | Low | High | Medium | Pratsinis, mail<br>Teoh et al., 2010<br>Wegner et al., 2011<br>Mueller et al., 2004 |
| LT plasma | Low | Very good | Medium | Different | Medium | N/A | Different | N/A | Vollath, 2007 |
| CS solution | Low | Very good | High | High | Low | N/A | High | N/A | Aruna and Mukasyan, 2008<br>Chung and Wang, 2012 |
| Sol-gel | Low | Very good | Very high | Different | Low | High | Different | High | Pini et al., 2014<br>Bahnajady, mail<br>Bahnajady et al., 2011<br>Gupta and Tripathi, 2012 |
| Solvothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | Gupta and Tripathi, 2012 |
| Hydrothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | Gupta and Tripathi, 2012 |
| Precipitation | Low | Very good | Very high | Different | Low | High | High | High | Gupta and Tripathi, 2012<br>Manda et al., 2012 |

Fig. 4 Comparison matrix

The results of "cradle to gate" assessment show that CFHS can compete with high-productive technologies (e.g. VAFS, Altair process, sulfate process) in terms of production rates, costs and environmental impacts but offers considerably higher variability, process controllability and product quality of NPs. Technologies like precipitation, sol-gel, and batch solvo/hydrothermal syntheses that can provide similar range of NPs with comparable quality parameters are associated with significantly higher environmental impacts and production costs and cannot offer sufficient productivity that would enable full industrial application in the end products.

For this reason, the combination of productivity, variability and quality can be considered as the major source of competitive potential of CFHS. The biggest challenge will be finding proper commercial product applications that fully utilize the high value of NPs produced by this new technology.

The following environmental benefits of the CFHS should also be highlighted:

- no use of organic solvents as in the case of solvothermal method and no risk of producing harmful emissions – product of incomplete combustion (NOx and CO);
- possibility for avoiding the use of expensive organic precursors with high environmental impacts as is the case for solvothermal method or FSP, no need for different gases – e.g. Ar, $H_2$, $O_2$, $CH_4$, $N_2$ as is the case of other methods;

- low risk of NP release: NP emission into the air are negligible because the product is in suspension form not dry powder; emissions into the WW are also very low as shown through the NanoMile project (http://nanomile.eu-vri.eu/).

Our main goal in this paper was to assess sustainability of newly developed technology based on the widest possible range of factors, compare it with existing production technologies and identify its major benefits, risks, strengths and weaknesses. For nanotechnology selection, we recommend to continue with a stochastic multi-criteria decision analysis as applied in e.g. Canis, L. et al. (2010) or Linkov, I., et al. (2011), where the uncertainties in performance assessment and in stakeholders' preferences are treated. For such an analysis additional parameters as demanded production volumes, requirements for production variability and quality, etc. has to be known. This analysis, however, is beyond the scope of this article.

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**References**


1. Aruna, S.T., Mukasyan, A. S., 2008. Combustion synthesis and nanomaterials. Current Opinion in Solid State and Materials Science 12, 44–50.
2. Behnajady, M.A., Eskandarloo, H., Modirshahla, N., Shokri, M., 2011. Investigation of the effect of sol–gel synthesis variables on structural and photocatalytic properties of $TiO_2$ NPs. Desalination. 278, 10–17.
3. Brugger, W. 1963. US Pat., 3076831 A.
4. Buchmüller, O., Diplomarbeit, Universität Augsburg, 2012.
5. Canis, L., Linkov, I., Seager, T.P., 2010. Application of stochastic multiattribute analysis to assessment of single walled carbon nanotube synthesis processes. Environmental Science and Technology, 44, 8704-8711.
6. Caramazana-González, P., Dunne, P. W., Gimeno-Fabra, M., Zilka, M. Ticha, M, Stieberova, B., Freiberg, F., McKechnie, J., Lester, E. H., 2017. Assessing the life cycle environmental impacts of titania nanoparticle production by continuous flow solvo/hydrothermal syntheses, Green Chem. 19, 1536-1547.
7. Dunne, P.W., Munn, A.S., Starkey, C.L., Huddle, T.A. and Lester, E.H., 2015. Continuous-flow hydrothermal synthesis for the production of inorganic nanomaterials. Phil. Trans. R. Soc. A, 373(2057), p.20150015.
8. Gottschalk, F., Nowack, B., 2011. The release of engineered nanomaterials to the environment. Journal of Environmental Monitoring. 13, 1145–1155.
9. Grubb, G. F., 2010. Improving the environmental performance of manufacturing systems via exergy, techno-ecological synergy, and optimisation. Ph.D. thesis. The Ohio State University.
10. Grubb, G.F., Bakshi, B.R., 2011. Life cycle of Titanium Dioxide Nanoparticle production, Impact of emissions and use of Resources. Journal of industrial technology, 15. 81–95.
11. Guinée, J.B., Gorrée, M., Heijungs, R., Huppes, G., Kleijn, R., de Koning, A., van Oers, L., Wegener Sleeswijk, A., Suh, S., Udo de Haes, H.A., de Bruijn, H., van Duin, R., Huijbregts, M.A.J.,2002. Handbook on life cycle assessment, Kluwer Academic Publishers, Dordrecht, Netherlands.
12. Gupta S. M., Tripathi, M., 2012. A review on the synthesis of $TiO_2$ nanoparticles by solution route. Central European Journal of Chemistry. 10(2), 279-294.
13. Hischier, R, Nowack, B., Gottschalk, F., Hincapié, I., Steinfeldt, M., Som, C., 2015. Life cycle assessment of facade coating Systems containing manufactured nanomaterials. Journal of Nanoparticle Research. 17,68-81.
14. Chen, J., Whittingham, M.S., 2006. Hydrothermal synthesis of lithium iron phosphate. Electrochemistry Communications. 8(5), 855-858.
15. Chung, S. L., Wang, Ch. M., 2012. Solution combustion synthesis of $_{TiO2}$ and its use for fabrication of photoelectrode for dye-sensitized solar cell. J. Mater. Sci. Technol. 28(8), 713–722.
16. International Organization for Standardization ISO 14044:2006, Geneva, Switzerland, 2006.
17. International Organization for Standardization, ISO 14040:2006, Geneva, Switzerland, 2006.
18. Jurewicz J. W., Boulos M. I., Brochu L., Crête J. P., Dignard,N., D. Héraud, D., Hudon, F., Ostiguy, C., 2011. Can induction plasma technology be nano-safe, "green" and energy efficient? Journal of Physics: Conf. Ser. 304, 012072.
19. Krewer C., 2005. Environmental LCA of utilizing red cabbage trimmings as novel products. Master of Science Thesis. Chalmers University of Technology. Göteborg, 2005.
20. Lester, E., Blood, P., Denyer, J. D., Giddings, D., Azzopardi, B., Poliakoff, M., 2006. Reaction engineering: The supercritical water hydrothermal synthesis of nano-particles. J Supercrit Fluids. 37, 209-214.
21. Liang, Y., Su, J., Xi, B., Yu, Y., Ji, D., Sun, Y., Cui, C. Zhu, J., 2017. Life cycle assessment of lithium-ion batteries for greenhouse gas emissions. Resources, Conservation and Recycling. 117, 285-293.
22. Linkov, I., Bates, M.E., Canis, L.J., Seager, T.P., Keisler, J.M., 2011. A decision-directed approach for prioritizing research into the impact of nanomaterials on the environment and human health. Nature Nanotechnology, 6, 784–787.
23. Majeau-Bettez, G., Hawkins, T. R., Strømman, A.H., 2011. Life cycle environmental assessment of lithium-ion and nickel metal hydride batteries for plug-in hybrid and battery electric vehicles. Environmental Science & Technology. 45 (10), 4548–4554.

24. Manda, B. M. K., Blok, K., Patel, M. K., 2012. Innovations in papermaking: An LCA of printing and writing paper from conventional and high yield pulp. Science of the Total Environment. 439, 307–320.
25. Middlemas, S., Fang, Z.Z., Fan, P., 2015. Life cycle assessment comparison of emerging and traditional titanium dioxide manufacturing processes. Journal of Cleaner Production 89: 137-147.
26. Moeller, A. 1965. US Pat., 3206281.
27. Mueller, R., Jossen, R., Pratsinis, S. E., Watson, M.A., Kamal, M., 2004. Zirconia nanoparticles made in spray flames at high production rates, Journal of the American Ceramic Society. 87 (2): 197-202.
28. Osterwalder, N., Capello, C., K. Hungerbuhler, K., Stark W.J., 2006. Energy consumption during nanoparticle production: How economic is dry synthesis? Journal of Nanoparticle Research. 8, 1–9.
29. Pine, T., Lu, X., Mumm, D.R., Samuelsen, G.S., Brouwer, J., 2007. Emission of pollutants from glycine–nitrate combustion synthesis processes. Journal of the American Ceramic Society. 90 [12], 3735–3740.
30. Pini, M., Rosa, R., Neri, P., Bondioli, F., Ferrari, A.M., 2014. Environmental assessment of a bottom-up hydrolytic synthesis of $TiO_2$ nanoparticles. Green Chem. 17, 518-531.
31. Pratsinis, S.E., 2011. History of manufacture of fine particles in high-temperature aerosol reactors. Ensor, D.S. (Eds.), Aerosol Science and Technology: History and Reviews. RTI Press, Research Triangle Park, NC, pp. 475-508.
32. PRé Consultants, SimaPro 8.0.4 (Ecoinvent inventory database v.3.), Amersfoort, Netherlands, 2013.
33. Roth, P., 2007. Particle synthesis in flames. Proceedings of the Combustion Institute. 31, 1773–1788.
34. Stark, W. J., Pratsinis, S. E., 2002. Aerosol flame reactors for manufacture of nanoparticles. Powder Technology 126: 103–108.
35. Teoh, W. Y., Amal, R., Madler, L., 2010. Flame spray pyrolysis: An enabling technology for nanoparticles design and fabrication. Nanoscale. 2, 1324–1347.
36. Tichá, M., Žilka, M., Stieberová, B, Freiberg, F., 2016. Life cycle assessment comparison of photocatalytic coating and air purifier. Integr Environ Assess Manag. 12(3), 478-85.
37. Vollath, D., 2007. Plasma Synthesis of Nanoparticles. KONA Powder and Particle Journal. 25.
38. Wegner, K., Schimmoeller, B., Thiebaut, B., Fernandez, C., RAO, T.N., 2011. Pilot plants for industrial nanoparticle production by flame spray pyrolysis. KONA Powder and Particle Journal. 29, 251-265.
39. Yu, Y., Wang, D., Huang, K., Wang, X., Liang, Y., Sun, W., Chen, B., Chen, S., 2014. Assessment of cathode active materials from the perspective of integrating environmental impact with electrochemical performance. Journal of Cleaner Production. 82, 213–220.
40. Zackrisson, M., Avellán, L., Orlenius J., 2010. Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles - Critical issues. Journal of Cleaner Production. 18, 1519-1529.

**Web references**

41. Nanocoatings market analysis by product by application and segment forecasts to 2020. http://www.grandviewresearch.com/industry-analysis/nanocoatings-market (accessed april 2016).
42. NanoMile project. http://nanomile.eu-vri.eu/.
43. Nanopowders production. http://www.tekna.com/technology/nanopowder-synthesis (accessed November 2013).
44. Nanosustain project. (http://www.tecdesign.uni-bremen.de/typo3/forschung/abgeschlossene-forschungsprojekte/nanosustain.html (accessed 5 June 2015).
45. Project on Emerging Nanotechnologies. www.nanotechproject.org (accessed June 2014).
46. Renard, F., 2015. 2020 cathode materials cost competition for large scale applications and promising LFP best-in-class performer in term of price per kWh. https://www.eiseverywhere.com/ehome/oreba1.0/204235/login.php (accessed 22 September 2015).
47. U.S. EPA, 2010. State of the science literature review: Nano titanium dioxide environmental matters. https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=498019 (accessed 16 november 2013).
48. Verhulst, D., Sabacky, B., Spitler, T., Prochazka, J., 2003. New developments in the altair hydrochloride $TiO_2$ pigment process. http://www.b2i.cc/Document/546/AltairHydro2003.pdf (accessed 8 october 2013).

**Figure Captions:**

Point-by-point response to the reviewer's comments on the manuscript

**Manuscript number JCLEPRO-D-18-02197**

# "Sustainability Assessment of Continuous-flow Hydrothermal Synthesis of Nanomaterials in the Context of Other Production Technologies"

The authors would like to thank the Reviewer for careful review of our manuscript.

## Reviewer #1

| | |
|---|---|
| **Comment:** | My comments were not addressed. Authors claimed that there are no need in MCDA because "We wanted to assess sustainability of newly developed technology based on the widest possible range of factors, compare it with existing production technologies and identify its benefits, risks, strengths and weaknesses." This is exactly why MCDA is required. The paper should be reviewed by more than one reviewer before it can be considered for publication. |
| **Response:** | Opponent's comments were not intentionally addressed. We still believe that the application of MDCA would not benefit our article and could move the focus completely outside the intended area. It could also diminish the clarity of the main ideas and messages of the paper. In our opinion, performing the MDCA without linking to a specific (product) application makes no sense, because the preferences and criteria weights may vary significantly for each application.<br>In addition, our paper is now very close to the upper word limit and incorporation of MDCA would mean that we would have to make significant cuts in the original text and remove some of the ideas we consider as very important.<br>We fully agree with the proposal of the Reviewer # 1 for an assessment by another reviewer before the final decision on publication in Journal of Cleaner Production. Due to the long time that has passed since the first submission, we respectfully ask for a quick evaluation and decision. |

Point-by-point response to the reviewer's comments on the manuscript

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| **Comment:** | My comments were not addressed. Authors claimed that there are no need in MCDA because "We wanted to assess sustainability of newly developed technology based on the widest possible range of factors, compare it with existing production technologies and identify its benefits, risks, strengths and weaknesses." This is exactly why MCDA is required. The paper should be reviewed by more than one reviewer before it can be considered for publication.<br>Reviewer #1: Even though I still believe that MCDA is an important component of the problem framing in the study, I respect authors' response and appreciate their addition of recommendation of MCDA as the next step at the end of the paper. From my end, I am done with this review and can not contribute more. Nevertheless, I believe the paper needs to be reviewed by an expert in technology. It seems like I have been the only reviewer |
| **Response:** | We also respect the reviewer's opinion on benefits of MDCA. For this reason, we have mentioned this method as the next step in choosing a suitable nanoparticle production technology. However, we still believe that without knowing the specific product application, MDCA will not provide relevant results. In this paper we wanted to characterise nanoparticles production technologies by using a wide range of criteria (technical, economic, environmental). The choice of the appropriate technology then depends on the prioritization of the selected criteria. Prioritizing for the health industry can be completely different from the priorities of the coating industry. Because we did not want to link the evaluated production technologies with a specific product application and wanted to make a comparison in general, MDCA is not part of our article. We still believe that the application of MDCA would not benefit our article and could move the focus completely outside the intended area.<br>In addition, our paper is now very close to the upper word limit and incorporation of MDCA would mean that we would have to make significant cuts in the original text and remove some of the ideas we consider as very important.<br>Like the reviewer, we have nothing to add to this issue. |