# COMPARATIVE STUDY OF NANOPARTICLE PRODUCTION TECHNOLOGIES FOCUSED ON ENVIRONMETAL ASPECTS

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**Abstract**

This article presents main results of a comparative study of different nanoparticle (NP) production technologies, e.g. flame pyrolysis, plasma synthesis, combustion synthesis, sol-gel, solvothermal and hydrothermal synthesis have been considered. Evaluation criteria were primarily focused on environmental impacts of compared technologies but also general criteria as productivity, quality, technical conditions or economic criteria have been envisaged. Available LCA studies assessing particular NP production technologies were used as an important source for this comparison. The study has been elaborated within 7. RP Sustainable Hydrothermal Manufacturing of Nanomaterials (SHYMAN), which aims to develop competitive and sustainable continuous NP production technology based on supercritical hydrothermal synthesis. The study will serve for the assessment of this newly developed and scaled up technology. Except general evaluation of different technologies on the basis of particular criteria presented in the table form, the article shows in detail, for the declared unit of 1 kg of produced NPs, the comparison of energy consumption, $CO_2$ emissions, unwanted emissions of nanoparticles and other pollutants. The evaluation has demonstrated that besides specific processes of different technologies it is the choice of precursor which has essential influence on energy demand of the whole life cycle of NPs; the CED (Cumulative energy demand) incorporated in the precursor could be higher than the process energy of selected technology.

**Keywords:**

LCA, environmental impacts, nanoparticles production technology, comparative study

## 1. INTRODUCTION

Nowadays, there is an intense increase of application of nanomaterials, number of registered nanoproducts has been augmented from 54 in 2005 to 1865 in 2013 [1]. As nanomaterials transfer from laboratories into everyday life, the need to assess its environmental impacts grows, especially in the stage of the development of new materials and new technologies. Therefore, the evaluation of environmental impacts is an integral part of 7. FP. project SHYMAN, which is focused on development of large-scale technology of nanoparticles production - continuous supercritical hydrothermal synthesis. To asses environmental impact of the developed technology this comparative study of different nanoparticle production methods has been elaborated. Available life cycle assessments studies of NP production methods were an important source.

## 2. LIFE CYCLE ASSASMENT

Life cycle assessment (LCA) according to [2] represents a complex method for an evaluation of environmental impacts. LCA analyses the whole life cycle of specified product – from raw material acquisition to the end of life of the product – “from cradle to grave”. The LCA study consists of four phases: goal and scope definition, inventory analysis, impact assessment, interpretation. Within the goal and scope definition phase the functional unit and system boundaries are defined. The second phase – inventory analysis consists of the defined system inputs and outputs aggregation and evaluation of all resources and pollutant emission in relation to the functional unit. Life Cycle Impact Assessment (LCIA) aims to describe, or at least to indicate, the impacts of the environmental loads quantified in the inventory analysis – the different impact categories can be calculated (global warming potential, acidification….). The overview of LCA studies focused on the production of particular nanomaterial and its application is in [3].

## 3. STRUCTURE OF THE STUDY AND INFORMMATION SOURCES

The aim of our study is to compare different NP production methods with respect to different criteria, mainly environmental. $TiO_2$ was taken as reference nanoparticle because of its wide use and availability of data. For this assessment following criteria have been selected: toxicity of inputs, energy consumption of the production of 1 kg of nano $TiO_2$ (including embodied energy in inputs), water consumption, emissions (mainly $CO_2$ eq. emissions related also to the production of 1 kg of nano $TiO_2$), risk of release of NP during production; necessary safety measures. For overall comprehension other criteria have been envisaged: productivity of technologies, quality of NPs, technical conditions (e.g. pressure, temperature,…); possible precursors and economic criteria - costs of inputs, costs of equipment, operational costs. A large variety of sources for our comparative study were used: existing LCA studies oriented on nano $TiO_2$ production, other literature sources focused on the production of the nano $TIO_2$ by different technologies, email communication with authors of different articles (prof. Pratsinis [4], Bahnajady [5]), partners from University of Nottingham (e.g. Prof. Lester [6]); Czech experts (e.g. prof. Procházka from Advanced Materials [7]); Ecoinvent database of SimaPro software [8]. The presented comparative study is built on the results of these LCA studies of nano $TiO_2$ production methods: the LCA of the Altair hydrochloride production [9]; the LCA of $TiO_2$ production by precipitation method for the use in paper industry [10]. An important source is analysis of energy demands and $CO_2$ equivalents for nano $TiO_2$ and nano $ZrO_2$ created by Osterwalder [11]. In this comparative study there are also included the preliminary results of LCA of supercritical hydrothermal syntheses scaling up within SHYMAN project.

## 4. RESULTS OF THE STUDY AND DISCUSSION

### 4.1 The overall comparison of selected technologies

The comparison of NP production technologies have been done on the basis of the detailed structured overview [12] elaborated for each of the selected NP production technology. The main results of the comparison have been transformed into the matrix form presented in the fig. 1.

| Technology/ criterion | Productivity | Quality | Variability | Cost of inputs | Cost of equipment | Energy Consumption process | Energy Consumption embodied | CO2 emissions | Important sources |
|---|---|---|---|---|---|---|---|---|---|
| HT plasma | High/ Medium | Good | High | Different | High | Very high | Different | Very high | [11] , [13], [14], [15] |
| LT plasma | Low | Very good | Medium | Different | Medium | N/A | Different | N/A | [13] |
| VAFS | High | Good | Low | Low | High | Low | Low | Low | [16] , [17] |
| FSP | Medium | Good | High | High | High | Low | High | Medium? | [4] , [17], [18] , [19] |
| CS solution | Low | Very good | High | High | Low | N/A | High | N/A | [20] , [21] |
| Sol-gel | Low | Very good | Very high | Different | Low | N/A | Different | N/A | [5] , [8], [22] , [23] |
| Solvothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | [23] |
| Hydrothermal | Low | Very good | Very high | High | Medium | N/A | High | N/A | [23] |
| Altair | High | Good | Low | Low | ? Medium | Low | Low | Low | [9] , [24] |
| Shyman | Medium | Very good | Very high | High | Medium | Low | Very high | High | [6] , [8] |
| Precipitation | Low | Very good | Very high | Different | Low | High | Medium | High | [10] , [23] |

**Fig. 1** The overall comparison of the different NP production technologies (HT- high temperat., LT- low temperat., VAFS – vapour-fed aerosol flame synth., FSP – flame spray pyrolysis, CS – combustion synth., Altair – Altair hydrochloride process, SHYMAN – continuous supercritical hydrothermal syntheses)

As regards the productivity, the highest production rate attains VAFP 25 t/h [16], for Altair hydrochloride process there is a pilot plant with production of 100 kg/hour [9], but these methods are not very versatile. The productivity of the typical HT plasma plant is several kg/hour [13], it could be 60 kg/hour (estimation), the SHYMAN technology is envisaged to be 12 kg/h, flame spray pyrolysis is up to 5 kg/h [4]. Wet production methods as sol-gel, hydrothermal and solvothermal method represent methods with low productivity.

The quality of produced NPs (particle size, distribution of particle size, BET surface, agglomeration and NP properties) – depends on the ability of production methods to control the large variety of factors. Wet methods in general perform better in the terms of quality – smaller particles, narrower size distribution and the NPs have better properties for special application than dry methods (e.g. hydrothermal and solvothermal methods produce nanoparticles suitable for the use as semiconductor materials (QD – CdSe, ZnO)). The particle size of TiO2 produced by wet technologies varied between 10-20 nm [22]. Altair hydrochlorid process produces anatase TiO2 NPs with the average diameter 40 nm [9]. Standard of the quality is represented by commercially produced nano TiO2 Degussa P25 (VAFP technology) with 80% of the anatase phase, particle size 21 nm, BET SSA 45.63 $m^2/g$. The size of NPs for HT plasma is between 100 and 50 nm [15]. Flame spray pyrolysis ZrO2 with 30 nm [19]. For supercritical hydrothermal syntheses, scaled up within this project, the highest quality of dispersed and formulated products is envisaged.

The main economic factors evaluated within this study were costs of inputs and costs of equipment. Regarding precursors used for NPs production, chlorides are cheaper than organic compounds: TiCl4 is available at less than $1000/ton [24]. FSP precursors and organic solvents will remain more expensive than the metal chlorides [18]. From this point of view the price of precursor – organic compound TIBALD used for the supercritical continuous hydrothermal synthesis is higher than the feed stock for the VAFP (TiCl4) and the Altair hydrochloride process (TiCl4 or Ilmenite). Organic compounds are also necessary for solvothermal and hydrothermal methods and for solution combustion synthesis. In the case of sol-gel and plasma synthesis there is a possibility of use both type of precursors. Concerning costs of equipment, high investment costs are needed for the FSP - Wegner et al. [18] have estimated investment costs to be 750 000 Euro for pilot plant with production of 1.25 kg/h located in Switzerland. As low investment methods can be considered sol-gel and combustion solution syntheses. Cost of equipment of continuous hydrothermal synthesis SHYMAN are estimated to be approx. 400 000 EUR.

Important environmental criteria are presented in detail in the next chapters.

### 4.2 Comparison of energy consumption

In the following graph there is a comparison of energy consumption for the production of 1 kg of TiO2 NPs for different production methods.

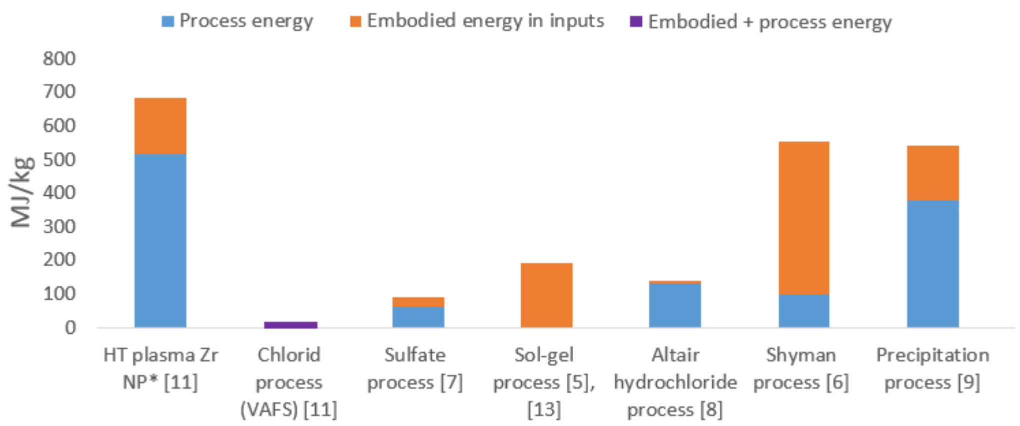


**Fig. 2** Energy consumption for the production of 1 kg of NP (* for HT plasma as the embodied energy were used energy consumption for 3,5 kg of TTIP [8], process energy is for Zr NP and it is taken from [11])

It should be noted, to complement the graph, that for vapour assisted flame pyrolysis and for flame spray pyrolysis the energy consumption is very small or that these plants typically generate within the reaction process more energy than they consume as in the case of Cabot's plant in Rheinfelden, Germany, excess heat is converted to electric energy and supplied to the local electric network [4].

The above mentioned data imply that continuous supercritical hydrothermal synthesis (SHYMAN) is ranked among the methods with the high energy consumption measured by means of CED (Cumulative energy demand). But the process itself consumes only 97 MJ for the production of 1 kg of $TiO_2$ and the overall CED is affected by the CED of the used precursor (TIBALD) which requires 457 MJ. There is a need to replace energy demanding precursors to diminish the environmental impact of SHYMAN technology. It should be pointed out that low variable technologies (e.g. sulphate and chloride process, Altair hydrochloride process) have considerably lower CED than SHYMAN technology but in comparison with technologies with similar variability (e.g. HT plasma, sol-gel..) SHYMAN technology does not perform badly in terms of CED. High temperature plasma is the method with the highest energy consumption, only for the dispersion of the Zr metal and the heating of the gas to process temperature 520 MJ is needed [11]. The consumption is inherently higher than for wet production methods but for the production of some metals NP high temperature plasma represents the only possibility [11].

### 4.3 Comparison of $CO_2$ emissions

In the following graph there is depicted a comparison of $CO_2$eq for the production of 1 kg of $TiO_2$ NPs for different production methods.

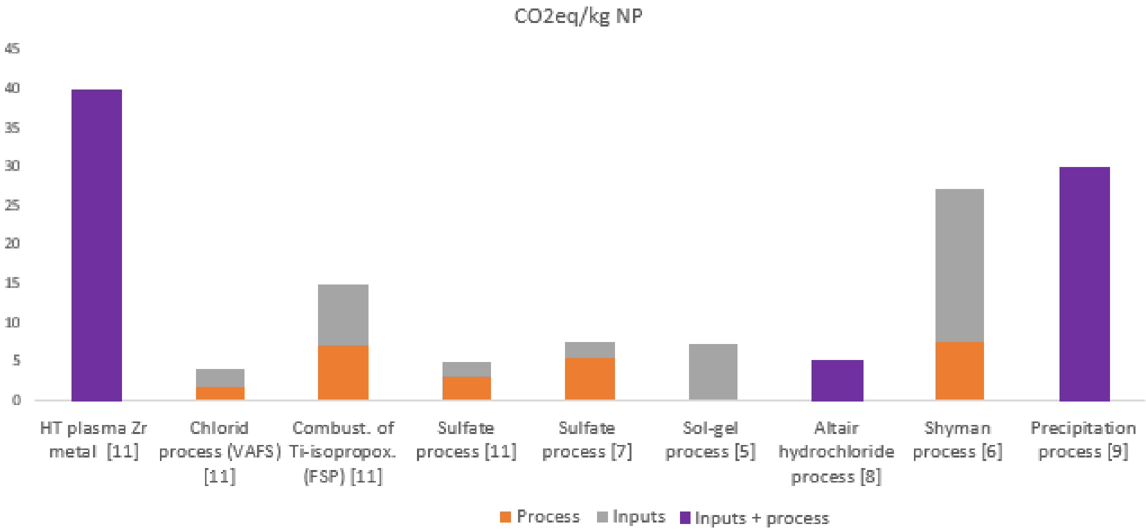


**Fig. 3** $CO_2$ eq./kg NP (only CO2 emissions are for chloride process [11], sulfate process [11] and inputs for Combustion of Ti-isopropoxide)

It is obvious that $CO_2$ emissions correspond to the energy consumption. To complete the graph - for flame assisted spray pyrolysis (FASP) there are no $CO_2$ emission during production of NP when using H2 flame [25]. $CO_2$ emissions produced during production of inputs are unknown.

### 4.3 Other emissions

Both liquid phase and gas phase processes generate pollutants (e.g., waste water, carbon dioxide, NOx, chlorine, hydrogen chloride, etc.) [26]. For dry processes there is a large amount of gas generated and released during reaction as it is stated in [21] for combustion solution synthesis. The emissions into environment depend on the efficiency of different separators which are required to use, for example in the case of using nitrate precursors there is a necessity to employ DeNOx treatment unit [18]. For Altair hydrochlorid process fugitive emissions of HCl in the early stages of process and fugitive emissions of methane in the stage of hydrolysis had been estimated to have the highest impact on human toxicity potential (HCl) and global warming potential (methane) [9]. Conservative 1% fugitive emission rate was assumed for the volatile organics [9]. For sol-gel process prof. Bahnajady [5] stated that if the production process is done 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 production of harmful emissions – product of incomplete combustion ($NO_x$ and CO) as have been proved for glycine nitrate process [27] - up to 4500 ppm of $NO_x$ and 9000 ppm of carbon monoxide.

### 4.4 Risk of nanoparticle release and safety measures

Dry methods represent methods with high risk of NPs release to the air so there is a need for severe measures to protect not only working environment. The measures are described in [14] for HT plasma synthesis and in [18] for flame spray pyrolysis (e.g. fully enclosed room, personal protection, submicron particle counters…,HEPA filters…) As it is mentioned in EPA review [28]: The quantity of dust emissions to air from handling and packaging solid powders depends on the air pollution control devices employed and that actual industrial practices employed by individual manufacturers are uncertain. The only available data of NPs release as it is concluded in the EPA review [28] are estimation using EPA/OPPT models – for example daily release rate in wt % of daily through-put was estimated to be 0.5 % for the activity of transferring solid nano-$TiO_2$ from product collector to packaging mechanism and 1 % for the cleaning solid nano $TiO_2$ residuals (powders) in process vessels.

In the case of dry NP production methods water is used for cleaning and maintenance and is treated very carefully as it is described in [18]: the resulting slurry after evaporation is recovered and disposed of as hazardous waste or is treated at high temperature by sintering [18]. For wet production methods there is the risk of leakage of NPs mainly to the water. For sol-gel process the value of NP release is very low in ppm level that is negligible [5]. This is also valid for the supercritical hydrothermal synthesis – the individual measures to prevent the release of NP are now in development. The impact of the leakage of NPs is not encompassed in the available LCA studies as it is very difficult to assess these impacts, but nowadays there is a trend to envisage and complete these data. As for example the existing LCA study of the Altair hydrochloride process [9] has been widespread [29]: with this result: the realistic release of NPs represents approximately 20 % of ecotoxicity impact of $TiO_2$ manufacture.

## 5. CONCLUSION

Continuous supercritical hydrothermal syntheses developed within the SHYMAN project of 7. RP will be classed among the method with medium productivity (12 kg/h), it will perform high versatility of production and it will produce high-quality dispersed and formulated NPs ready for application in customer’s products. In terms of the environmental impacts there are no toxic inputs, the risk of leakage of NPs into environment is planned to be negligible and the energy consumption of the production of 1 kg of $TiO_2$ is low. The highest potential for improvement from the environmental point of view is the reduction of CED by using suitable precursors, which have lower amount of embodied energy and simultaneously do not compromise the quality of production. This evaluation has demonstrated that it is the choice of precursor, which could have essential influence on energy demand of the whole life cycle of NPs.

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