Environmental sustainability of some synthetic processes of TiO_2 nanoparticles

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Outline

- ➢ Introduction and aim
- ➢ EATOS and Life Cycle Assessment as Green Metrics evaluation tools
- ➢ SCS *vs*. other soft chemistry routes
  - hydrolytic sol-gel
  - non hydrolytic sol-gel (benzyl alcohol route)
- ➢ Conclusions and future perspectives

Introduction

- conventional metrics: **Yield**, reaction **Time** and **Cost** of the precursors

- engineered nanomaterials ➔ **size** and **shape**

- **Green metrics**

mass index $$MI = \frac{\sum_i mass_{reagent_i}}{mass_{product}}$$

environmental-factor $$E-factor = \frac{\sum waste(g)}{product(g)}$$

atom efficiency $$AE = \frac{MW_{product}}{\sum_i MW_{reagent_i}}$$

atom utilization $$AU = \frac{mass_{product}}{\sum_i mass_{by-products_i}}$$

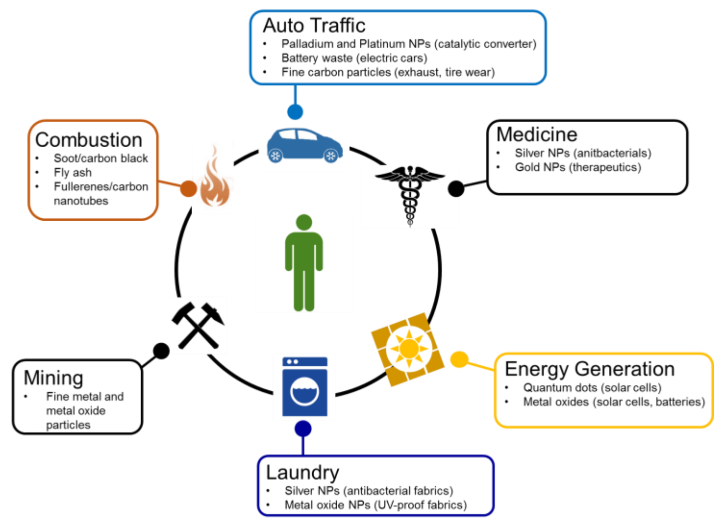
P.T. Anastas, J.C. Warner, in Green Chemistry: Theory and Practice, Oxford University Press, NY, 1998.
P.T. Anastas, J.B. Zimmerman, Design through the 12 principles of green engineering, Environ. Sci. Technol. 37, 2003, 94A-101A.
T. Van Gerven, A. Stankiewicz, Structure, energy, synergy, time – the fundamentals of process intensification, Ind. Eng. Chem. Res. 48, 2009, 2465-2474.

Introduction

In organic synthesis several works already exist…

S. Protti et al., Green Chem. 11, 2009, 239-249
D. Ravelli et al., Green Chem. 13, 2011, 1876-1884
C. Villa et al., Curr. Org. Chem. 15, 2011, 284-295

… Surprisingly the environmental assessment of the different synthetic strategies for the obtainment of engineered nanomaterials is scarce…..



Aim of the work

To realize for the first time a complete (from the **cradle to the grave**) and **quantitative** environmental assessment of SCS of TiO_2 nanoparticles

Solution combustion synthesis of TiO_2 nanoparticles

$$Ti(C_4H_9O)_4 + 3H_2O \rightarrow TiO(OH)_2 + 4C_4H_9OH$$
$$TiO(OH)_2 + 2HNO_3 \rightarrow TiO(NO_3)_2 + 2H_2O$$
$$9TiO(NO_3)_2 + 10C_2H_5NO_2 \rightarrow 9TiO_2 + 14N_2 + 20CO_2 + 25H_2O$$

S.L. Chung, C.M. Wang, Solution combustion synthesis of TiO_2 and its use for fabrication of photoelectrode for dye-sensitized solar cell, J. Mater. Sci. Technol. 28, 2012, 713-722.

Hydrolytic sol-gel synthesis

$$Ti(C_3H_7O)_4 + 2H_2O \rightarrow TiO_2 + 4C_3H_7OH$$

M. Pini, R. Rosa, P. Neri, F. Bondioli, A.M. Ferrari, Environmental assessment of a bottom-up hydrolytic synthesis of TiO_2 nanoparticles, Green Chem. 17, 2015, 518-531.

Non hydrolytic sol-gel synthesis: Benzyl alcohol route

$$2C_6H_5CH_2OH + TiCl_4 \rightarrow TiO_2 + 2C_6H_5CH_2Cl + 2HCl$$

M. Niederberger, M.H. Bartl, G.D. Stucky, Benzyl alcohol and titanium tetrachloride – a versatile reaction system for the nonaqueous and low-temperature preparation of crystalline and luminescent titania nanoparticles, Chem. Mater. 14, 2002, 4364-4370.

tools employed

EATOS (Environmental Assessment Tool for Organic Syntheses)

Free, data easily available (MSDS),……

$$MI = \frac{\sum substrate(g) + solvent(g) + auxiliary\_materials(g) + catalyst(g) + ...}{product(g)}$$

$$E - factor = \frac{\sum waste(g)}{product(g)}$$

$$EI\_in = \frac{\sum substrate(g) \cdot Q_{tot} + solvent(g) \cdot Q_{tot} + auxiliary\_materials(g) \cdot Q_{tot} + catalyst(g) \cdot Q_{tot} + ...}{product(g) \cdot Q_{tot}}$$

$$EI\_out = \frac{\sum waste(g) \cdot Q_{tot}}{product(g) \cdot Q_{tot}}$$

$$Q_{tot} = \frac{\sum_{i=1}^{i=n} Q_i}{n}$$

Weighting categories: claiming of resources, risk, human toxicity, chronic toxicity, ecotoxicology, ozone creation, air pollution, accumulation, degradability, greenhouse effect, ozone depletion, nutrification and acidification (MSDS)

NO ENERGY CONTRIBUTIONS ARE CONSIDERED!!!!!!

M. Eissen, J. O. Metzger, EATOS, Environmental Assessment Tool for Organic Synthese; the software can be obtained free of charge via http://www.chemie.uni-oldenburg.de/oc/metzger/eatos.

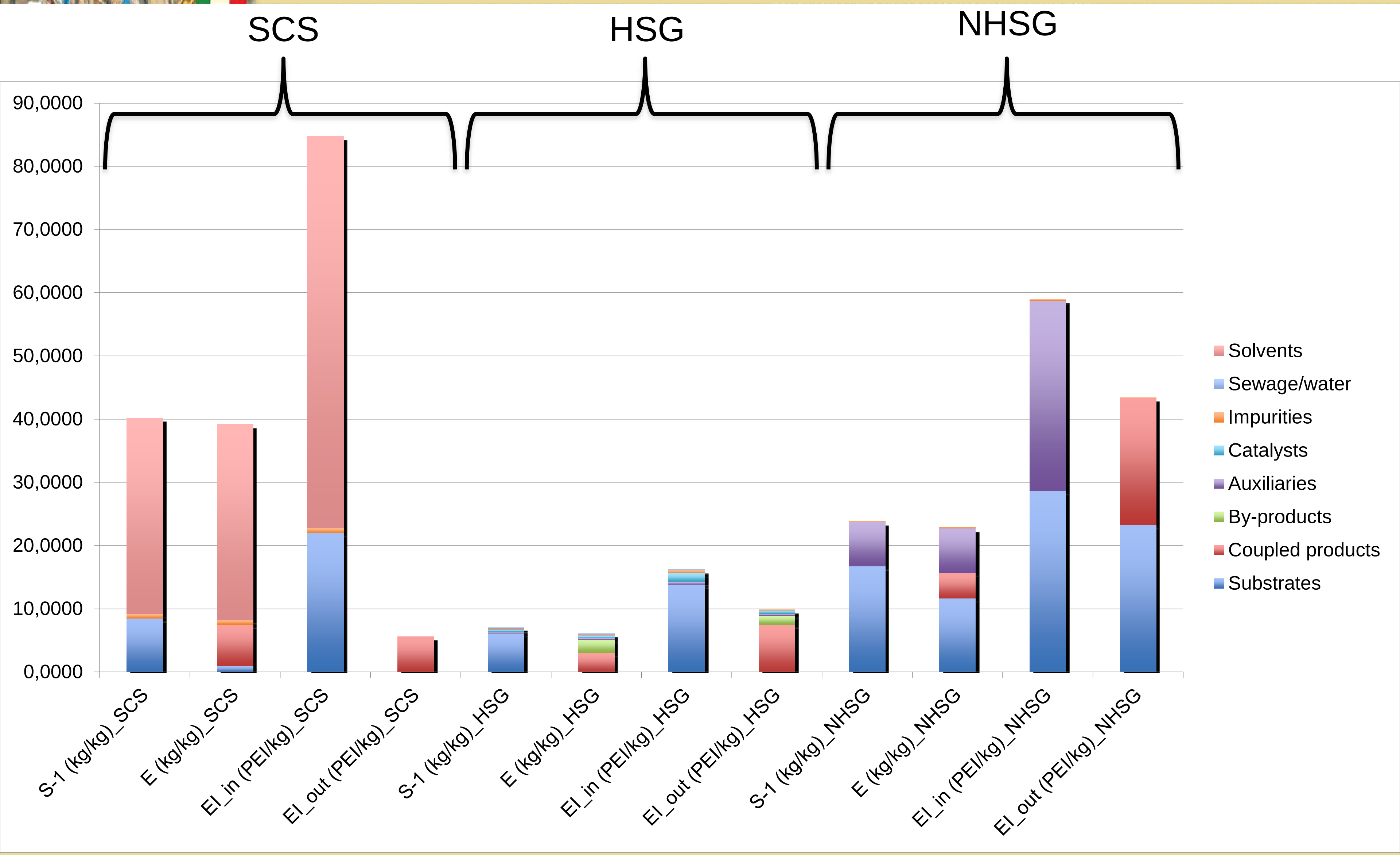
tools employed

Life cycle assessment (LCA)

- from the cradle to the grave
- quantifies ecological and human health impacts of a product or a system over its complete life cycle
- accounts for a wide range of damage categories, including energy contributions, transportation, extraction of natural resources, packaging, disposal, end of life…
- is standardized by the ISO 14040 and 14044

ISO 14040, Environmental management – Life cycle assessment – Principles and framework, International Standards Organization, ISO 2006.
ISO 14044, Environmental management – Life cycle assessment – Requirements and guidelines, International Standards Organization, ISO, 2006.

EATOS results



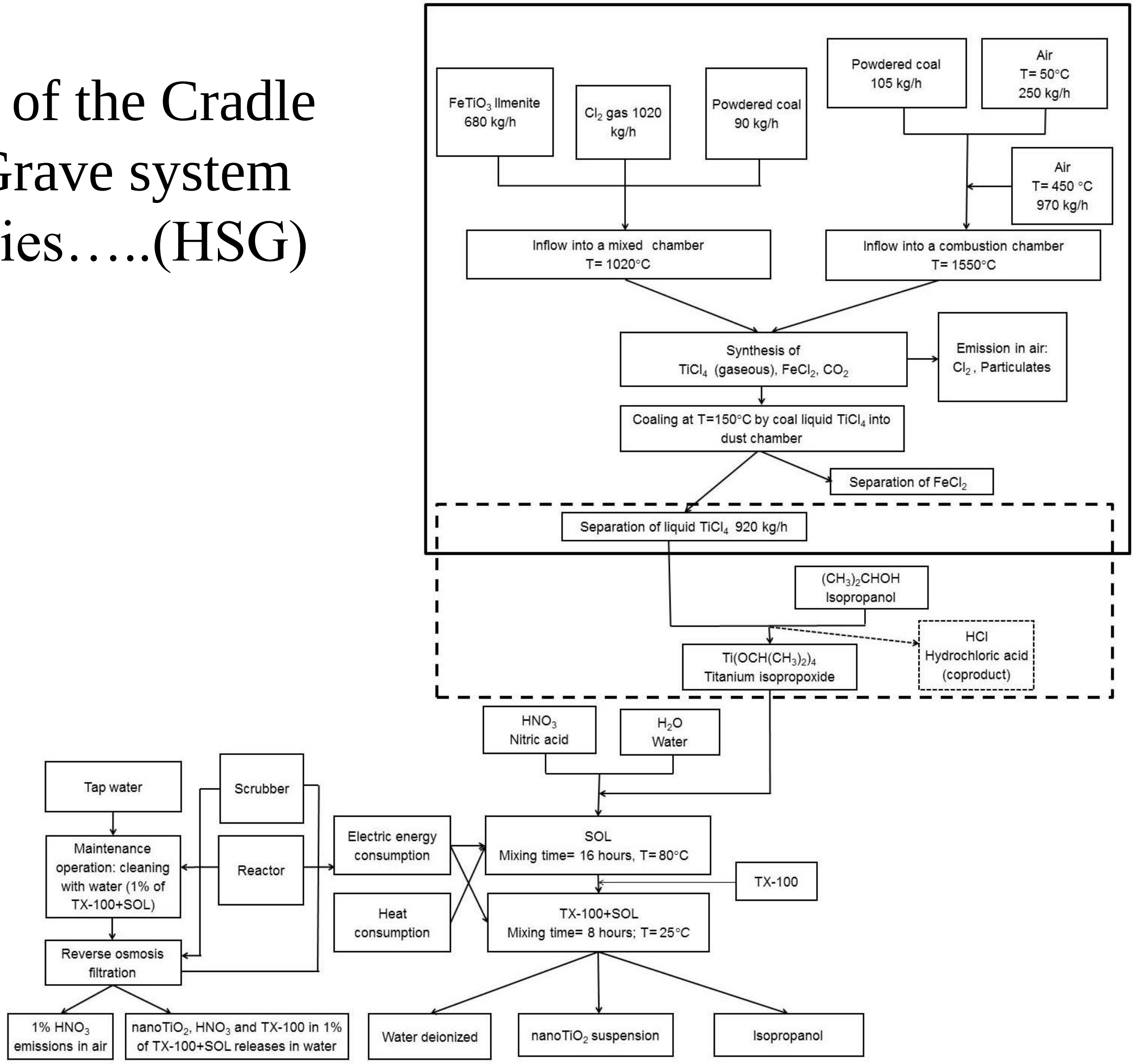
LCA results

- objective: environmental and human health assessment of three different synthetic strategies for TiO_2 and their comparison
- studied system: industrial scale production starting from the lab scale
- function of the system: production of chemical syntheses for the obtainment of TiO_2 NPs
- functional unit: 145.5 g TiO_2 NPs
- system boundaries: cradle to the grave (from the extraction of raw materials)
- data quality: literature data, database (Ecoinvent, Unimore-LWG), *new processes created if needed*
- software: SimaPro 8.0.4.28
- evaluation method: Impact 2002+ (modified)

ISO 14040, Environmental management – Life cycle assessment – Principles and framework, International Standards Organization, ISO 2006.
ISO 14044, Environmental management – Life cycle assessment – Requirements and guidelines, International Standards Organization, ISO, 2006.

LCA results

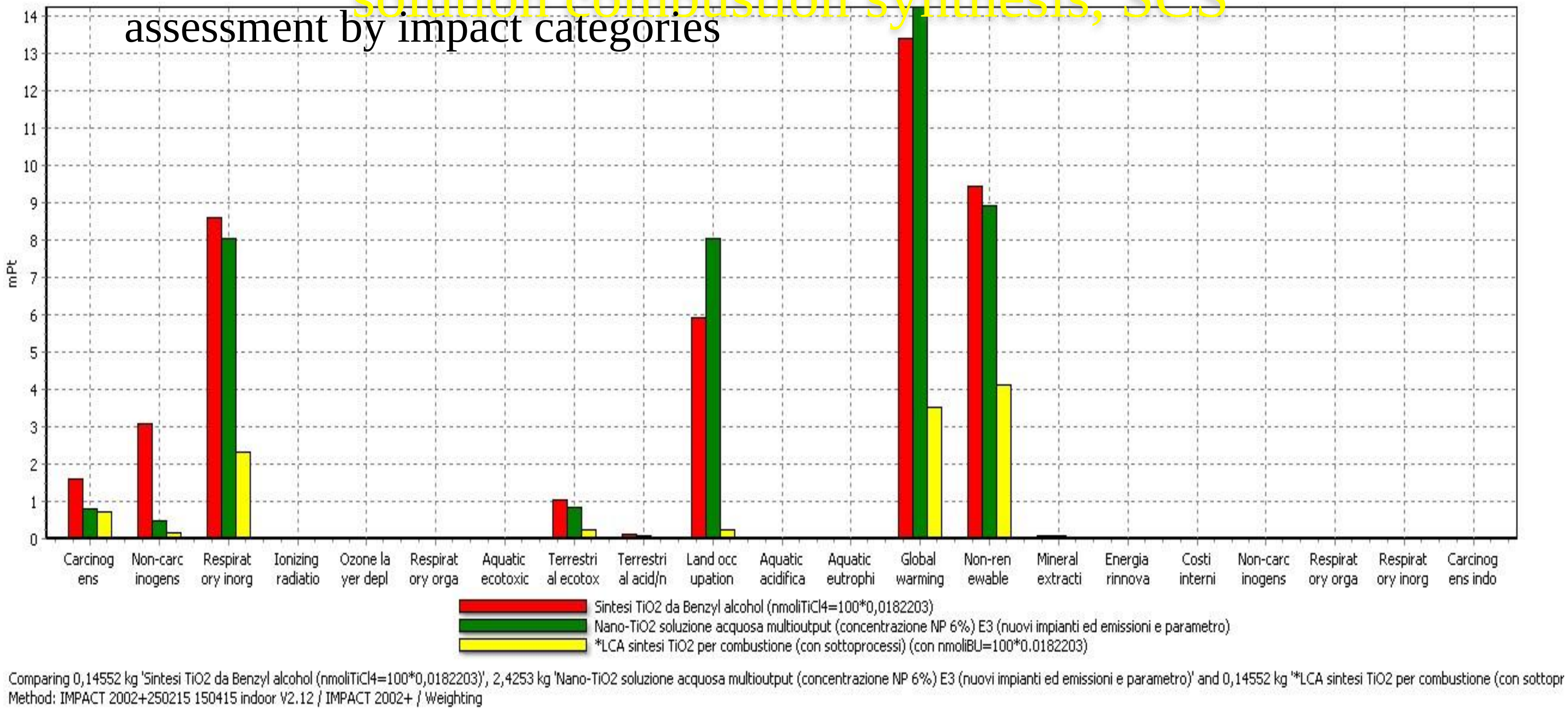
example of the Cradle to the Grave system boundaries…..(HSG)



LCA results

non hydrolytic sol gel synthesis, NHSG (benzyl alcohol)
hydrolytic sol-gel, HSG
solution combustion synthesis, SCS

assessment by impact categories



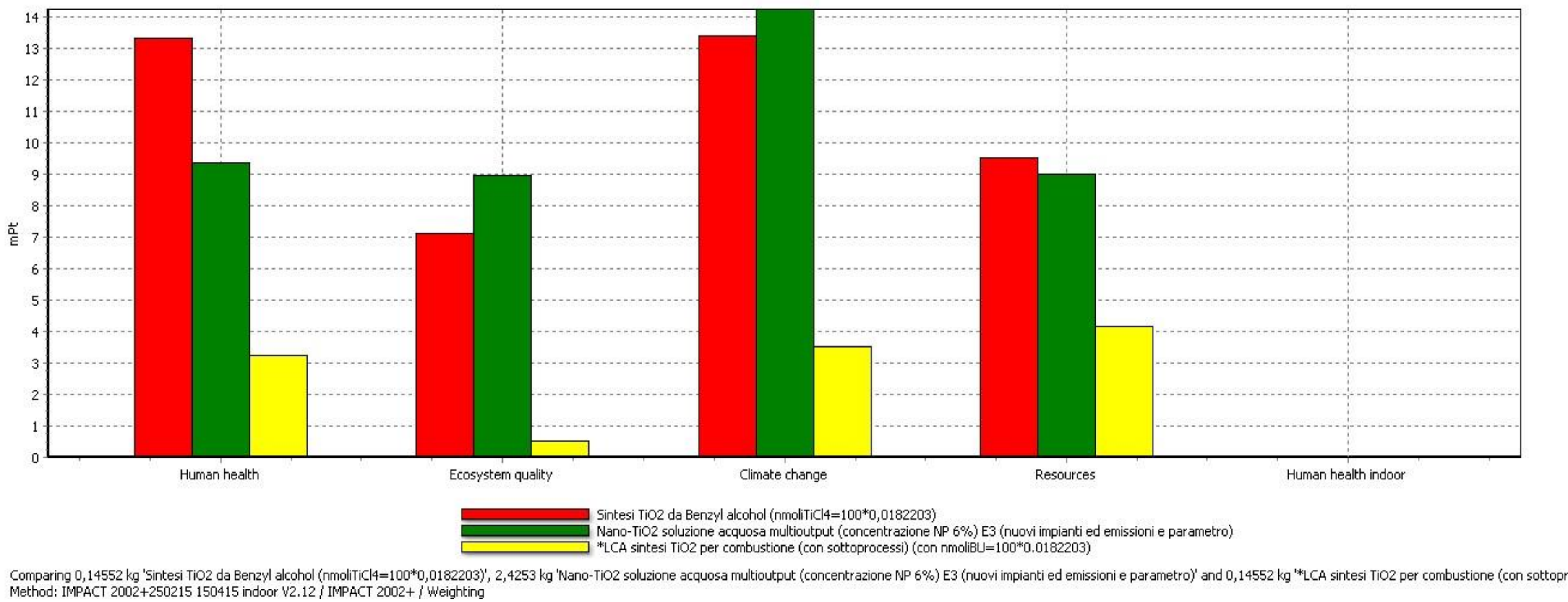
LCA results

non hydrolytic sol gel synthesis, NHSG (benzyl alcohol)

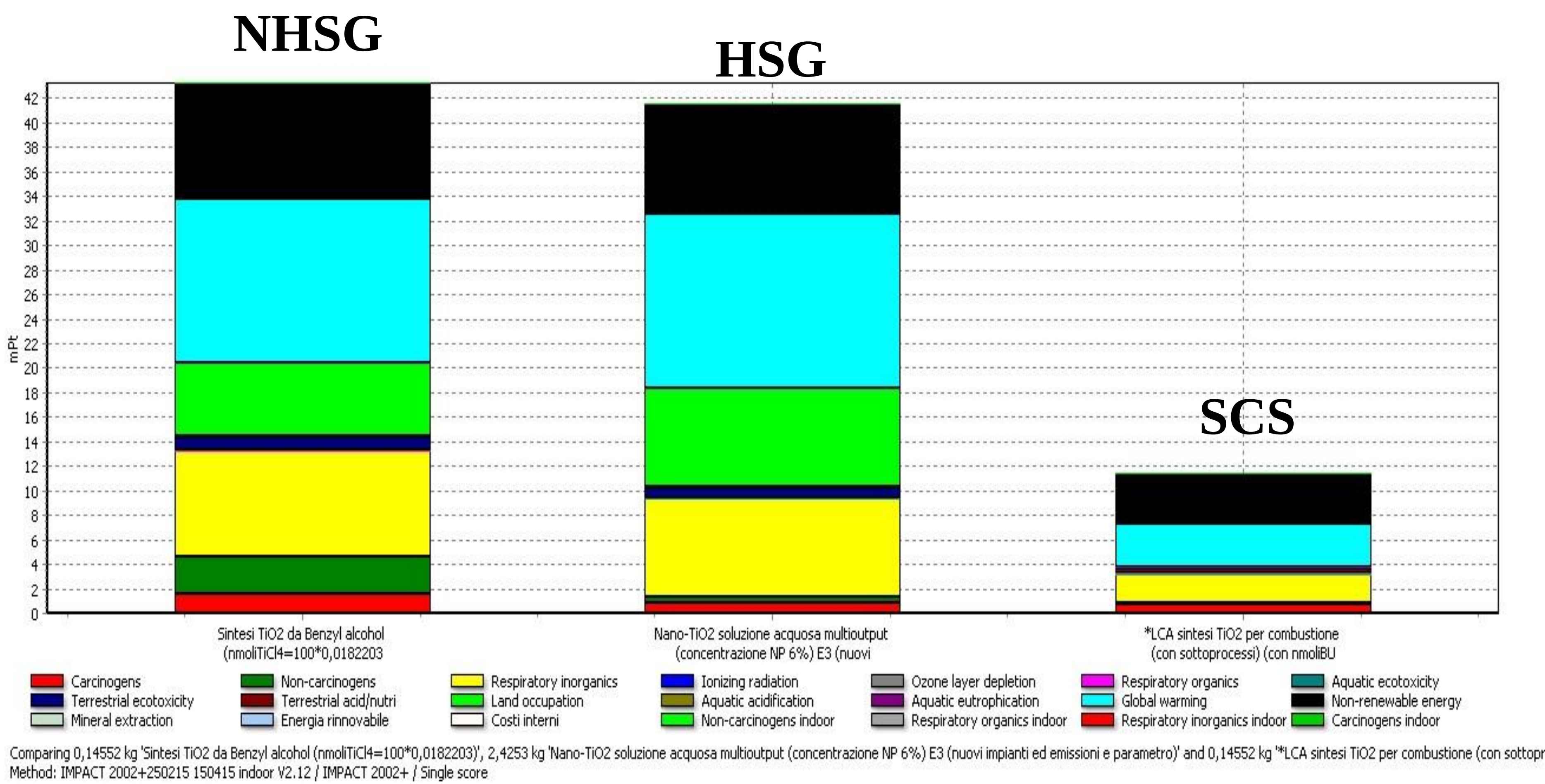
hydrolytic sol-gel, HSG

solution combustion synthesis, SCS

assessment by damage categories



LCA results


NHSG
HSG
SCS
mPt
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
Sintesi TiO2 da Benzyl alcohol (nmoliTiCl4=100*0,0182203
Nano-TiO2 soluzione acquosa multioutput (concentrazione NP 6%) E3 (nuovi
*LCA sintesi TiO2 per combustione (con sottoprocessi) (con nmoliBU
Carcinogens
Non-carcinogens
Respiratory inorganics
Ionizing radiation
Ozone layer depletion
Respiratory organics
Aquatic ecotoxicity
Terrestrial ecotoxicity
Terrestrial acid/nutri
Land occupation
Aquatic acidification
Aquatic eutrophication
Global warming
Non-renewable energy
Mineral extraction
Energia rinnovabile
Costi interni
Non-carcinogens indoor
Respiratory organics indoor
Respiratory inorganics indoor
Carcinogens indoor
Comparing 0,14552 kg 'Sintesi TiO2 da Benzyl alcohol (nmoliTiCl4=100*0,0182203)', 2,4253 kg 'Nano-TiO2 soluzione acquosa multioutput (concentrazione NP 6%) E3 (nuovi impianti ed emissioni e parametro)' and 0,14552 kg '*LCA sintesi TiO2 per combustione (con sottopr
Method: IMPACT 2002+250215 150415 indoor V2.12 / IMPACT 2002+ / Single score

Conclusions

- combine environmental assessment to a particular synthetic strategy for engineered nanomaterials can be the first step towards the sustainable development of nanotechnology

- SCS can be effectively considered a “green” synthetic procedure mainly as a consequence of its reaction rate and its low energy requirements (at least for the specific syntheses considered)

- metrics which do not account for energy, heat, time contributions can lead to un-reliable data

- environmental assessment of further synthesis (hydrothermal, solvothermal) and further ignition strategies (MWs)

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Environmental assessment of a bottom-up hydrolytic synthesis of TiO_2 nanoparticles

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A green metrics evaluation of the bottom-up hydrolytic sol–gel synthesis of titanium dioxide (TiO_2) nanoparticles has been performed by following two different approaches, namely, EATOS software and LCA methodology. Indeed, the importance of engineered nanomaterials is increasing worldwide in many high-technological applications. Due to the as yet completely un-established environment and human health impact of nano-sized materials, the possibility of at least choosing a greener synthetic strategy through an accurate comparison of detailed environmental assessments will soon be of absolute importance in both the small and large scale production of these advanced inorganic materials. The present LCA study has been carried out following an ecodesign approach, in order to limit the environmental impacts and protect human health. The results of LCA analysis suggest that the highest environmental impact is mainly due to energy and the titanium isopropoxide precursor used in the synthesis process. Concurrently, software EATOS has been employed to calculate the environmental parameters that account for the environmental and social costs related to all the chemicals involved in the analyzed synthesis. As the EATOS approach is based purely on synthetic chemical mechanism considerations, thus neglecting any energy contributions, and its results cannot be directly compared to those arising from LCA analysis. However, similar and comparable outcomes are obtained by simply neglecting the energy contributions, broadening the application fields of the combined EATOS-LCA approach to the inorganic synthesis of engineered nanomaterials, highlighting the great potential of their synergy.

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Thanks for Your kind attention

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