Integrated approach EATOS-LCA for the environmental sustainability evaluation of a bottom-up hydrolytic synthesis of TiO_2 nanoparticles

Martina Pini

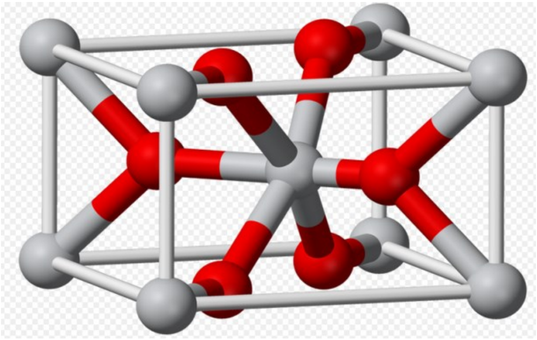
Overview of research activities

ARACNE

www.aracne.emr.it

Bando Regione Emilia Romagna "Dai distretti produttivi ai distretti tecnologici - 2" DGR n. 1631/2009

- ARACNE Italian project
  - 3 companies of Emilia-Romagna region
  - University of Modena and Reggio Emilia
  - University of Bologna
- Aim: study new and eco-friendly building materials with higher technological properties obtained by the addition of nano-TiO_2



EATOS & LCA (1)

- The synthesis of nanomaterials is currently one of the main research areas of inorganic chemistry and materials science.
- No completely environment and human health impacts of nano-sized materials have been still established.

a greener synthetic strategy of nanoparticles through an environmental assessments is important to be developed.

EATOS & LCA (2)

COLOROBBIA®

COLOROBBIA - US 2008/0317959 A1, Dec. 25, 2008.
Method for preparation of aqueous dispersion of TiO_2 in the form nanoparticles, and dispersions obtainable with this method. Inventors: Baldi G. et al.

A green metrics evaluation of the
bottom-up hydrolytic sol-gel synthesis of nano-TiO_2
has been performed following:

EATOS software and LCA methodology

<u>Publication</u>

Pini M., Rosa R., Neri P., Bondioli F. and Ferrari A.M. (2015) Environmental assessment of a bottom-up hydrolytic synthesis of TiO_2 nanoparticles, Green Chem., 17 (1), 518 – 531.

EATOS vs LCA

Software EATOS (Environmental Assessment tool for Organic Synthesis)	Metodologia LCA (Life Cycle Assessment)
➢ immediate ➢ user friendly data ➢ no energy consumptions and emissions ➢ free of charge	➢ complex and detailed ➢ data not always available in the LCA software Database ➢ energy consumptions, transport, distribution, emissions, waste materials, end of life treatment ➢ from cradle to grave ➢ it requires expensive software (SimaPro software)

The hydrolytic sol-gel synthesis of nano-TiO_2

$$Ti(OiPr)_4 + 4H_2O \rightarrow TiO_2 + 2H_2O + 4iPrOH$$

The reaction mechanism involving subsequent hydrolysis and condensation reactions:

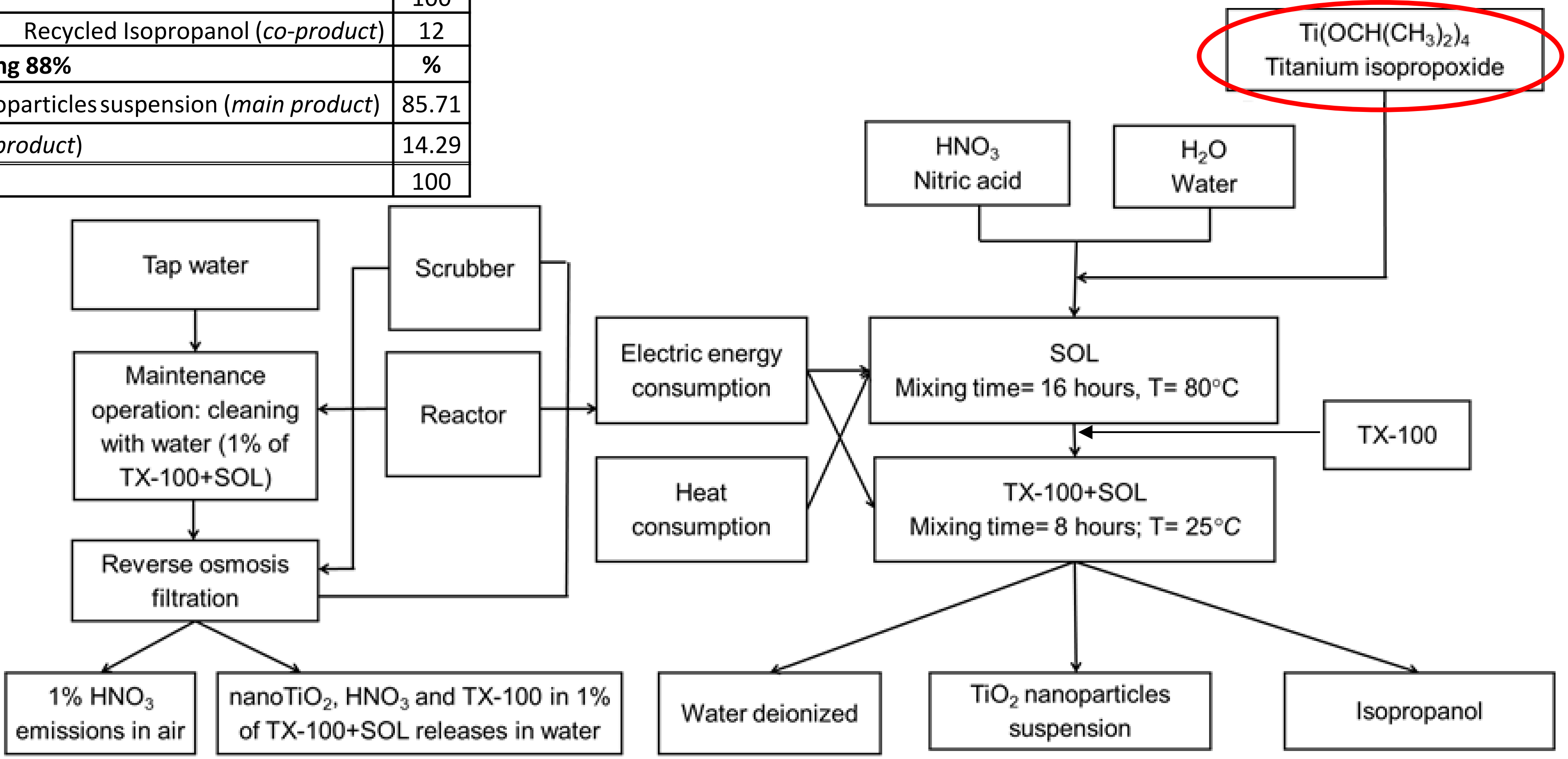
$$Ti(OiPr)_4 + nH_2O \rightarrow Ti(OiPr)_{4-n}(OH)_n + niPrOH$$

$$\equiv Ti\text{-}OH + HO\text{-}Ti\equiv \rightarrow \equiv Ti\text{-}O\text{-}Ti\equiv + H_2O$$

$$\equiv Ti\text{-}OiPr + HO\text{-}Ti\equiv \rightarrow \equiv Ti\text{-}O\text{-}Ti\equiv + iPrOH$$

Flow chart of hydrolytic sol-gel synthesis of nano-TiO_2

Chemicals	**wt%**
Titanium isopropoxide	23.22
Water	73.40
Nitric acid 63%	2.38
Triton X-100	1
Total	100
Recycled Isopropanol (*co-product*)	12
Remaining 88%	**%**
TiO_2 nanoparticles suspension (*main product*)	85.71
H_2O (*co-product*)	14.29
Total	100



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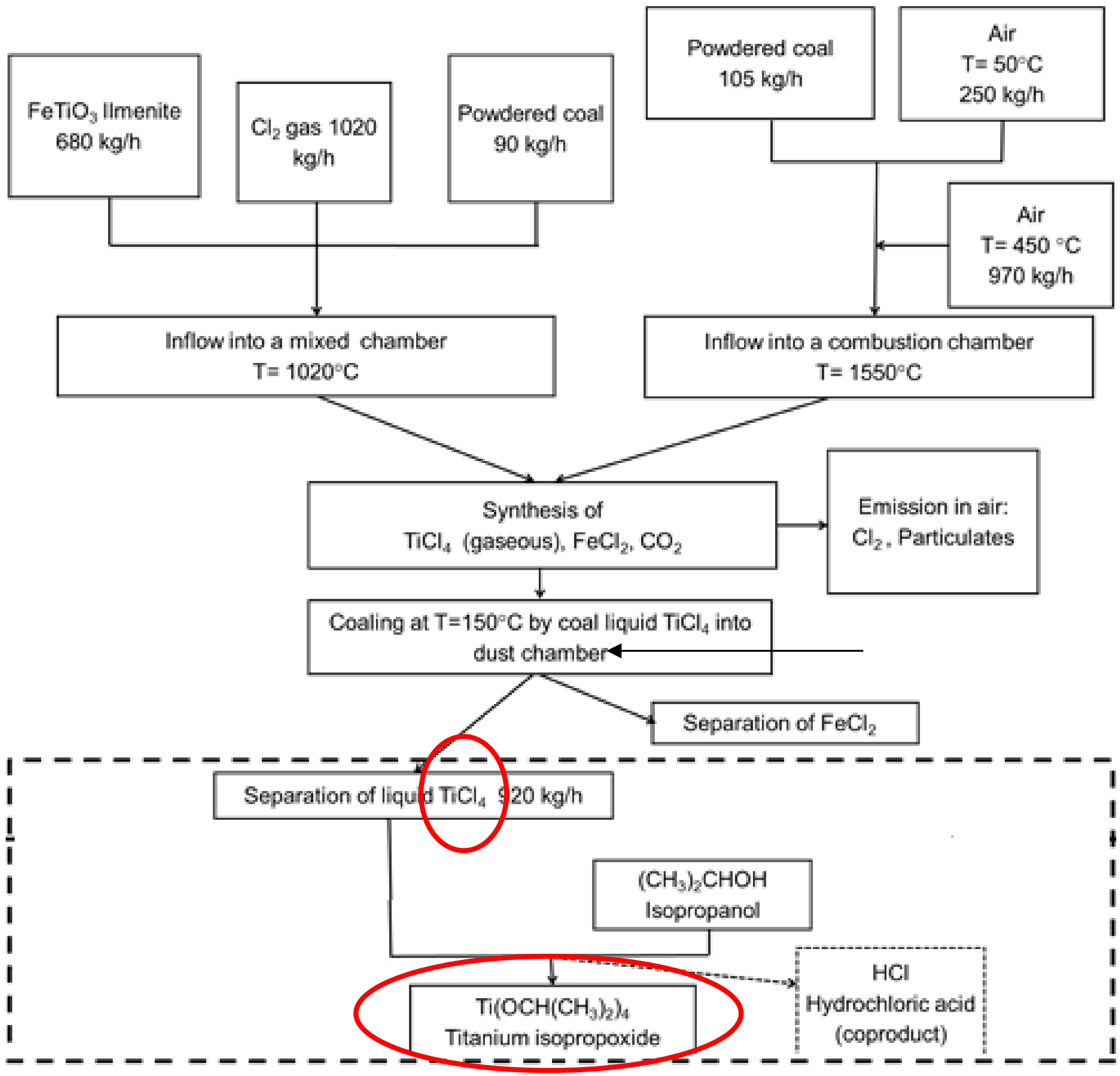
Flow chart of Titanium Isopropoxide



Method for preparatio

Life cycle assessment (LCA)

- Goal definition: assess the environmental impacts of the nanoTiO_2 suspension obtained by a liquid-phase process.
- Functional unit: multi output process

Products	UF	Unit	Mass allocation
Nano TiO_2 suspension	0.75425=1kg*88%*85.71%	kg	75.425%
Coproduct			
Isopropanol	0.12=1kg*12%	kg	12%
H_2O deionized	0.12575=1kg*88%*14.29%	kg	12.575%

- Function of the system: functionalizing building materials.
- System boundaries: *"from cradle to gate"*.
- Data quality: primary data and secondary data (literature and DB data).
- Calculation software: SimaPro 7.3.3
- LCIA method: modified IMPACT 2002+

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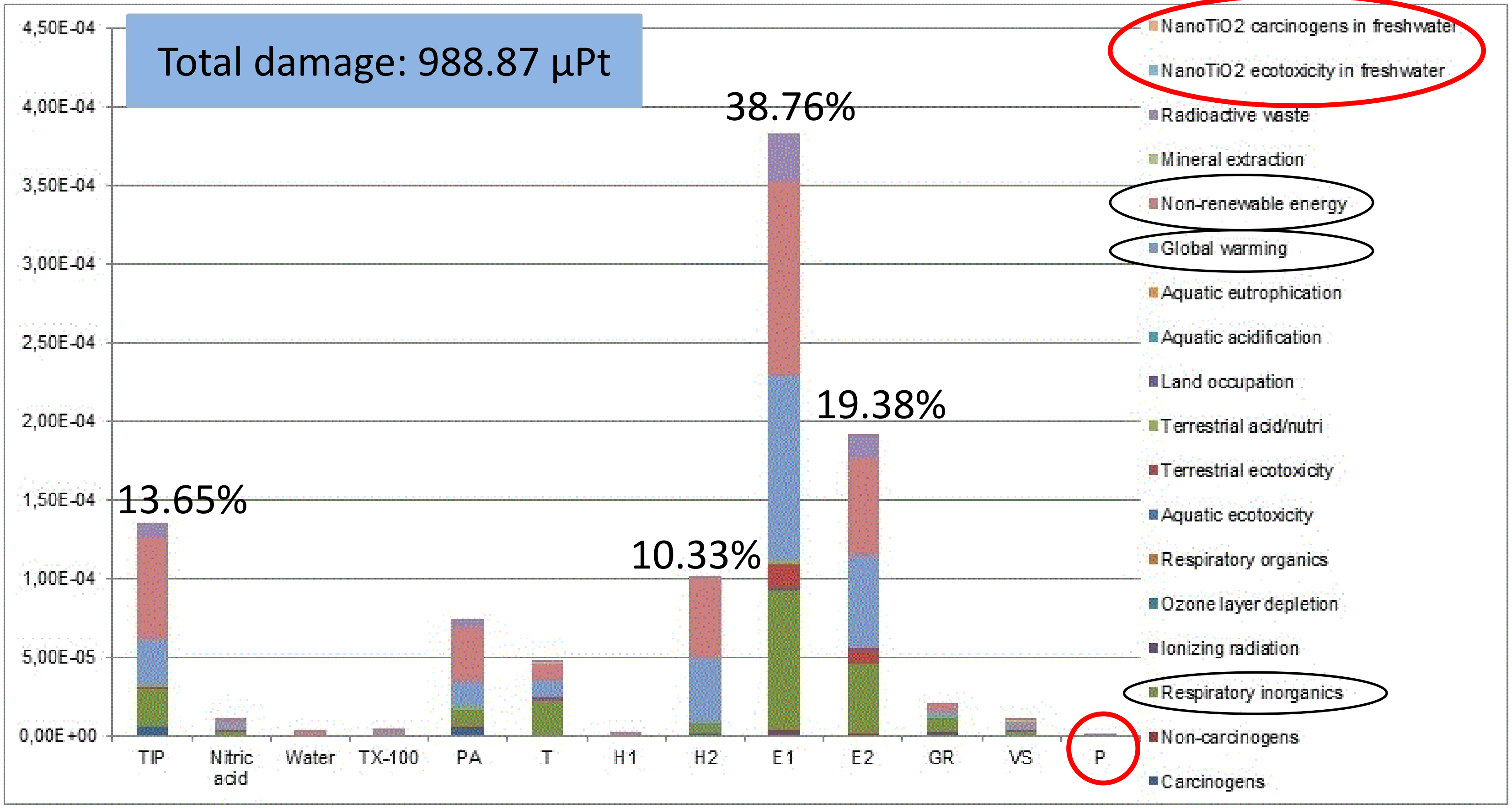
- Land use: basic indicators of transformation
- Mineral extraction: additional resources (*silver, gravel, sand, lithium, bromine and water*)
- Radioactive waste category was added. Waste and its occupied volume have been evaluated.
- Toxicity of TiO_2 nanoparticles released in water on:
    - ✓ freshwater ecosystem (*Salieri B., Righi S., Pasteris A., Olsen S.I. " Freshwater ecotoxicity characterisation factor for metal oxide nanoparticles: A case study on titanium dioxide nanoparticle", Sci. Total Environ., 2015, 505:494–502. DOI: 10.1016/j.scitotenv.2014.09.107*)
    - ✓ human health (*Pini M., Neri P., Montecchi R., Ferrari A.M., "Life Cycle Assessment of nanoTiO2 functionalized porcelainized stoneware tiles", 247th ACS National Meeting & Exposition, Dallas, Texas, March 16-20, 2014*)

LCIA results of 1kg of nano-TiO_2 suspension



TIP = titanium isopropoxide; **TX-100** = Triton X-100; **PA** = packaging of raw materials; **T** = transport of raw materials; **H1** = heat to warm up the solution at 80 °C; **H2** = heat to maintain the solution at 80 °C; **E1** = electric energy to mix the sol for 16 hours; **E2** = electric energy to mix the sol and TX-100 for 8 hours; **GR** = glass reactor; **VS** = vacuum system; **P** = water purification

EATOS calculation

Performed by Roberto Rosa (roberto.rosa@unimore.it)

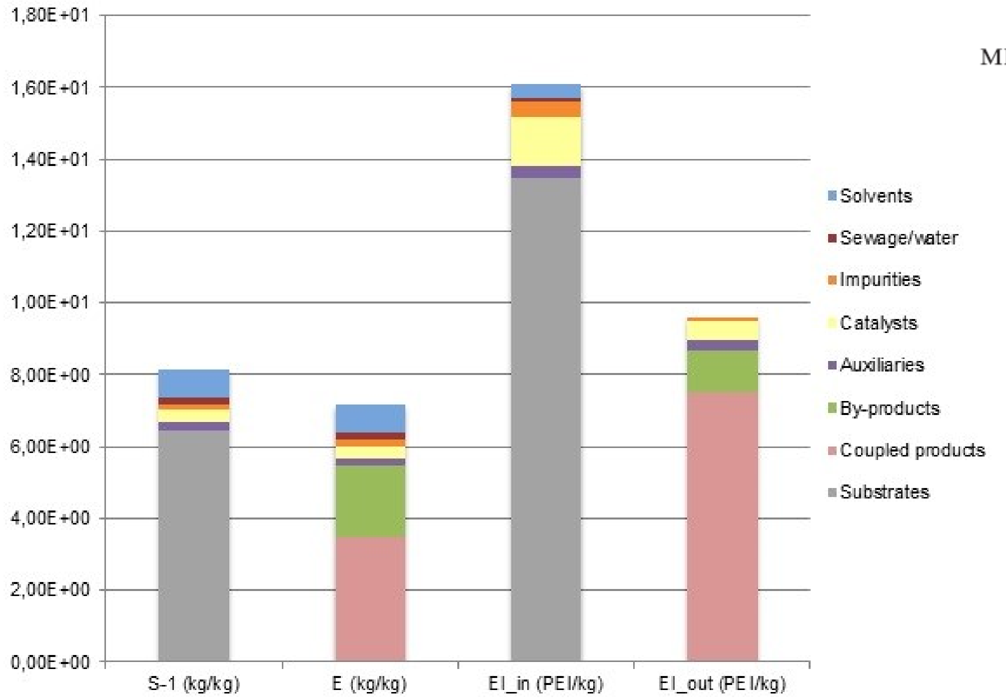
- List of the product and coupled products considered in the EATOS environmental assessment.

Substance	Category	Molecular weight (g mol^{-1})	Quantity (g)
$Ti(OiPr)_4$	Key substrate	284.2308	232.2
H_2O	Substrate	18.0152	58.87
H_2O	Solvent	18.0152	675.13 (recyclable quantity = 100%)
HNO_3, 63%	Catalyst	63.0128	23.8
Triton X-100	Auxiliary material	646.8572	10

- List of starting substances used for the EATOS environmental assessment of the hydrolytic sol-gel synthesis of TiO_2 nanoparticles.

Substance	Category	Molecular weight (g mol^{-1})	Useful quantity (% or g)	Yield (%), referred to the key substrate
TiO_2	Product	79.8788	—	69.34
H_2O	Coupled product	18.0152	69.34%	—
C_3H_8O	Coupled product	60.0956	120 g	—

EATOS results



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

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

EATOS software allows you to calculate four environmental parameters:

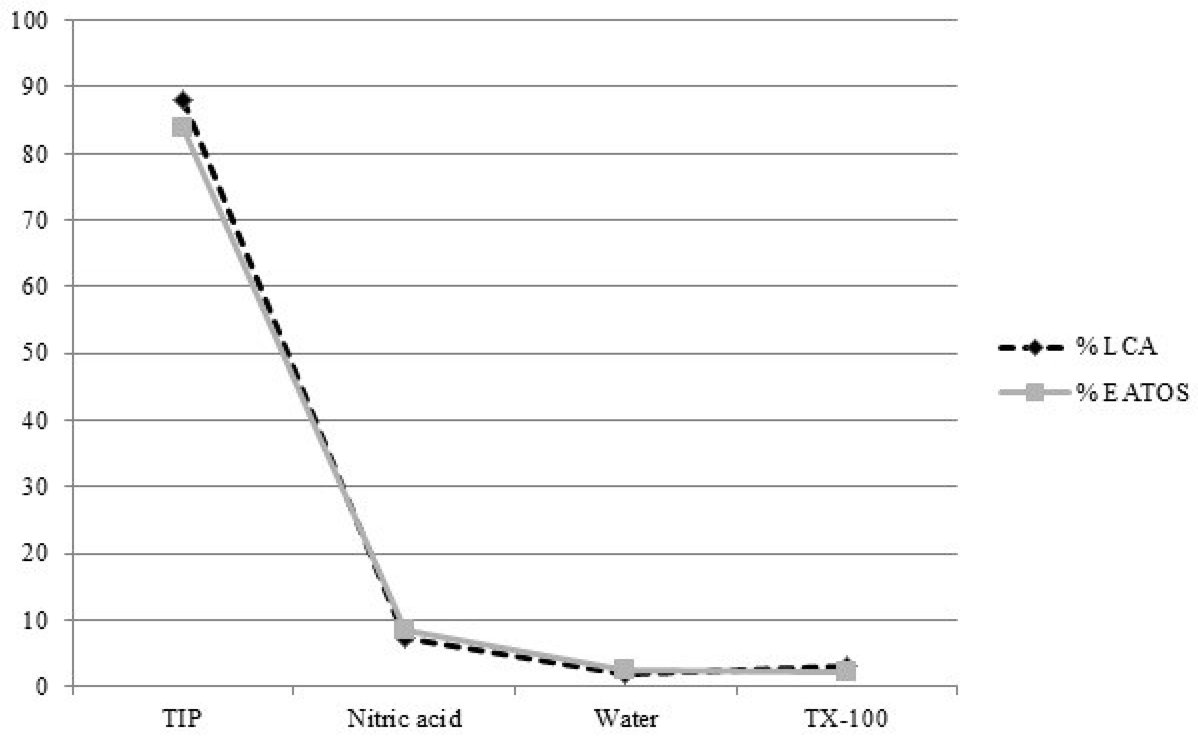
1. mass index [MI] (S-1)
2. impact factor E
3. EI_In
4. EI_out

(3–4) Corresponding to MI and E, but weighted on a specific risk category *(human toxicity, ecotoxicology, ozone creation, air pollution, degradability, greenhouse effect, etc.)*

Category	Substance	S^{-1} (kg of starting material/kg of product)	E (kg of waste/ kg of product)	EI_in (PEI kg^{-1})	EI_out (PEI kg^{-1})
Substrates	Titanium isopropoxide and water	6.4728	0.0402	13.4997	—
Coupled products	Isopropanol and water	—	3.4604	—	7.5233
By-products	Unspecified	—	1.9723	—	1.18
Auxiliaries	Triton X-100	0.2278	0.2278	0.3418	0.2848
Catalysts	Nitric acid	0.3416	0.3416	1.3665	0.5124
Impurities	Unspecified	0.1587	0.1587	0.3968	0.119
Sewage/water	Water + unspecified	0.2006	0.2006	0.1003	—
Solvents	Water	0.7691	0.7691	0.3845	—
Total		8.1706	7.1707	16.0896	9.6195

EATOS and LCA results comparison

-excluding energy consumptions and transports-



Conclusions

- The environmental assessment of the bottom-up hydrolytic sol–gel synthesis of nano-TiO_2 was concurrently performed by the software EATOS and by LCA methodology → similar conclusions.
- The present work represents the first example in which the synergy between LCA methodology and EATOS software has been applied to a green metrics evaluation of the inorganic synthesis of nanoparticles.
- The LCA results showed that most environmental loads are generated by the total electric energy consumption (58.14%), followed by TIP (13.65%) and heat consumption (10.33%).
- A better environmental performance can be achieved by the following:
  - *using renewable energy sources (e.g. solar power, geothermal, biomass, etc.);*
  - *using microwave dielectric heating of reaction mixture;*
  - *substituting titanium tetraisopropoxide with a different metal oxide precursor.*
- The main conclusion is to always combine an environmental assessment with any new proposed strategy for the synthesis of nanoparticles, so that the strict requirement of using the most environmentally friendly procedure could very soon accompany traditional requests of a desired size and shape.

Grazie per l’attenzione

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