CONAMA 2018
CONGRESO NACIONAL DEL MEDIO AMBIENTE

GRUPO ANTOLIN INGENIERIA

RUMBO 20.30.

Congreso Nacional del Medio Ambiente
Madrid del 26 al 29 de noviembre de 2018

SAFE BY DESIGN, NANOREG2 PROJECT

GRUPO ANTOLIN INGENIERÍA, SA
ACM Advanced Carbon Materials

NanoReG2

Project #646221, Funded by the Horizon 2020 Framework Programme of the European Union

Dr. César Merino Sánchez
GT-14 Oportunidades y retos de los nanomateriales
#conama2018

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03 NANOREG2 OBJECTIVES

04 ACM SbD CASE STUDY

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01 GRUPO ANTOLIN

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GRUPO ANTOLIN

Talent

28,000 individuals drive us direct to success

Financial Strength

2017 annual sales of 5,037 million euros

Global Presence

151 production plants and centers Just in Time across 25 countries

Innovation

We innovate today to obtain a sustainable future for the automobile

BU

Overheads
Doors
Lighting
Cockpits

NanoReg2

Project #646221, Funded by the Horizon 2020 Framework Programme of the European Union

GRUPO ANTOLIN

Overheads & Trunk Trim BU

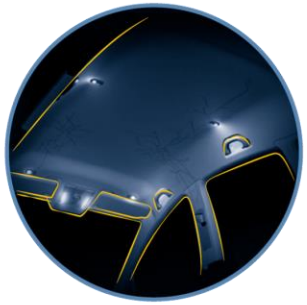
- Modular headliner
- Substrate
- Sunvisors
- Lighted headliner
- Trunk Trim

Number 1 Worldwide

Doors & Hard Trim BU

- Carrier solutions
- Door panels
- Window regulators
- Mechanisms

Multi-Technological Offer



Lighting BU

- Complete solutions
- Interior:
  - Functional
  - Mood lighting
- Exterior

Leading ambient lighting supplier

Cockpits & Consoles BU

- Cockpits
- Instrument panels
- Central console

We Improve Life on Board

NanoReG2

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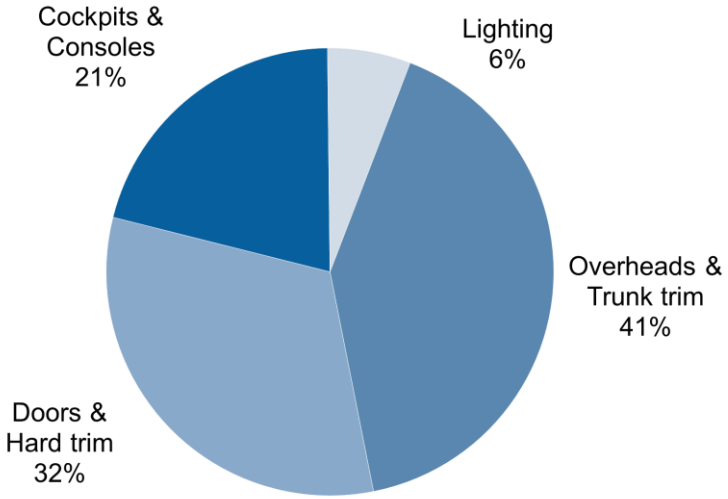
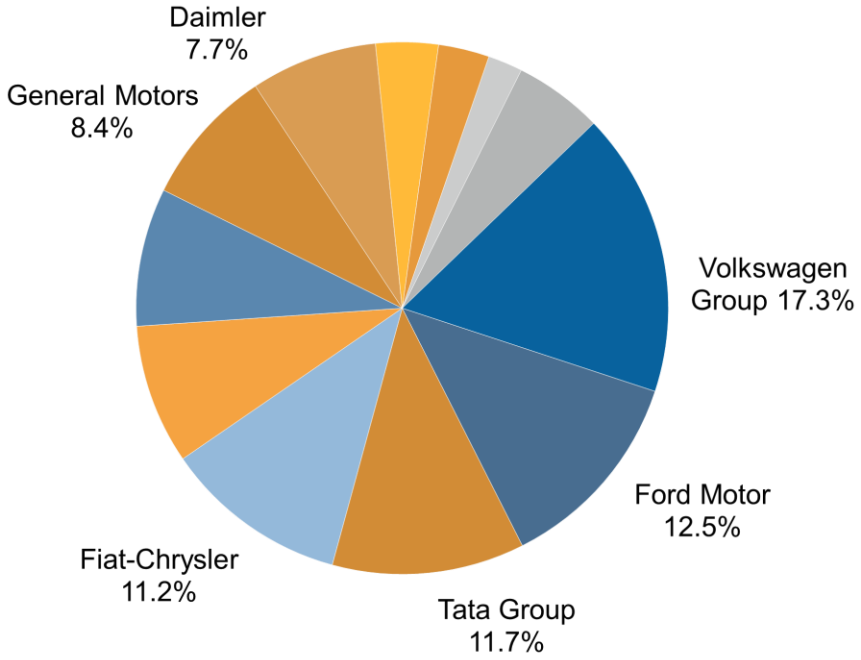
GRUPO ANTOLIN





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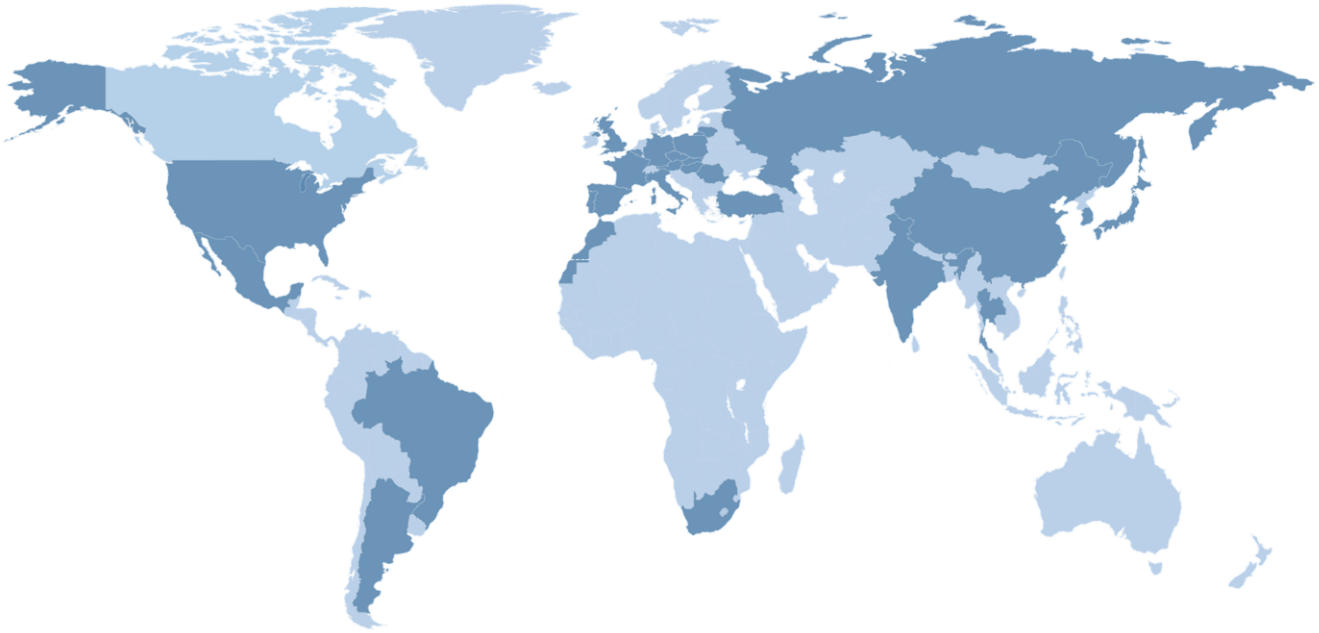
GRUPO ANTOLIN



25 Countries

Spain
Argentina
Austria
Brazil
China
Czech Republic
France
Germany
Hungary
India
Italy
Japan
Mexico
Morocco
Poland
Portugal
Romania
Russia
Slovakia
South Africa
South Korea
Thailand
Turkey
United Kingdom
United States

Grupo Antolin is present in 9 of the top 10 best selling cars in the world

NanoReg2

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GRUPO ANTOLIN

Materials & Processes

Focused mainly on weight reduction to minimize CO_2 emissions and the use of green materials (recyclable/recycled)

Industrial flexibility

Innovative processes to produce different functions. Adapting to meet evolving market demands with minimum investment

Smart Interiors

Supporting our customers' brand strategy is key to end user experience and perceived quality based on customization

Innovative solutions

NanoReG2

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02 ACM Advanced Carbon Materials

NanoReg2

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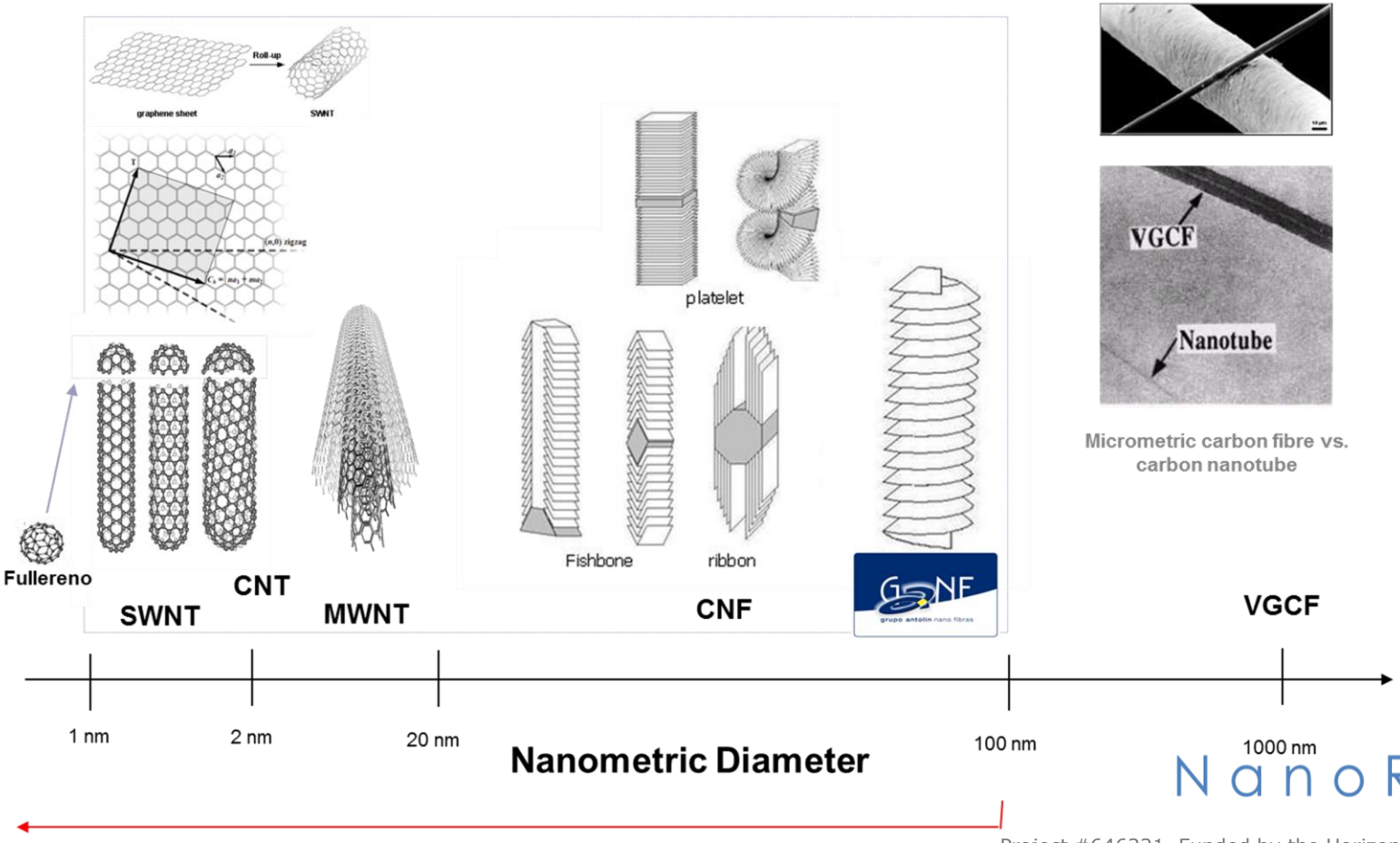
GRAPHITIC NANOFILAMENTS AND GRAPHENE



Human hair diameter vs. micrometric carbon fibre

Micrometric carbon fibre vs. carbon nanotube

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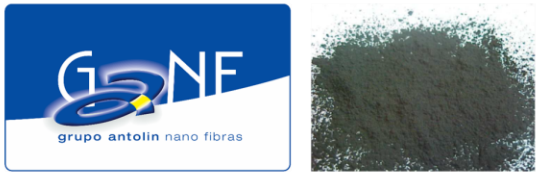
ACM ADVANCED CARBON MATERIALS

- **Grupo Antolin was the first European producer of carbon nanofibers at industrial scale using the continuous production process known as "floating catalyst technique". Trade mark GANF®, since 2004.**



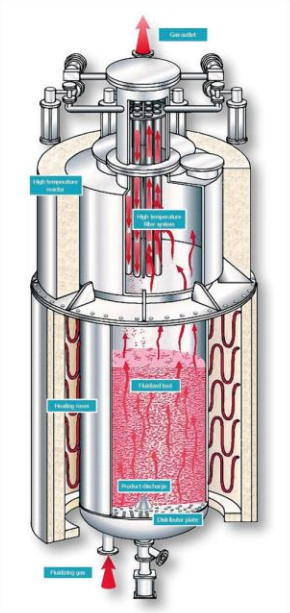
- **Grupo Antolin division of Advanced Carbon Materials provides high quality graphene products for high-tech applications since 2010. Trade mark GRAnPH®.**

- **ACM technologies are protected by 8 patents: Production process of graphene, reduced graphene oxide and graphene oxide obtained from GANF. Carbon nanofiber production and tailoring for different applications.**

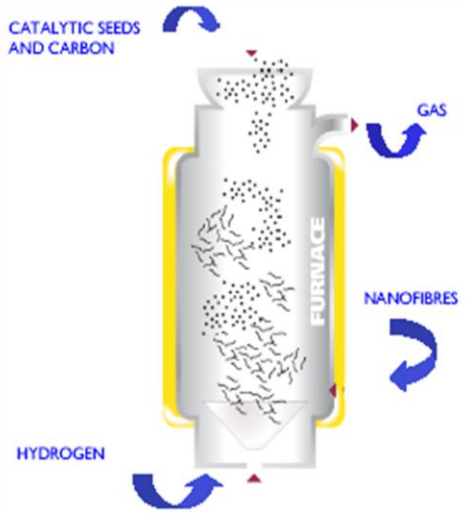
CONTINUOUS PRODUCTION OF CARBON NANOFILAMENTS

- There are mainly two technologies for industrial production of carbon nanotubes and nanofibres:

Fluidized bed substrate



Floating catalyst technique

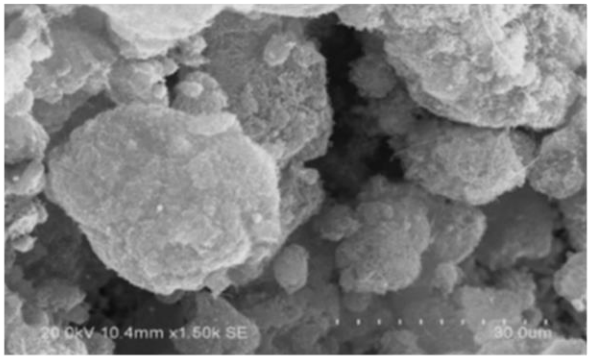


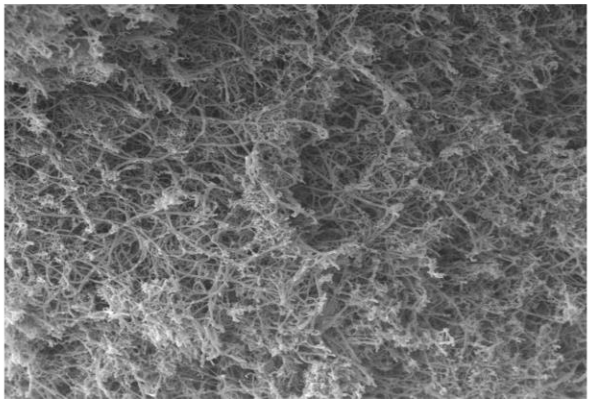
The floating catalyst technique needs shorter reaction times

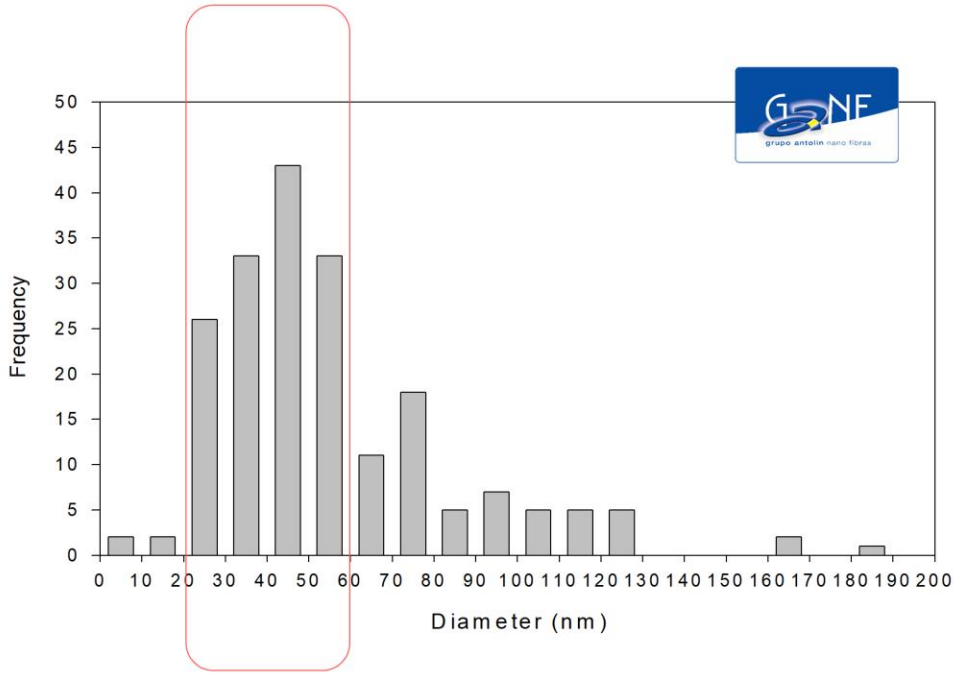
ACM avoids parallel non-catalytic reactions: Soot formation and filaments thickening

ACM CARBON NANOFIBRES

- **GA is the only producer using the floating catalyst using a Ni compound: Homogeneous product and repetitive process.**

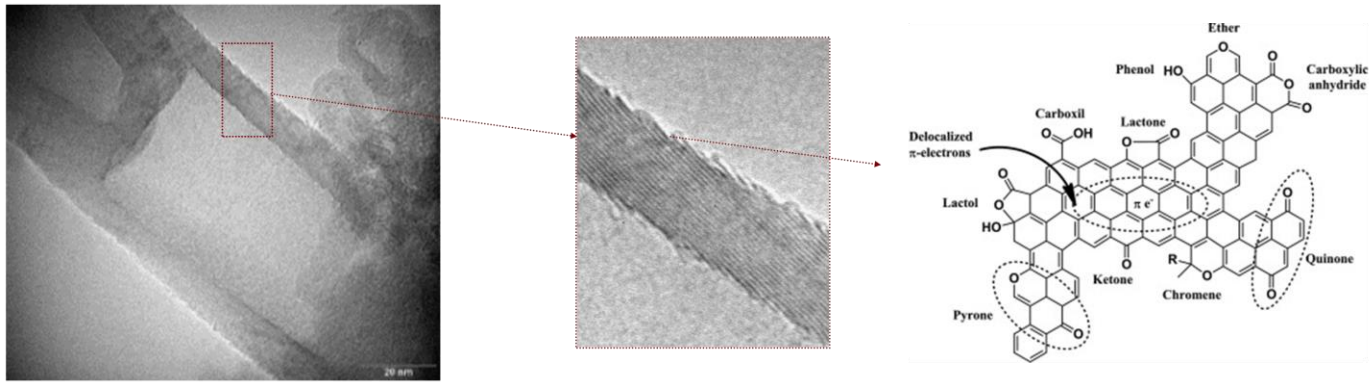


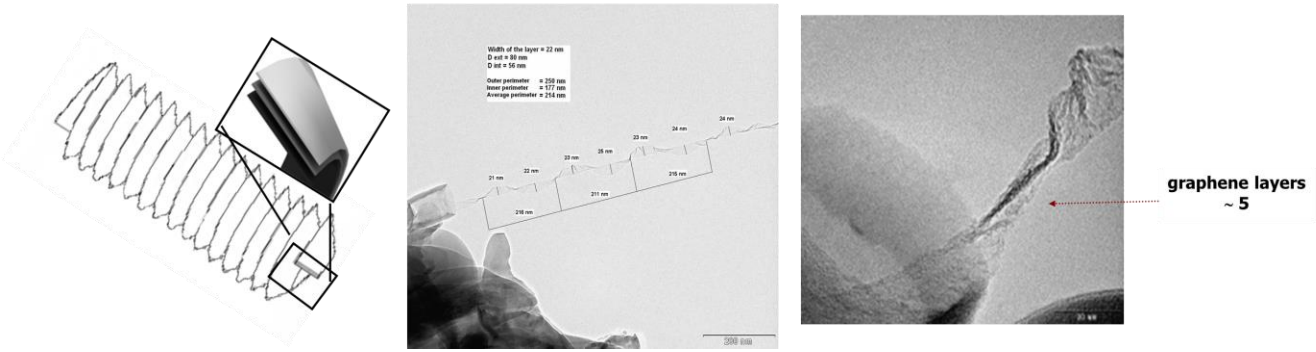




ACM CARBON NANOFIBRES

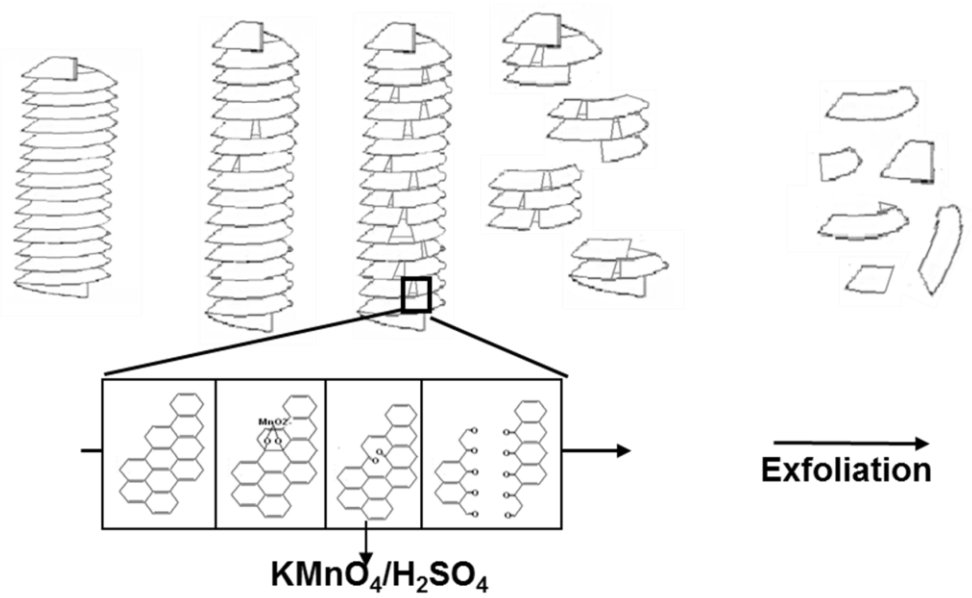
- **Good chemical interaction with functional groups from polymers due to the graphitic structure and their surface chemical groups.**

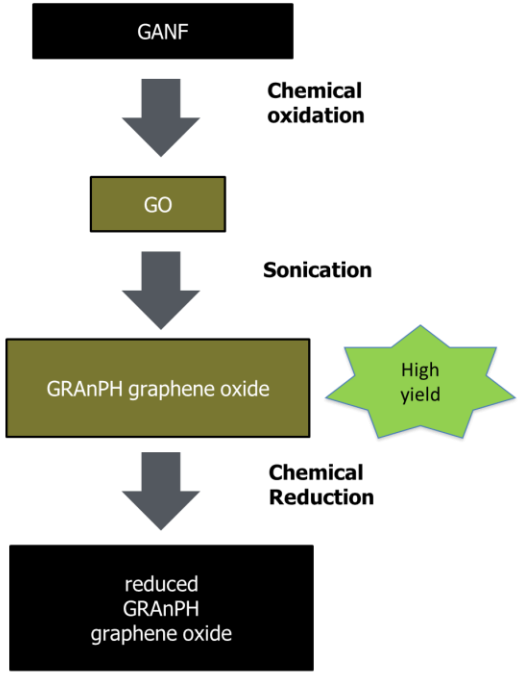




ACM GRAPHENE OXIDE

- **Chemical oxidation (unzipping and fragmenting) + sonication (exfoliation of GO sheets in liquid media).**

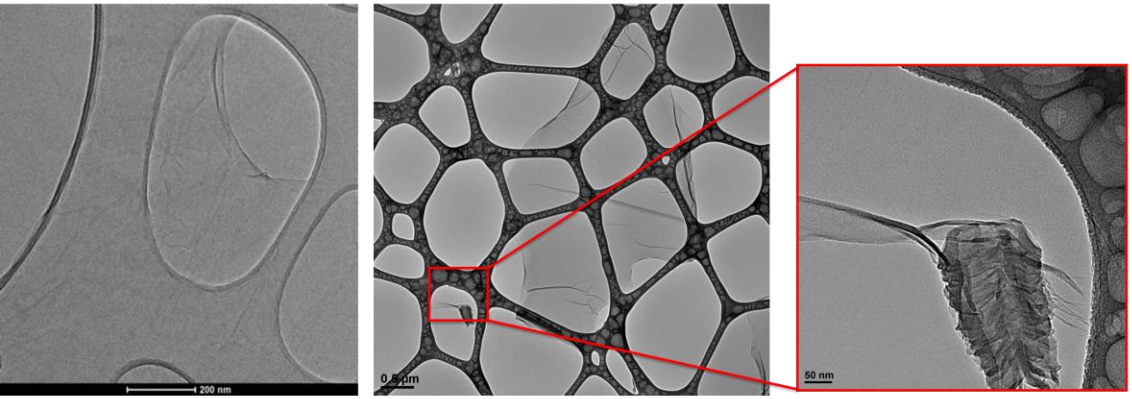




- **Main advantages versus GO obtained from graphite:**
  - **High purity and reproducibility.**
  - **Production of mainly single and few layers graphene oxide sheets.**

ACM GRAPHENE OXIDE

- **GANF as precursor obtaining graphene oxide sheets with singular properties:**
  - **Different crystallinity, lateral size and functional groups than standard graphene oxide obtained from graphite.**



	GRAnPH®	GO (Graphite)
UV-Vis	λ_{max}=235nm	λ_{max}=230 nm
XPS	60% C-C 26% C-O 14% C=O	49% C-C 45% C-O 6% C=O
XRD	$d_{(002)}$=0.77 nm	$d_{(002)}$=1.02 nm
Raman	I_D/I_G = 1.03	I_D/I_G = 1.4

DISPERSION: INTERMEDIATE PRODUCTS

- Grupo Antolin has developed different dispersion technologies for achieving good dispersion of GANF and GRAnPH in some composite end products.
- Most of our sales are intermediate products.
- Easier to use by customers and higher added value for ACM.

GAcomp

- Polymers doped with GANF or GRAnPH.
- Applications related to automotive, sports, aeronautics, etc.

IQNet
THE INTERNATIONAL CERTIFICATION NETWORK
CERTIFICATE
ISO 9001:2008

GAqUA

- Dispersions of GANF in water.
- Applications related to water based systems such as adhesives, etc.

THERMOSET HIERARCHICAL COMPOSITE PRODUCTS

- **Paddle tennis rackets production in series by hand lamination of epoxy resin with different reinforcing fabrics. Collaboration with highly recognized paddle rackets producers.**

- **Formulation and processing of prepregs for automotive bodyworks or sports equipment production.**

THERMOSET HIERARCHICAL COMPOSITE PRODUCTS

Graphene Flagship: Airbus, Aernnova, UC3M, GA

- **Leading edge Horizontal Tail Plane – Made of epoxy/carbon fibre composite.**
- **Target: integration of GRM in the Leading Edge in order to improve their mechanical performance – impact resistance → demonstration in full scale part.**

THERMOSET HIERARCHICAL COMPOSITE PRODUCTS

Headliners functionalized by GRMs

Current commercial application: Headliners using bio-based polyurethane.

- **July, 2016. Grupo Antolin has developed and gained type-approval the first automotive headliner on the market to feature graphenic material.**
- **This breakthrough generates a microstructure that is more resistant (20% more stiffness than conventional materials), lighter (between 25% and 40% depending on the technology it is compared with), and additionally reduces environmental impact.**
- **The product also uses a new system of low density vegetable origin polyurethane foam, formulated with up to 3 times more vegetable oil compared to other green foams on the market. In this case, vegetable oils make up more than 15% of it by weight.**

03 NANOREG2 OBJECTIVES

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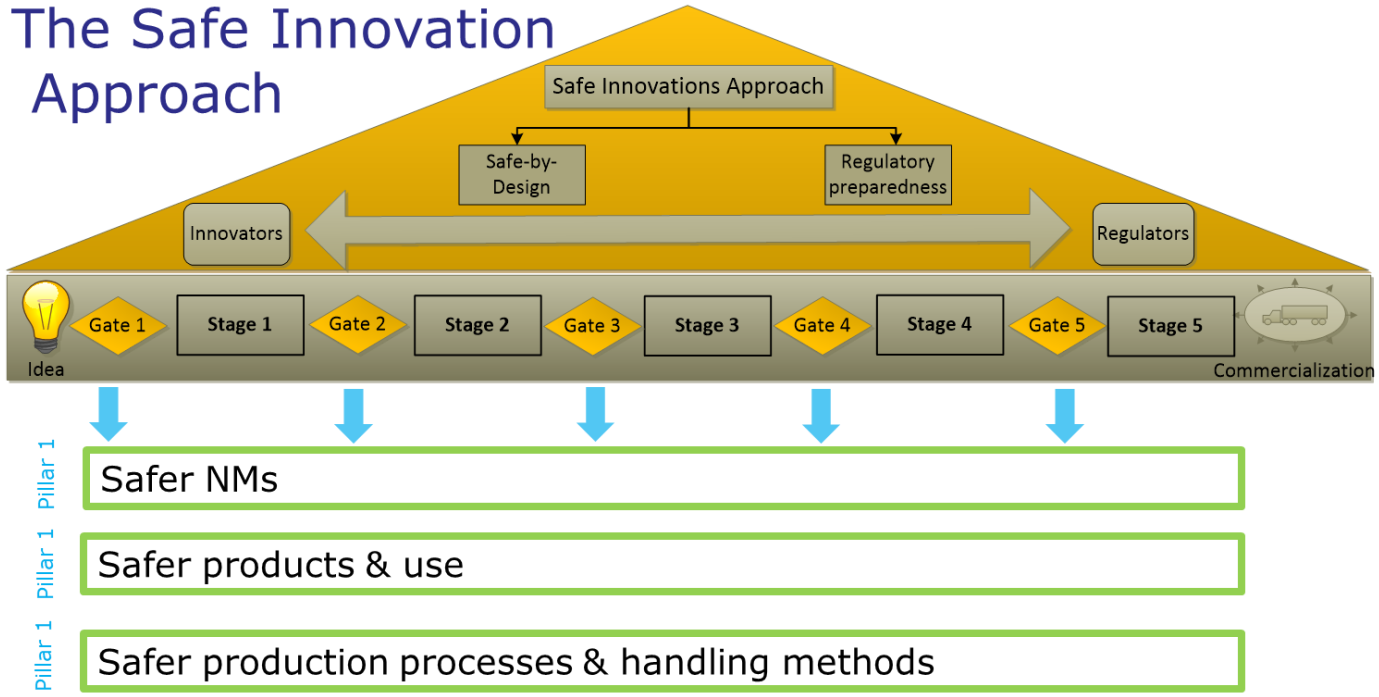
NANOREG2 OBJECTIVES

The challenge is to build a **regulatory system** which is **flexible enough** to be able **to deal** with new targets and **requirements in the future.**

This can be helped by the introduction of Safe by Design (**SbD**) principles **in the innovation process in a cost effective** and rapid **manner**.

- **Safer NMs, products & processes**
- **Efficient innovation process**
- **Faster to market**
- **Knowledge sharing**

https://www.youtube.com/watch?v=qc9t_ISCpGI



SbD concept aims at reducing uncertainties and risks of human and environmental safety of nanotechnology, starting as early as possible during the innovation process

Regulatory preparedness: improving anticipation of regulations for innovative MNMs, their applications and potential safety issues

04 ACM SbD Case Study

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CASE STUDY OUTLINE

Descriptor	Description
Nanomaterial/s	Carbon nanofibres (CNFs): GANF, GAtam
Final Product/s	Dispersion of CNFs in polymers
Potential applications	Additive for polymeric formulations
Aim of the innovation	Scale-up of the production
Main exposed target/s (workers, consumers, environment)	Workers, environment
Scope of the application of the Safe by Design approach	To study a safe scale-up and to select the NMs (GANF or GAtam) that would be safer

CASE STUDY OUTLINE

- Risk Assessment for both NMs at different production stages. Testing needs and hot spots identified.
- Ecotox and tox of GANF and GAtam performed.
- Environmental and occupational exposure assessment before and after SbD process improvements.
- Changes in the design of the production process and cleaning operations to reduce risk (safer production).
- LCA study for the production of GANF and GAtam.

CASE STUDY: CNFs PRODUCTION STAGES

Production stages for RA

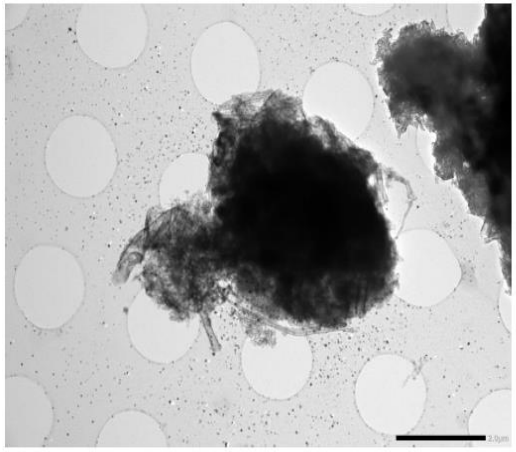
Stage 1. Metal catalyst production and dosing.
Stage 2. CNFs production: growth, filtering and collection
Stage 3. Surface treatment: Burning of volatiles and CNFs oxidation
Stage 4. CNFs dispersion in liquid media and packaging

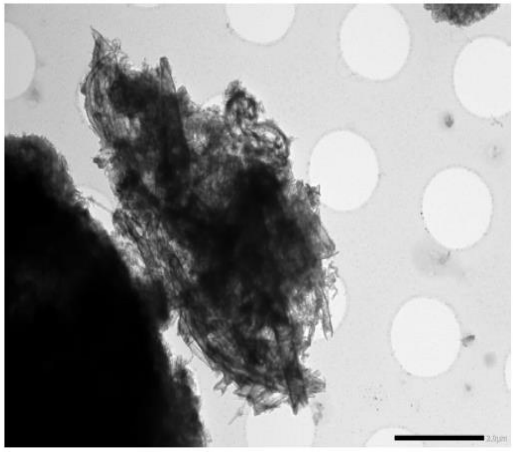
Main properties of GANF and GAtam

Measured property	Unit	GANF	GAtam
FIBRE DIAMETER (TEM)	nm	20 - 80	20-80
CARBON PURITY (TGA)	%	>85	>80
OXYGEN CONTENT	%	> 5	> 10
SPECIFIC SURFACE AREA (BET N_2)	m^2/g	100-170	70-140
GRAPHITIZATION DEGREE (XRD)	%	≈70	≈60

TEM ENVIRONMENTAL AND OCCUPATIONAL EXPOSURE RESULTS - INERIS

Sample	Sample Location
S1	1st chimney: Direct exhaust gas scrubber
S2	2nd chimney: Outside exhaust gas scrubber
S3	3rd chimney: Exit cleaning production furnace GANF
S4	4th chimney: Exit surface treatment furnace
S5	Collector: Production furnace GANF
S6	Collector: Surface treatment furnace exit
S7	HEPA filter exit: packing and dosing GANF hood
S8	Collector: Ash container cleaning production GANF
S9	Filter: Surface treatment furnace
S10	5th chimney: Exit gas analyser GANF production





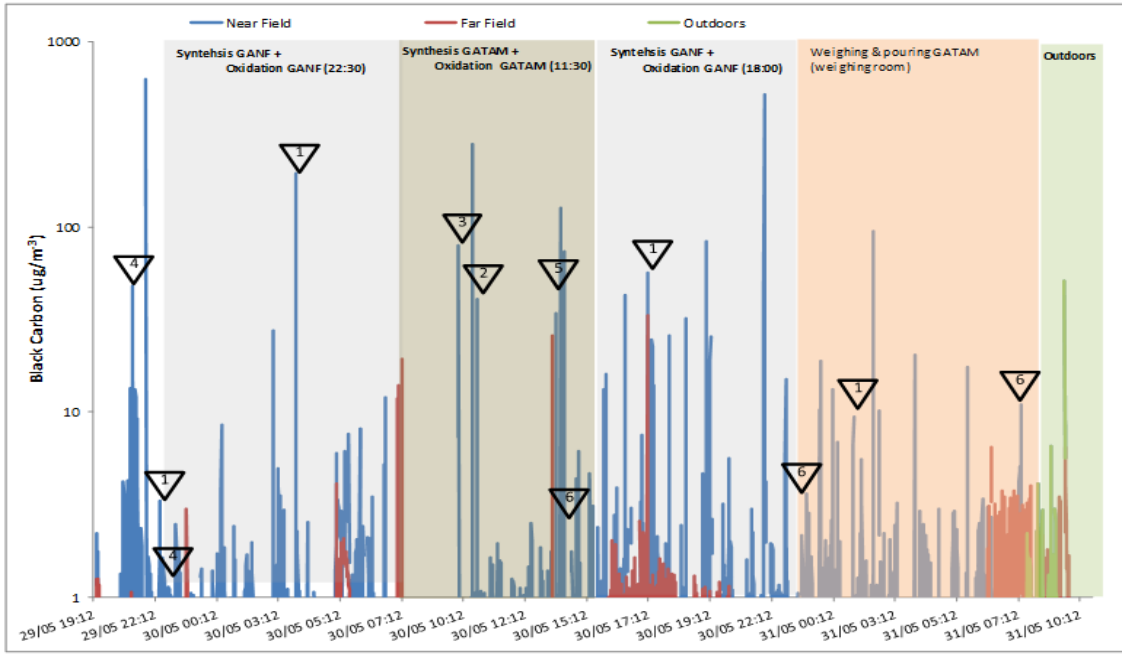
Occupational: In both cases - a low number of big (micrometric) agglomerates of tubes and rods (nanostructured) corresponding to GANF and GAtam. Nanometric nickel particles inside the agglomerates and also outside these agglomerates.
Some samples contain CNFs particles but others contains objects not clearly related.

Environmental: There is not enough NMs emitted to be able to obtain measurable concentrations in the surrounding ambient air.

OCCUPATIONAL EXPOSURE RESULTS - IOM

The synthesis of GANF and GATAM show relatively high concentrations of black carbon (Aethalometer A51) and high concentrations of particles in the range 10-300 nm with low diameters (DISCMINI).

However the samples analysed by SEM and EDX did not show single CNFs. the fibres emitted are agglomerated into large agglomerates.



Sample	Description
PC1	Middle zone in the production area
PC2	Collection of GANF
PC3	Collection of surface treated GANF
PC4	Collection of GAtam
PC5	Collection of surface treated GAtam
PC6	Filter cleaning surface treatment GAtam
PC7	Area for handling powdered CNFs
PC8	Area for preparing dispersions

PROCESS CHANGES TO IMPROVE SAFETY

Considering the occupational exposure results obtained it has been decided to consider the following SbD production process improvements:

- Automated pneumamatic collection of GAtam.
- Pneumatic collection of surface treated CNFs.
- Improve ventilation in the dispersion and powdered material handling areas.
- External centralized vacuum cleaner for maintenance operations.
- Automated gravimetric dosing unit for preparing CNFs dispersions and packaging.
- Plant layout modifications.

OTHER NANOREG2 PARTNERS CONTRIBUTIONS

- GAIKER: Technical partner. ROS, Inflammatory effects, clearance, Skin irritation. RA and LCA before and after SbD.
- NRCWE: Dustiness, Zeta potential/hydrochemical reactivity, Biopersistency, Genotoxicity.
- Univ. Utrecht: Stability (Raman, ICP-MS)
- NILU: Genotoxicity
- CEA: Cytotoxicity
- INERIS: Inhalation tox (ALI in vitro), In vivo regulatory test OECD on algae and microinvertebrates, Exposure assessment after SbD process improvements.
- INIA: Continue in vitro on fish cell lines
- UCO: Continue i*n vitro* and *in vivo* toxicity on mussels
- IOM: Exposure assessment after SbD process improvements

RISK ASSESSMENT: APPROACHES

a. The application of the control banding tools used in the screening risk assessment
   i) without and with experimental data;
   ii) before and after SbD measures implementation

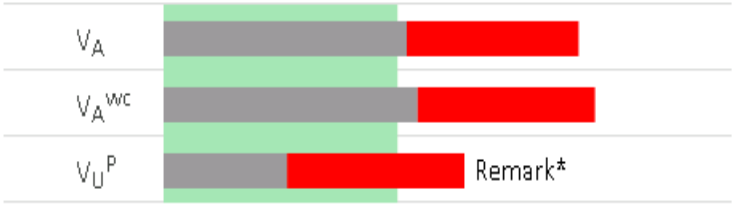
b. The application of SUNDS. It is a powerful tool to carry out a risk assessment of different scenarios (i.e. before and after SbD) but it requires the calculation of a benchmark dose (BMD), i.e. a dose of no toxic effect. Only possible with an *in vivo* assay.

c. The application of a Weight of Evidence (WoE) approach. Combines the available data (evidences) into hazard and exposure classes through a system of weights and algorithms. Weights are defined to give to each data their relevance for the risk assessment and the data quality in the integration process.

Last two approaches are being developed with the help of Greendecision, srl and colaboration with caLIBRAte project

SWISS PRECAUTIONARY MATRIX: RESULTS

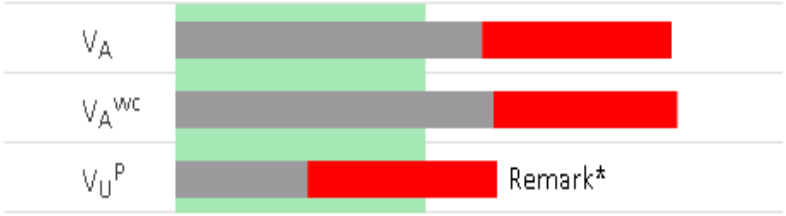
Stage 3: GANF surface treatment



* Further clarification can possibly allow these values to fall into the green zone.

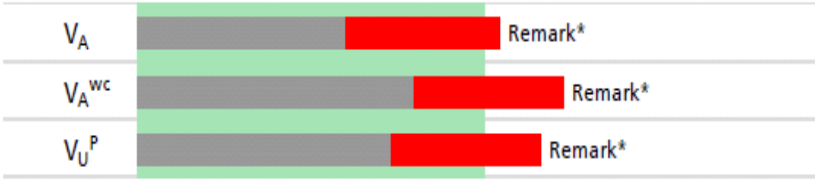
Stage 3: GAtam surface treatment

Before SbD



* Further clarification can possibly allow these values to fall into the green zone

after SbD



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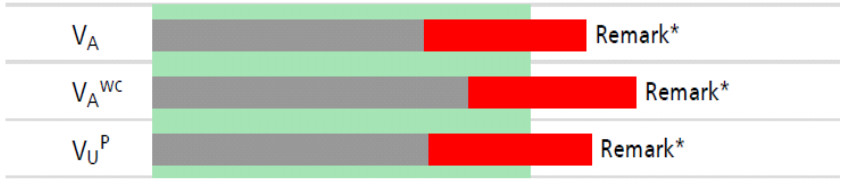


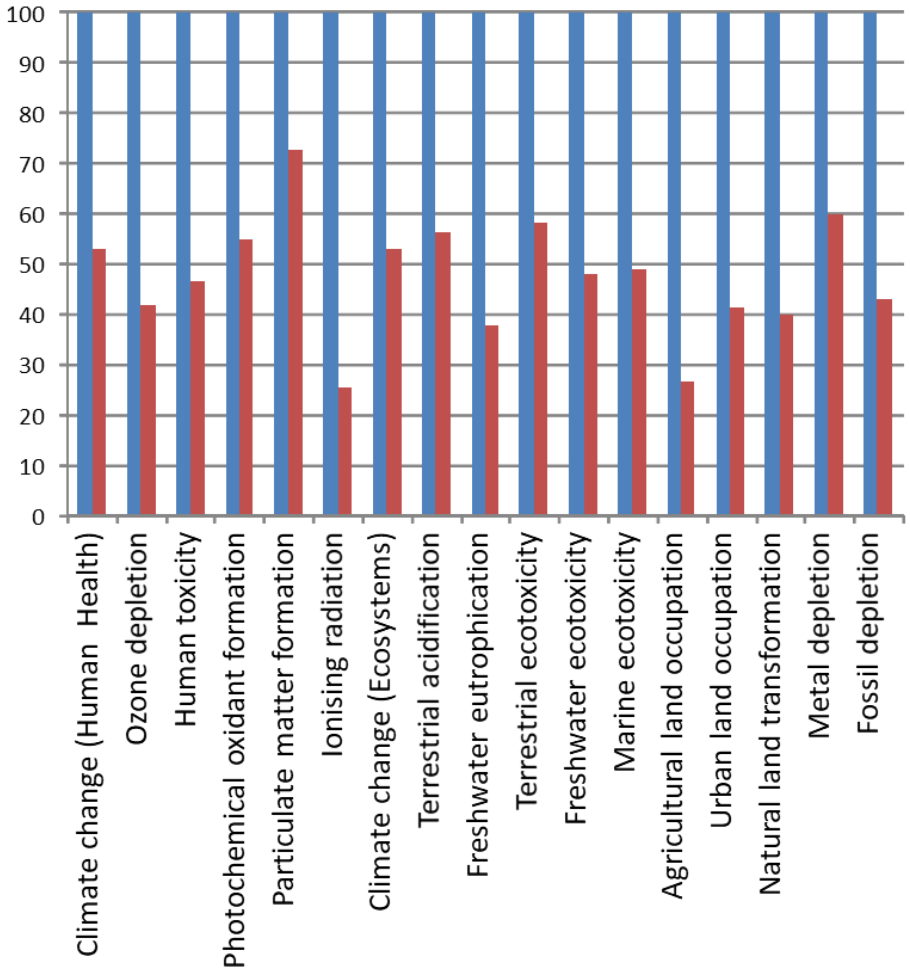
* Further clarification can possibly allow these values to fall into the green zone.

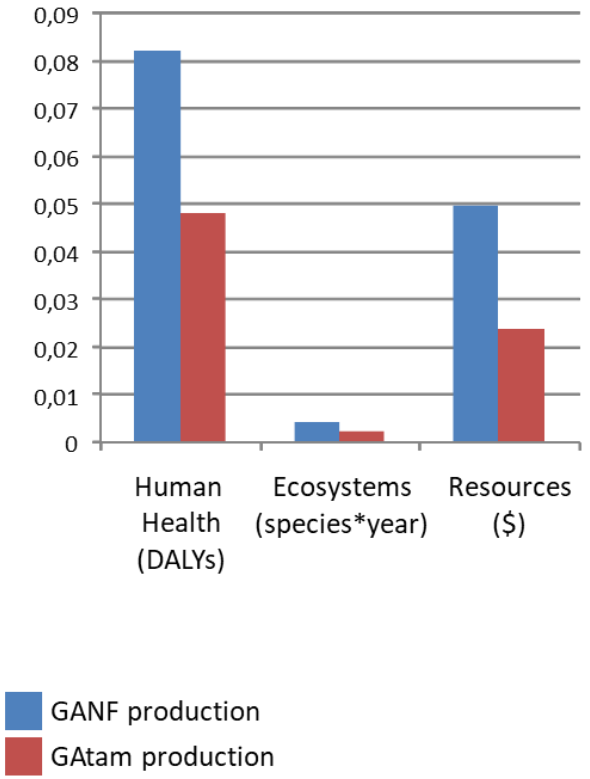
Conclusions: After the safe by design, automatization of the process, the exposure is expected to be reduced and the red bar that before was outside the safety zone has now fallen inside it. There is still an uncertainty zone due to unknown stability.

ENVIRONMENTAL EVALUATION FROM LIFE CYCLE ANALYSIS PERSPECTIVE

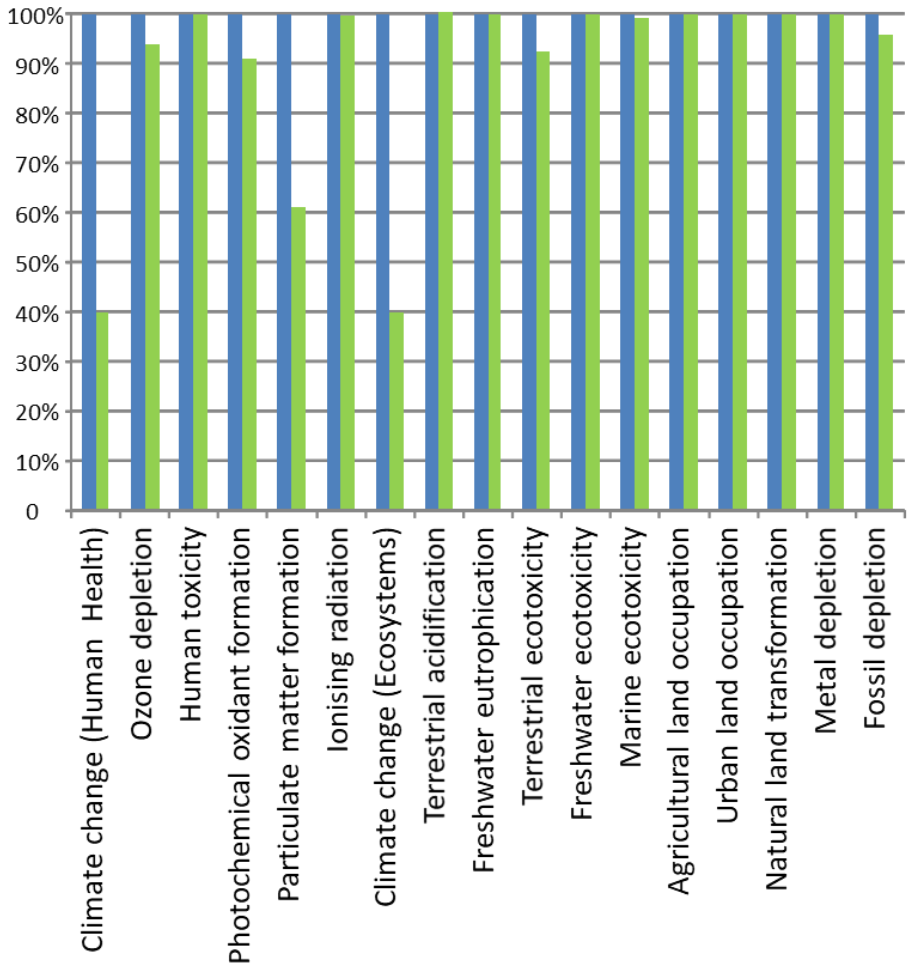
- LCA study for the production of 1kg carbon nanofibers GANF and GAtam (manufacturing and packaging stage):
- Results show that the main environmental impacts are due to chemicals used during the process, followed by energy consumption.
- LCA will be further updated with new data regarding emission of NPs, as well as data related to the use stage and end-of-life stage of both NPs.
- Comparative LCA between 'before' and 'after' SbD. An estimation of SbD improvements has been made considering burning methane emissions generated during the process for energy recovery.

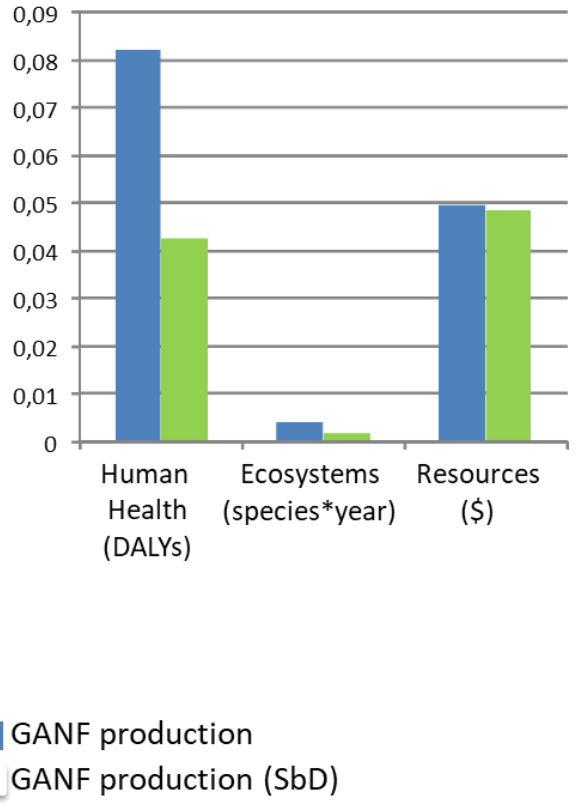
LCA ANALYSIS BEFORE SbD





LCA ANALYSIS AFTER SbD





¡Gracias!

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Acknowledgements

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