Comparative Life Cycle Assessment of Sunscreen Lotion Using Organic Chemicals Versus Nano-Titanium Dioxide as UV Blocker

by

Ankita Thakur

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Graduate Supervisory Committee:

Kevin Dooley, Co-Chair
Lenore Dai, Co-Chair
Mary Laura Li

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ABSTRACT

The production of nanomaterials has been increasing and so are their applications in various products, while the environmental impacts and human impacts of these nanomaterials are still in the process of being explored. In this thesis, a process for producing nano-titanium dioxide (nano-TiO_2) is studied and a case-study has been conducted on comparative Life Cycle Assessment (LCA) of the application of these nano-TiO_2 particles in the sunscreen lotion as a UV-blocker with the conventional organic chemical sunscreen lotion using GaBi software. Nano-TiO2 particles were identified in the sunscreen lotion using Transmission Electron Microscope suggesting the use of these particles in the lotion.

The LCA modeling includes the comparison of the environmental impacts of producing nano-TiO_2 particles with that of conventional organic chemical UV-blockers (octocrylene and avobenzone). It also compares the environmental life cycle impacts of the two sunscreen lotions studied. TRACI 2.1 was used for the assessment of the impacts which were then normalized and weighted for the ranking of the impact categories.

Results indicate that nano-TiO_2 had higher impacts on the environment than the conventional organic chemical UV-blockers (octocrylene and avobenzone). For the two sunscreen lotions studied, nano-TiO_2 sunscreen variant had lower environmental life cycle impacts than its counterpart because of the other chemicals used in the formulation. In the organic chemical sunscreen variant the major impacts came from production of glycerine, ethanol, and avobenzone but in the nano-TiO_2 sunscreen variant the major impacts came from the production of nano-TiO_2 particles.

Analysis further signifies the trade-offs between few environmental impact categories, for example, the human toxicity impacts were more in the nano-TiO_2 sunscreen variant, but the other environmental impact categories viz. fossil fuel depletion, global warming potential, eutrophication were less compared to the organic chemical sunscreen variant.

DEDICATION

To my parents

Ravinder Thakur

Anju Thakur

Sister Nimisha Thakur

And Brother Vidit Thakur

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER 1

INTRODUCTION

1.1 Motivation for Research

The field of nanotechnology is changing and growing rapidly will have significant impact on every sector in the coming years. Nanotechnology is concerned with the creation or handling of particles and materials, that as a minimum: (i) have one nanometric dimension, normally 1 nm to 100 nm, and (ii) are produced through the structured organization of groups of atoms and molecules or through reduction at the nanometric level of macroscopic materials (Ostiguy, Roberge, Woods, & Soucy, 2010). Nanoparticles have new and unusual properties that are not obvious in the corresponding bulk material. This is because a nanoparticle has a large surface area in relation to its size and is consequently highly reactive. Applications of nanoparticles include nanoparticulate titanium dioxide for sunscreens, and as photocatalytic agent in coatings that can be applied to stay-clean windows (Ion Publishing Ltd., 2014). These materials are being used in the expanding array of consumer products (Eastern Research Group, 2010, August). In 2005, the global production of nano-TiO_2 was estimated to be 2000 tons, of which, 1300 tons was used in personal care products especially topical sunscreens and cosmetics. By 2010, it had increased to 5000 tons (Weir, Westerhoff, Fabricius, Hristovski, & Goetz, 2012)

Below are the estimated upper and lower bounds for annual U.S. production of five engineered nanomaterials (ENM) in ton per year (tpy) (Hendren C.O et. Al, 2011)

Table 1: Estimated upper and lower bounds for Annual U.S. production of 5 ENMs

product	lower bound (tpy)	upper bound (tpy)
nano-TiO_2	7800	38,000
nano-Ag	2.8	20
nano-CeO_2	35	700
CNT	55	1101
fullerenes	2	80

Although, there are a lot of publications in last few decades about the growth of nanotechnology, but these publications contain very less scientific data on the feasible approaches of dealing with nano waste streams generated at various phases of the nanotechnology-based products and materials life cycle (Musee, 2011). In 2007, Environmental Protection Agency (EPA) released a review draft of the white paper on nanotechnology which discussed the potential environmental benefits of nanotechnology, risk management issues, risk assessment challenges, and the research needs in both environmental applications and its implications (Science Policy Council, 2007). The potential advantages and disadvantages of nanomaterials and the products using them over the conventional products have not been investigated completely and there is a need to understand the full implications of these nanomaterials (Klopffer et al., 2007).

1.2 Life Cycle Assessment (LCA)

With the growing demand for green manufacturing and for the sustainable development of nanotechnology there is a need to use a life-cycle based approach, in order to better understand the potential problems and how the system around us will be impacted throughout the life span of these particles (Sustainability, 2010). Life cycle assessment tool can be used to analyze and evaluate the environmental and health effects of nanotechnology. The International Organisation of Standardization (ISO) have published the ISO 14040 for the life cycle assessment principles and framework. LCA concepts study five stages of the complete life span of the product where the potential impacts might occur :

1. Raw material extraction : Where all the raw materials are acquired from the nature such as mining and harvesting.
2. Raw material processing : Where the acquired raw materials are processed, purified and prepared for use in the product manufacturing.
3. Product manufacture: Where the product is manufactured and is transported to the consumers.
4. Product use : Use and maintainance of the product by the consumer
5. End-of-life : After the life span, disposal of the product by the consumer, it includes landfilling, recycling and waste water treatment.

LCA is adequate to answer many questions on environmental and human health impacts of nanotechnology and comparing different products performing the same function.

1.3 Problem Statement and Contributions

In this thesis, we are using LCA to answer the question: " How do the life cycle impacts of a consumer product differ depending on whether it uses nanomaterials or conventional materials that achieve the same function?". As nanotechnology is emerging, conducting an LCA can be difficult due to insufficient knowledge of the detailed inputs and outputs of the nanoproduct system. But assessing the life cycle of nanotechnology and nanoproducts at an early stage can reduce or prevent the potential impacts on human health and the environment. This LCA study is divided into two parts. Firstly, we have investigated the environmental burdens or benefits of producing nano- titanium dioxide particles. Secondly, we have compared their application in the sunscreen lotion with that of conventional organic chemical based sunscreen lotion. Existing research on this topic, have only addressed the cumulative energy and exergy demands of the nano-titanium dioxide particles production (Grubb & Bakshi, 2010). In this study, additional impact categories namely global warming potential, human toxicity, resource depletion, ozone depletion, eutrophication, ecotoxicity and acidification were analysed for both nano-titanium dioxide production process and their application in sunscreen lotions as UV blocker. These impact categories are then compared to the impacts of the already existing conventional materials which are used as UV blockers, thereby, providing valuable information on the comparison of nanotechnology to the already existing technology used in consumer products across the spectra of impact categories. The results in this LCA study can be used for making decisions in product design, marketing and other R&D decisions.

1.4 Organization of Thesis

This thesis is structured into 5 chapters. Chapter 2 gives an overview of nanomaterials, background and properties of nano-titanium dioxide particles, description about the life cycle assessment (LCA) methodology, the environmental impact categories studied and uncertainity assessment in LCA.

Chapter 3, discusses the methods and tools used in this project. It also explains the production process of nano-titanium dioxide particles and sunscreen lotions. Further, this chapter defines the functional unit, scope, system boundary and assumptions used for this LCA study. Chapter 4, presents the results of applying the LCA and characterization tools to the study. The results from the life cycle impact assessment of the model of titanium dioxide particle production process and comparative life cycle model of sunscreen lotions are included in this chapter.

Chapter 5 summarizes and concludes the results of this thesis and explores the future scope of research.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 gives an overview of nanomaterials, background and properties of nano-titanium dioxide particles, a description about the life cycle assessment (LCA) methodology, the environmental impact categories studied, and a uncertainty assessment in LCA.

2.1 Overview – Nanomaterials

The term nano stands for 1 billionth of meter in a physical length scale. The major attraction of this size is that the materials have enhanced properties compared to the same materials at a larger size. This is due to the increase in surface area, and at this size, quantum effects occur that significantly change the material's optical, magnetic and electrical properties. As such, nanomaterials have gained attention and are used in many applications. A few applications of nanomaterials are given below:

1. Cosmetics applications- Sunscreen lotions
2. Nanocomposite materials: Silicate nanolayer and nanotubes used as a reinforced filler.
3. Fuel cells: nano-engineered membranes to improve efficiency of small-scale fuel cells.
4. Displays: Displays using carbon nanotubes as emission device for the next generation of monitors and televisions.
5. Nanocoatings: Surface coating with nanosized layers of nanomaterials improve properties like scratch resistance or hydrophobic properties. (Nanocompositech, 2010)

Despite the seemingly obvious benefits of nanomaterials, there could be unintended environmental implications. Nanoscale manufacturing can be energy and resource intensive and might have unintended human health impacts.

Sengül et al., n.d. have discussed various nano-manufacturing methods and have summarized their energy and resource requirements as follows:

1. Stricter purity requirements
2. Lower process yields
3. Repeated processing, post-processing or reprocessing steps of a single process or batch
4. Use of toxic, acidic or basic chemicals and organic solvents
5. Need for moderate to high vacuum
6. Use of or generation of greenhouse gases

The manufactured quantities of nanomaterials are expected to increase and displace the conventional materials in products. Also, acquiring the starting materials used for the nanomaterial manufacturing involves resource intensive extraction and processing that strains the natural resources and increases the overall environmental life cycle impact of the product in which these nanomaterials are ultimately used (Sengual, Theis, & Ghosh, n.d.)

2.2 Nanomaterials in Cosmetics:

Nanomaterials used in cosmetics differ from nanomaterials used by other industries. In cosmetics, nanomaterials are used in the form of nanoemulsions, nanosomes, and nanopigments, which are minerals already present in the natural environment. These materials are used for example in sunscreens, skin creams and oral hygiene products. Titanium dioxide (TiO_2) is one of the best known nanopigments used in sunscreens and toothpastes, and in cosmetic products as UV-filters. As of 2014, The European Commission has permitted one mineral UV-filters, which are usually used in the nanoscale for sunscreen products.

2.2.1 Background of Nano-Titanium dioxide (Nano-TiO_2):

After its first commercial production, titanium dioxide has been widely used as a pigment in sunscreens, paints, ointments, toothpaste, food and many other applications (Chen & Mao, 2007) Titanium dioxide occurs in both nano and bulk form. The physical and the chemical properties of nano-titanium dioxide make it an attractive component of various consumer products (Eastern Research Group, 2010). Different properties of nano-TiO_2 are described below:

1. Phases:

There are three phases of nano-TiO_2 that exist: Rutile, Anatase, and Brookite. Rutile is the stable phase at high temperatures, but brookite and anatase are the common forms that exist at nano-scale levels. Heating the product produces the following transformation: anatase to brookite to rutile, brookite to anatase to rutile, anatase to rutile, and brookite to rutile (Chen & Mao, 2007).The crystal structure of the particles is highly dependent on the preparation method of the particles. For smaller particles with size <50 nm anatase is the stable form, but this is transformed into the rutile form at higher temperatures.

2. Physical Properties:

For the use of titanium dioxide in the consumer products the following physical properties are studied: density, melting point, and refractive index. (Eastern Research Group, 2010)

Table 2: Physical properties of nano-titanium dioxide

Properties	Anatase	Rutile
Density (kg/m^3)	3895	4250
Melting point (deg.)	Anatase form converts to rutile form before melting	1830-1850
Refractive index	2.54	2.75

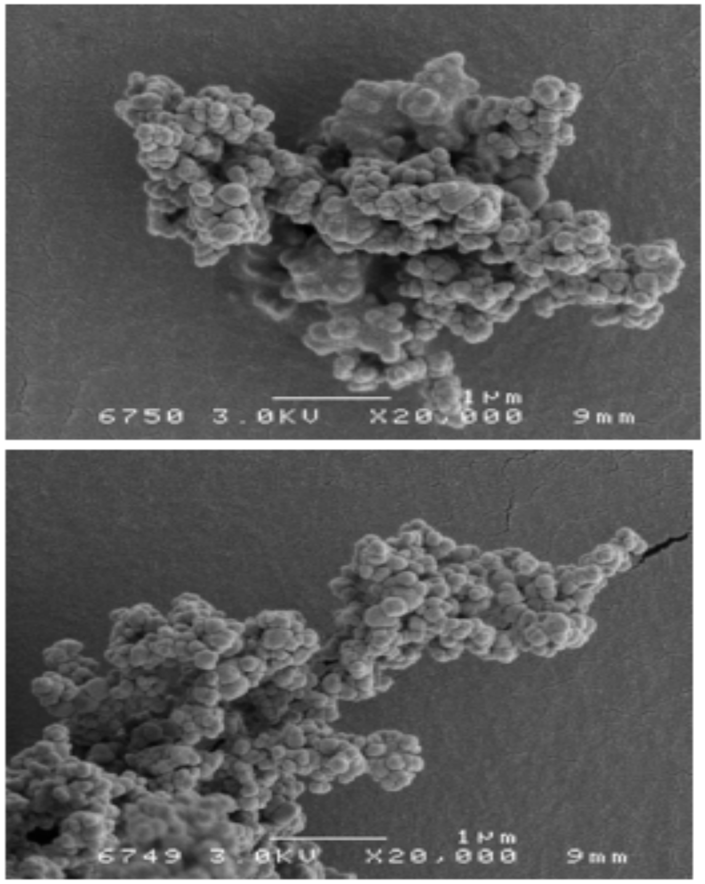
2.2.2 Nano-Titanium dioxide (Nano-TiO_2) as a UV Blocker in Sunscreen

Titanium dioxide is a good inorganic UV-blocker and has applications in many consumer products because of its chemical stability at high temperature and UV exposure. (Yang, Zhu, & Pan, 2004). Compared to the already existing organic UV blockers used in the sunscreens such as avobenzone, octocrylene etc., inorganic UV blockers are preferred because of their unique features, including nontoxicity and chemical stability under both high temperature and UV-ray exposure. A UV-ray is a segment of the electromagnetic spectrum, with the wavelength ranging from 100 to 400 nm, and is divided into 3 bands: UVA (315 or 320 to 400nm), UVB (290 to 315 or 320 nm), and UVC (100- 290nm).

Nano-TiO_2 are defined as particles in a three-dimensional form on the order of 100 nm or less, but greater than 1 nm (Cosmetics Europe, n.d). The main difference between the nano-TiO_2 and the pigment TiO_2 is the greater surface area of the nanoparticles. These particles have shown much better properties than their counter pigment Titanium dioxide particles, such as catalytic activity and ultra-violet rays (UV) absorption (Eastern Research Group, 2010).

Nano-TiO2 is available in anatase, rutile and brookite form. The anatase form is considered more photocatalytic than the rutile form and the rutile form is considered less photo reactive than anatase form and is extremely photostable. Although the photostable form is generally preferred for the sunscreen applications, the less photostable form is also used with coatings, which aids stability.

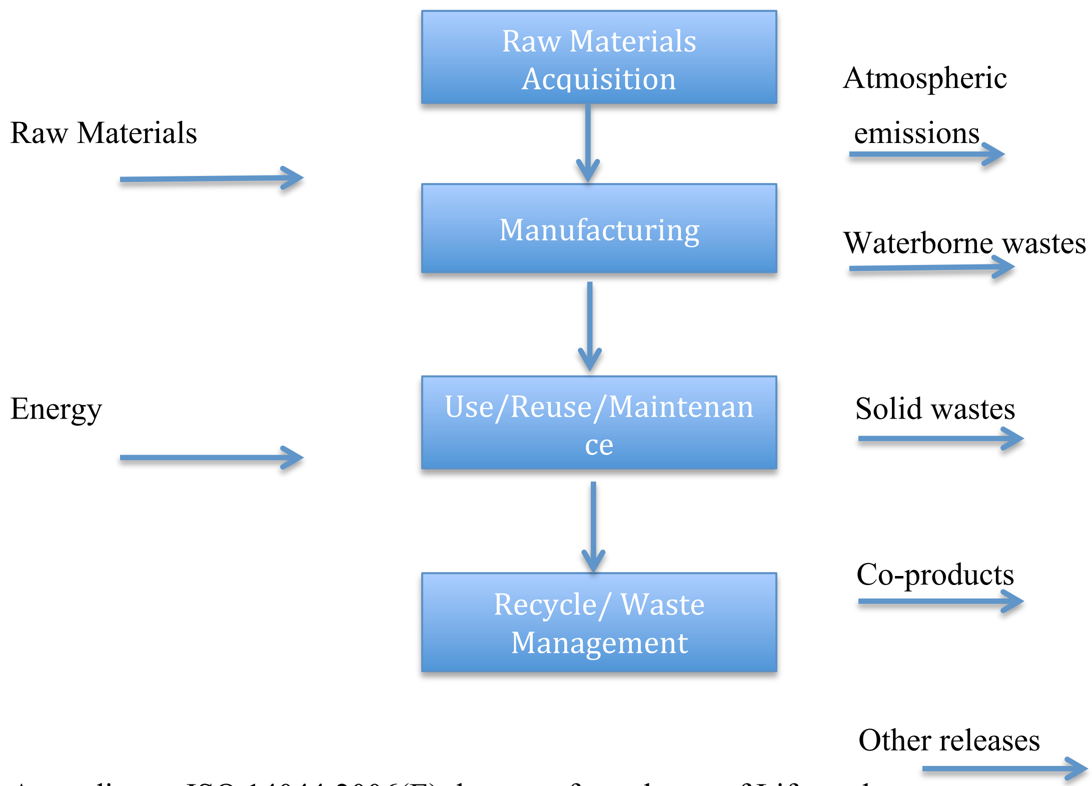
Figure 1: Nano-TiO2 agglomerates in sunscreen lotion (Cosmetics Europe, n.d.)



2.3 Life Cycle Assessment (LCA) Methodology:

Life cycle assessment (LCA) addresses the environmental aspects and the potential environmental impacts throughout the product's life cycle from raw material extraction to end-of-life (i.e. cradle-to-grave). It evaluates all stages of a product's life from the perspective that they are interdependent and one operation leads to the other. It helps in viewing the cumulative environmental impact coming from all life cycle stages of the product. By considering the product's cumulative effects, we can view the picture of the tradeoffs between the product and the environment and also the tradeoffs between different products. Typical life cycle stages that can be considered in an LCA are shown in Figure 2.

Figure 2: Typical life cycle stages of a product



According to ISO 14044:2006(E) there are four phases of Life cycle assessment:

1.) The goal and scope phase
2.) The inventory analysis phase
3.) The impact assessment phase, and the
4.) Interpretation phase.

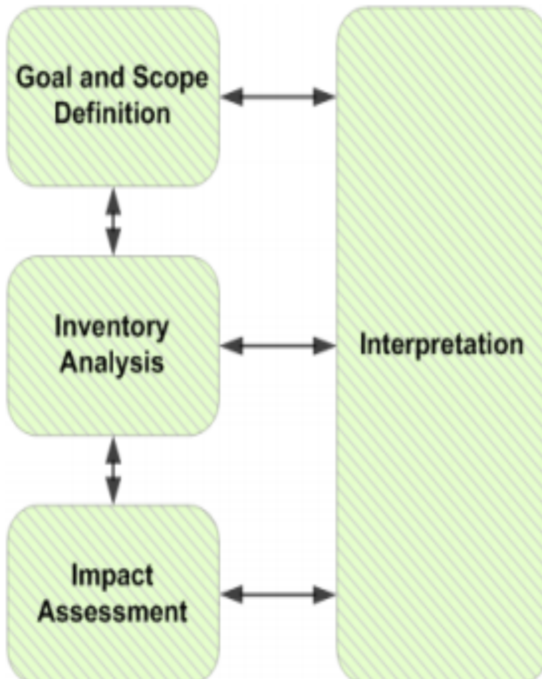
The goal and scope phase includes defining the system boundary and the level of detail in the study. It also includes defining the functional unit for the product being studied.

The Life cycle inventory phase is related to data collection in order to study the system. The data can be measured, calculated or estimated, or collected directly from industry. This stage includes all the data of material and energy streams entering and exiting the system.

Life cycle impact assessment is a relative approach based on the functional unit and is totally dependent on the data entered, data omitted and the sources of uncertainty. It includes impact categories, category indicators and the characterization models. The impact categories are standardized to equivalents of the common emissions. This causes all the impact categories to be in different units. For that reason, to compare across the categories, the results have to be normalized against the estimated total damage for that impact category in the country or world.

Life cycle interpretation phase of an LCA is the identification of the significant issues based on the results from the LCI study. It evaluates consistency and sensitivity of the results, as well as conclusions, limitations, and recommendations.

Figure 3: Illustration of LCA Phases (ISO, 2006)



2.4 Environmental Impact Categories:

1.) Acidification

According to TRACI 2.1 “Acidification is increase of concentration of hydrogen ion in the environment. This can be the result of addition of acids into the local environment, or by the addition of other substances which increase the acidity of the environment due to various chemical reactions and/or biological activity, or by natural circumstances such as the change in soil concentrations because of the growth of local plant species.”

These substances are basically air emissions which travel hundreds of miles before their deposition as acids, rain, fog or snow or dry deposition as dust or smoke. So to provide an assessment TRACI characterizes using acidification model which incorporates the increasing of hydrogen ion potential within the environment.

2.) Eutrophication:

According to US Environmental Protection Agency (US EPA), 2008d, "Eutrophication is the enrichment of an aquatic ecosystem with nutrients (nitrates, phosphates) which accelerate biological productivity (growth of algae and weeds) and an undesirable accumulation algal biomass." Although Nitrogen and phosphorous are good for agricultural activities, but the excess release of both the substances can cause negative impacts on freshwater lakes, streams and coastal regions. Some of the substances which contribute to this impact category are very difficult to characterize such as emissions from waste water treatment plants.

TRACI 2.1 uses a characterization model which includes substances, which can cause potential eutrophication.

3.) Global Climate Change:

According to US Environmental Protection Agency (US EPA), 2008b, "Global warming is an average increase in the temperature of the atmosphere near the Earth's surface and in the troposphere, which can contribute to changes in global climate patterns. Global warming can occur from a variety of causes, both natural and human induced. In common usage, "global warming" often refers to the warming that can occur as a result of increased emissions of greenhouse gases from human activities."

TRACI 2.1 uses global warming potentials (GWPs) for the calculation of the potency of greenhouse gases relative to carbon dioxide.

4.) Ozone Depletion:

According to US Environmental Protection Agency (US EPA), 2008j "Ozone within the stratosphere provides protection from radiation, which can lead to increased frequency of skin cancers and cataracts in the human populations. Additionally, ozone has been documented to have effects on crops, other plants, marine life, and human-built materials. Substances which have been reported and linked to decreasing the stratospheric ozone level are chlorofluorocarbons (CFCs) which are used as refrigerants, foam blowing agents, solvents, and halons which are used as fire extinguishing agents."

World Meteorological organization proposed a metric to calculate Ozone depletion potentials (ODPs), but there has been a consensus going on the use of this metric. US EPA maintains websites and lists all the various options for the ODPs. TRACI 2.1 uses the most recent sources of ODPs and use them for each substance.

5.) Human Health Particulate:

According to US Environmental Protection Agency, 2008n "Although this category may be called the human health criteria pollutants category, it deals with a subset of the criteria pollutants, i.e., particulate matter and precursors to particulates. Particulate matter is a collection of small particles in the ambient air which have the ability to cause negative human effects including respiratory illness and death. Numerous epidemiology studies show an increased mortality rate with elevated levels of ambient particulate matter."

The particulate matter is mostly produced due to combustion of fossil fuel, wood and particles from roads and fields. They are divided into two major groups:

1.) Inhalable coarse particles: diameter of 2.5 to 10 micrometers

2.) Fine particles: diameter of less than 2.5 micrometers.

The human health impacts due to these kind of particles is calculated by modeling the fate and exposure of the fractions which are inhaled by the human being. The fraction inhaled in calculated as the function of the amount of substance released in the environment and hence increases the air concentration and this air concentration is the function of the location of the release of the substance. In TRACI 2.1 all the substances are characterized using PM 2.5 as the reference substance.

6.) Human health cancer, non-cancer, and ecotoxicity:

There were number of models which existed to calculate human toxicity potentials and research has been conducted to find out the sources of uncertainties/ variability in these models. Under the Life Cycle Initiative of the United Nations environment Program (UNEP), developers created a model called USEtox and was used to develop human health cancer and non-cancer toxicity potentials and freshwater ecotoxicity potentials for over 3000 substances including organic and inorganic substances. USEtox is developed with two spatial scales: continental and global. The continental scale includes urban air, rural air, agricultural soil, industrial soil, freshwater, and coastal marine water. The units for the USEtox human health cancer, noncancer, and ecotoxicity are: CTUcancer, CTUnoncancer, and CTUeco, respectively. USEtox allows the combination of cancerous and non-cancerous impacts, but TRACI maintains these categories independently.

7.) Photochemical Smog Formation:

According to US Environmental Protection Agency, 2008e "Ground level ozone is created by various chemical reactions, which occur between nitrogen oxides (NOx) and volatile organic compounds (VOCs) in sunlight. Human health effects can result in a variety of respiratory issues including increasing symptoms of bronchitis, asthma, and emphysema. Permanent lung damage may result from the prolonged exposure to ozone. Ecological impacts include damage to various ecosystems and crop damage. The primary sources of ozone precursors are motor vehicles, electric power utilities and industrial facilities."

In TRACI 2.1, Photochemical smog formation is modeled with Maximum Incremental Reactivity (MIR). This model is selected because it was developed specifically for the US and had comprehensive substance coverage for human health and environmental impacts and it covers nearly 1200 substances leading to potential photochemical smog formation.

8.) Resource Depletion:

Resource depletion is an important issue, but it is very difficult to quantify this issue while minimizing the value choices and assumptions. While all the other impact categories have legislation or international agreements related to the fate, transport, and potency, there is no trace which exists for the resource depletion categories.

TRACI 2.1 addresses initial categories for resource depletion, fossil fuel use, land use, and water use (Bare, 2012).

2.6 Uncertainty Analysis

Weidema and Suhr Wesnaes, 1996 proposed a qualitative method for assessing the quality of the data collected for the LCA study called pedigree matrix which was further modified by Ciroth, 2008. The matrix is shown below in figure 4. The quality is assessed over different indicators:

1.) Reliability: This indicator conveys the quality of the source of data used for conducting the LCA study.

2.) Completeness: This indicator conveys the properties of the sample itself and if the sample includes the sufficient number of data.

3.) Temporal differences: This indicator co-relates the time of the study and the study from which the data is obtained.

4.) Geographical differences: This indicator is the co-relation of the defined area in the LCA study and the study from which the data is obtained.

5.) Technological differences: Technological indicator is concerned with the temporal and geographical differences. Even if the study is of the desired age and geographic area, it may not represent the technology under study. Therefore, it is necessary to use the data older data or the data from a different geography.

Figure 4: Pedigree matrix for assessing the quality of the LCA study (Ciroth, 2009)

Indicator score	1	2	3	4	5
Reliability of source	Verified data based on measurements	Verified data partly based on assumptions or non-verified data based on measurements	Non-verified data partly based on assumptions.	Qualified estimate (e.g. by industrial expert)	Non-qualified estimate or unknown origin
Completeness	Representative data from a sufficient sample of sites over an adequate period to even out normal fluctuations	Representative data from a smaller number of sites but for adequate periods	Representative data from an adequate number of sites but from shorter periods	Representative data but from a smaller number of sites and shorter periods or incomplete data from an adequate number of sites and periods	Representativeness unknown or incomplete data from a smaller number of sites and/or from shorter periods
Temporal differences	Less than 0.5 years of difference to year of study	Less than 2 years difference	Less than 4 years difference	Less than 8 years difference	Age of data unknown or more than 8 years of difference
Geographical differences	Data from area under study, **same currency**	Average data from larger area in which the area under study is included, **same currency**	Data from area with slightly **similar cost conditions, same currency, or with similar cost conditions, and similar currency**	Data from area **with slightly similar cost conditions, different currency**	Data from unknown area or area with very **different cost conditions**
Further technological differences	Data from enterprises, processes, and materials under study	Data from processes and materials under study from different enterprises, **similar accounting systems**	Data from processes and materials under study but from different technology, **and/or different accounting systems**	Data on related processes or materials but same technology	Data on related processes or materials but different technology

2.7 Existing work in the field of Nanotechnology and Life cycle assessment

Lloyd & Lave, 2003, have estimated the economic and environmental impacts associated with the use of nanotechnology in the automotive industry. They projected on the on material processing and fuel economy benefits associated with using a clay-polypropylene nanocomposite which is used instead of steel or aluminum in light-duty vehicle body panels. They found out that although the manufacturing cost is higher, the assessment showed benefits in using a nanocomposite design with reduced energy and less environmental discharges. Estimated annual CO_2 reductions from vehicle use are 65 million t from aluminum substitution and 49-87 million t from nanocomposite substitution. Because of the uncertainties, in the performance of nanocomposites, Lloyd &Lave have discussed that aluminum costs less than the nanocomposite and offers better performance than the lower bound nanocomposite, although the nanocomposite is better at the upper bound.

In 2005, Lloyd &Lave performed a study on catalytic design of platinum-group metal (PGM) used in automotives. They employed economic input-output and process-based LCA to estimate the relative change in life cycle environmental effects from changes in PGM usage. According to the study, techniques which enable the control over the shape and size of the nano-platinum group metal particles results in reduced PGM loading levels and which also leads to reduction in energy consumption and improves environmental quality. They have estimated that the amount of PGM required to meet U.S. vehicle emissions standards through 2030 based on current catalyst technology which is lower than what was used in 2005. They have then estimated the range of PGM that could be saved from potential nanotechnology advances.

Steinfeldt et al., 2004 performed a case study on ìNano-innovations within the display sectorî and investigated the potential for eco-efficiency using the application of nanotechnology-based products in the display sector. The OLEDs and CNT-FED were compared to the conventional displays CRT, LCD and plasma displays. According to that study, many indicators pointed to an increase in material and energy efficiency when using nanotechnology-based products. They also performed a case study on "The Ecological efficiency of Nano-varnishes" investigating the ecological potential of new, nanotechnology-based coating methods. The coating of aluminum with the new nano-varnish using a sol-gel technology was compared to a water-based varnish, a solvent-based varnish, a powder varnish and an evaluation was done on the ecological benefits by applying a comparative ecological life-cycle assessment method. The study concluded that the application of nanotechnology-based coatings shows a great potential for eco-efficiency in terms of emissions and environmental effects. From the literature, it was found that there is a lack of life cycle assessment studies for nanotechnology used in the personal care consumer products. One of the application is in the sunscreen lotions. In order to determine significant impacts during the life cycle of sunscreen lotion which uses these nanoparticles, a life cycle impact study is done. In this thesis, comparative life cycle assessment is done to study the tradeoffs of this new emerging technology with the already existing conventional technology.

CHAPTER-3

METHODOLOGY

Chapter 3, discusses the methods and tools used for this project. It also explains the production process of nano-titanium dioxide particles and production process of sunscreen lotions, used for the purpose of this thesis. Further, this chapter defines the functional unit, scope, system boundary and assumptions used for the Comparative LCA study.

3.1 Application of ISO Framework to Nanomaterials and Nanoproducts

The ISO framework (14044:2006) is applicable to the LCAs related to nanomaterials and nanoproducts. Although there is no generic LCA for the nanomaterials, the impacts can be calculated from cradle-to-grave of a specific nanoproduct. As the nanomaterials are increasing in the market place and showing up in a lot of products, it is necessary to study their environmental impacts and safety.

1. **Goal and Scope Definition Phase**: It is important to see and define the goal and scope of the LCA study of the nanoproduct as the nanomaterials can serve different functions to their alternatives. One should define the exact conditions of how the nanoproduct is different from the traditional product in the case of comparative analysis.
2. **The Inventory Analysis Phase**: The Inventory phase deals with the collection of complete and reliable data. The disadvantage with the collection of data for the nanoproducts is the transparency of the use of nanomaterials in the products by the companies. The data is always subject to confidentiality constraints and it is a difficult

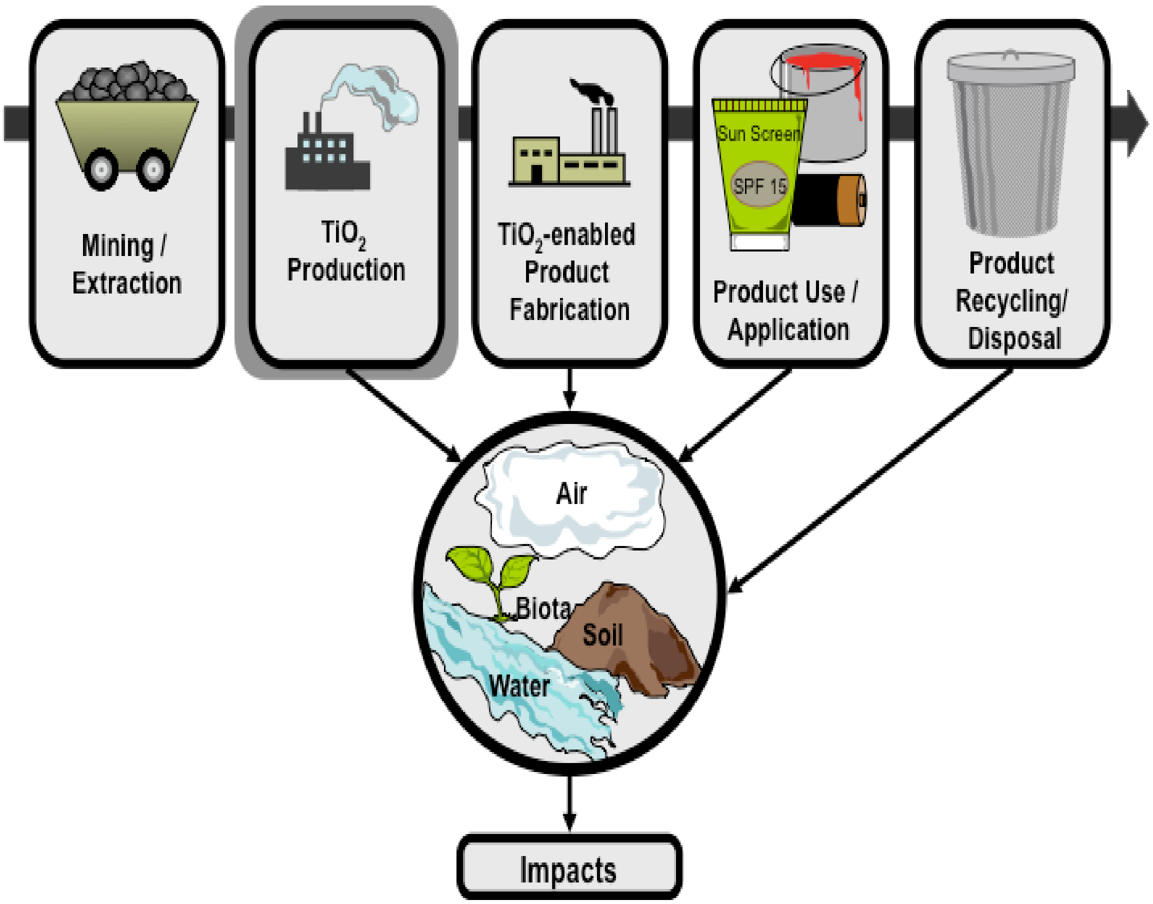
task to collect the proprietary information from companies. The nanoproducts have already entered the market and the release of nanomaterials to the environment can be in any life cycle stage. As of today, it is still unclear where the exact release is happening. Mostly the release is at the use phase of the product (additives, food, sunscreens), but the exact rate is not always available. The potential tool identified with the given problems is the input-output based life cycle assessment approach. This approach considers all the inputs and outputs of the product’s supply chain. It includes all the purchases that go into the final product direct or indirect. The inventory analysis should always be followed with the impact assessment, in standard LCI only the quantities of the emissions are reported. Also, the factors affecting the toxicity of the nanomaterials include the particle size, shape, aspect ratio, crystal structure, surface area, charge and solubility, for some applications the nanomaterials be coated and that can also change the properties. During the life cycle of a nanoproduct, these particles can change due to aging, pressure or weathering, so it is necessary to describe and keep in mind all the changes that occur and describe them properly.

3. **The Impact assessment phase**: Once the life cycle inventory is developed for the nano product, the emissions from the LCI are classified into impact categories at mid-point level such as climate change, human toxicity, eco-toxicity, ozone depletion etc. and end point level such as resource depletion, climate change, human health. For each of these impact categories, the relevant emissions are multiplied by the characterization factors. The characterization factors can be selected from the standard LCIA methods available

like CML 2001, Eco-Indicator 99, Impact 2002+, Recipe, TRACI. Within each impact category, the emissions are then normalized or weighted to a common reporting basis. Although, Normalization and weighting are optional.

4. **Interpretation Phase**: The interpretation phase of the LCA of nanomaterials and nanoproducts is not different from any other product. Uncertainty and sensitivity analysis are done for the uncertain production impacts (Klopffer et al., 2007).

Figure 5: Value chain of a typical nanoproduct (Hendren C.O et. al, 2011)



3.2 GaBi 6 Software:

The GaBi 6 software is developed by PE International. This software system is used for measuring the product sustainability performance. The software offers number of applications like Life Cycle assessment, Life Cycle Costing, Life Cycle Reporting and Life cycle working Environment. The tool used for the study is Life cycle Assessment (LCA). The GaBi Software allows access to the number of databases, which contains thousands of processes and flows measuring the environmental impacts. In the software, whole life cycle of the product is built and can be viewed as 'plan'. The plan contains several upstream and downstream processes. In addition, each process contains inputs and outputs named as "flows".

3.3 TRACI 2.1

TRACI – "Tool for reduction and assessment of chemical and other environmental impacts" is used in the impact assessment stage of an LCA study. This tool allows the quantification of stressors that have potential effects. The impact categories that TRACI 2.1 quantifies are ozone depletion, global warming, acidification, eutrophication, photochemical smog formation, human health particulate effects, human health cancer, human health noncancer, ecotoxicity, and fossil fuel depletion effects.

The TRACI framework starts after the inventory stage of the LCA.TRACI utilizes the amount of the chemical emission or resource used and the estimated potency of the stressor (Bare, 2012).

3.4 Production of Nano-titanium dioxide (TiO_2) particles

To model the production process of nano-TiO_2 particles in GaBi software, Altair nano-production process is studied. As its patent was released in a detailed paper in which production process were reported with mass and energy balance, the Altair nano production process provides the most detailed information to model as realistic as possible in addition to the constraints of the GaBi software. In the commercial databases provided by GaBi, currently, there are two processes available for the production of titanium dioxide, both the processes produce pigmentary (>100nm) titanium dioxide particles. The two processes are: chloride process and sulphate process. The chloride process uses titanium slag as the precursor with hydro chloric acid, while the sulphate process uses ilmenite with sulphuric acid. The Altair nano-TiO2 production process which is discussed below uses Ilmenite ore with hydrochloric acid to produce nano sized titanium dioxide.

The Altair nano-TiO2 process is derived from spray-hydrolysis which is used to produce the nano-TiO2 from ilmenite ore ($FeTiO_3$). The feed to the process is titanium chloride aqueous solution. This feed solution is subjected to total evaporation to form dry, hollow titanium dioxide particles which are amorphous in nature. The amorphous material from the total evaporation step is calcined in the presence of other additives. The additives promote crystallization into nano-sized particles like addition of phosphates stabilizes the anatase structure. Other additives also influence on the size and the phase purity. After this step the product is subjected to milling and final processing. The milling has to be mild so that it doesn't break individual crystallites, which would quickly broaden the particle- size distribution by generating a fraction of undersized material. The final product may be the milled slurry and the slurry is spray dried to produce loosely agglomerated balls or micronized product to produce dispersed powder.

The reactions that occur during the process are as following:

$2FeTiO_3 + 4HCl \text{ -----}\rightarrow 2FeCl_2 + 2TiOCl_2 + 2H_2O + O_2$

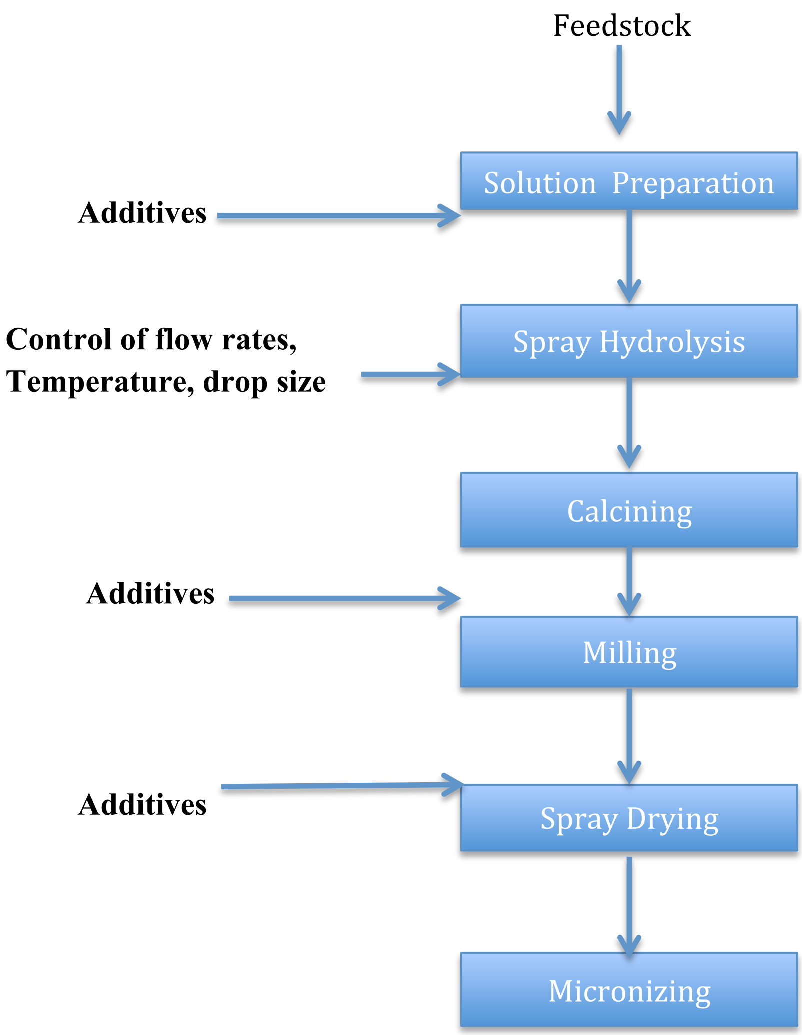
$2Fe^{3+} + Fe \rightarrow 3Fe^{2+}$

$TiOCl_2 + H_2O \rightarrow TiO_2 + 2HCl$

$2FeCl_2 + 2H_2O + \frac{1}{2} O_2 \rightarrow Fe_2O_3 + 4\ HCl$

The end product is 40-nm anatase phase TiO_2 nanoparticles. This current pilot-scale plant produces 100 kilograms of titanium dioxide per hour. Iron oxide is produced as a by-product and the regenerated hydrochloride acid is recycled back. (Verhulst et. al., 2002)

Figure 6: Flow diagram of nano-TiO2 particle production (Verhulst et. al., 2002)



It is a relatively new approach for the production of Nano-TiO_2 .The figure and the description of the process is published in the open literature as patents and articles.

The figure of the process was published in Verhulst et al., 2002 with mass and energy requirements for the nano-TiO_2 product which is produced at the rate of 97 kg/hour. From the figure, the inputs of the materials were identified and are listed in table 3. The mass requirements for each of the material were calculated for the 100kg of titanium dioxide produced.

Figure 7: Mass and Energy balance of the Altair production process (Verhulst et. al., 2002)

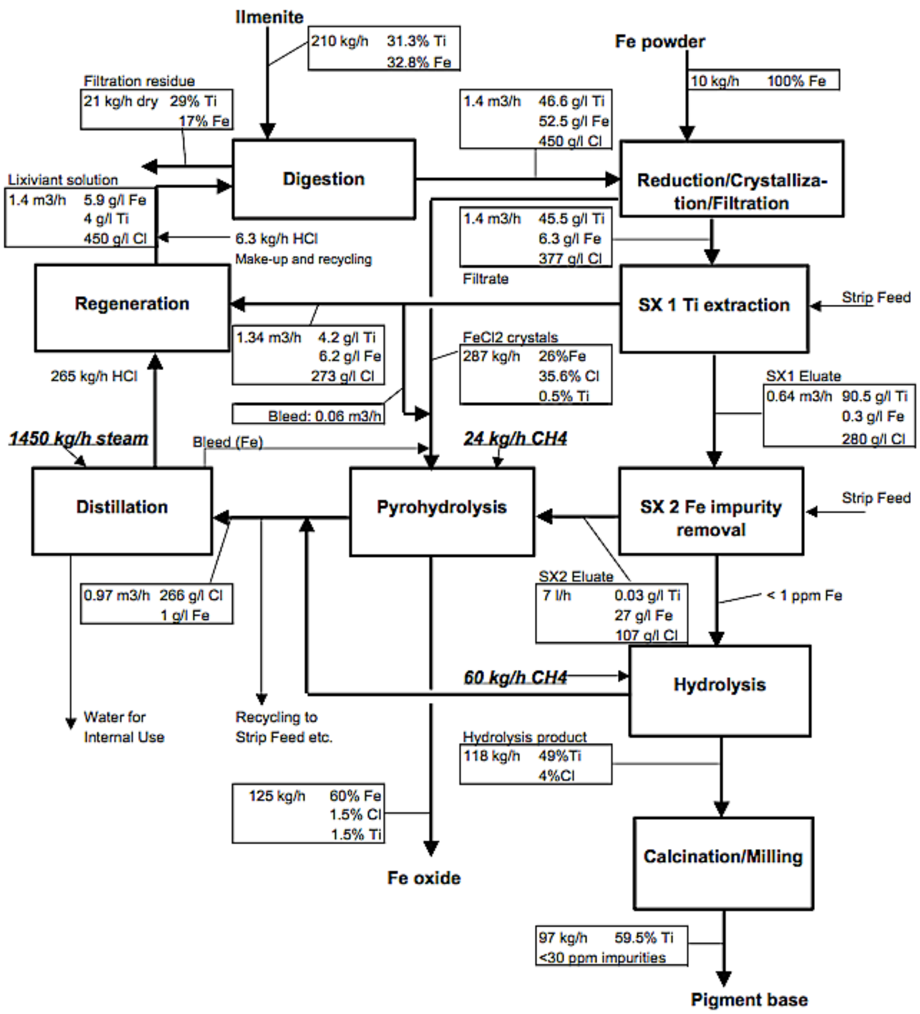


Table 3: Mass and Energy requirements for the Altairnano production process

Material Inputs to the Process	**Mass [kg / 100 kg of TiO2]**
Ilmenite Ore	**216.49**
Iron Powder	**10.30**
Hydrochloric acid	**6.49**
Methane	**86.59**
Steam	**14.97**

Electricity requirements for the process were not available in the open literature from the Altairnano Inc. So the value was taken from the work of Grubb and Bakshi i.e. 10.44 MJ/kg of titanium dioxide production (Grubb & Bakshi, 2010). This production process was then modeled in GaBi software, using ecoinvent database. The model was built to calculate the cradle-to-gate impacts of the emissions and energy requirements for the process. These impacts were then compared to the cradle-to-gate impacts of emissions and energy requirements for the production of conventional organic chemical UV-blockers, octocrylene, azobenzone etc., for which Nano-titanium dioxide is considered a less toxic substitute in sunscreens.

3.5 CASE STUDY: Application of nano-TiO_2 particles – Comparative Life Cycle Assessment case study of sunscreen lotions.

Sunscreen lotions play a major role in protecting skin from the solar ultra violet rays which are considered to be harmful and cause skin cancer and skin damage. Sunscreens need to absorb these harmful rays (UVA and UVB) to be effective. Nano titanium dioxide is used as a UV blocker in sunscreens, it absorbs UVA and UVB radiations. There has been an increasing use of nano-TiO_2 in the sunscreen lotions. Nano-TiO2 serves two purposes by absorption and scattering of UV rays. These particles are also an attractive alternative to the organic chemical based sunscreen lotions such as avobenzone, octocrylene, benzophenone which are known for crossing the skin barrier, causing skin reactions, including blisters and are suspected as endocrine disruptors. The sunscreen lotions are applied by the consumer on the body and after washing it reaches the environment (Stefanik, 2012).

For the purpose of this study, two models are built in GaBi Software using the ecoinvent database for the life cycle of both the alternatives of the sunscreens. Both the sunscreen lotions were then compared at different stages of the life cycle using the TRACI 2.1 impact assessment tool.

3.5.1 Functional Unit:

1 kilogram of sunscreen lotion, with titanium dioxide as the UV blocker. This one kilogram of sunscreen lotion is compared to the equivalent 1 kilogram of sunscreen lotion, with octocrylene and avobenzone as the UV blocker.

3.5.2 Scope and System boundary:

This comparative LCA of sunscreen lotion used in this study covers the phases of raw material production, product manufacturing, and end-of-life of product in wastewater treatment plants. The packaging, transportation, and the retail is equivalent in both formulations hence excluded from the LCA. The sunscreen formulations used for the purpose of the study are the standard products which are available in any retail store across United States. For each chemical ingredient, an equivalent eco invent process has been identified as shown in Table 6 and 7 . For the ingredients whose specific production process is not identified by ecoinvent, a proxy process is used in this model.

Figure 8: System boundary for the LCA

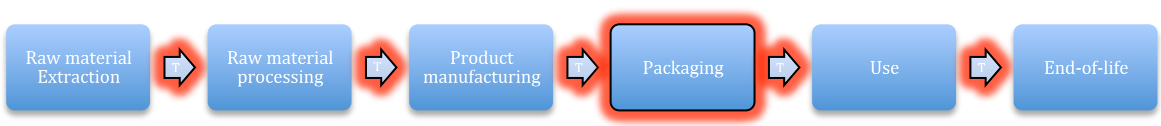


Table 4: Summary of system boundary

Included	**Excluded**
Raw materials extraction	Capital equipment and maintenance
Energy and fuel inputs	Packaging of the product (primary, secondary and tertiary)
Processing of raw materials	Transportation of raw, processed and manufactured products
Manufacture of final product	
Use of product	
Disposal of product	

3.5.3 Assumptions for the Comparative LCA study

1. One formula is generated for each sunscreen, in consideration of available processes in the eco invent database. It has been noted that there are different formulations available in the market in terms of inactive ingredients.
2. Only one active ingredient, Titanium dioxide is assumed to be used in the sunscreen formulation.
3. Titanium dioxide is compared with two organic sunscreen agents. Noted that different organic sunscreen agents are present in combinations in the sunscreen lotions.
4. It is assumed that the nano-TiO2 particles are used in anatase form.
5. The nano-TiO2 particles are used without any coatings.
6. The nano-TiO2 is assumed not to change properties during any life cycle stage due to aging, weathering or mechanical stress.
7. The nano-TiO2 particles used in the sunscreen lotion are produced with Altairnano production process.
8. Glycerin production and the impacts associated are assumed to be from the palm oil. Although, it has been noted that glycerin can be produced from different types of methods (for e.g. soy oil).
9. Transportation and packaging phase is excluded from the comparison of two sunscreens because the impacts from both the types of lotion are same.
10. It is assumed that the consumer uses 100 percent of the product and do not dispose the product with the packaging.

11. The transportation distances for the raw material supply to the manufacturing plants and from the manufacturing plants to the retailer stores are assumed to be equal in both the sunscreen types.

3.5.4 Characterization of nanoparticles in sunscreen lotions:

Although nano-TiO_2 particles have been used in personal care products for decades, particle size is never disclosed on the product packaging. The U.S. Food and Drug Administration does not specify how to label or describe these particles. For the purpose of this study, three mineral sunscreens that included titanium dioxide and zinc oxide as the UV-blocker in the active ingredient list were chosen from a local retail store. All three sunscreens were available without prescription and were made in the United States. Engineered nanoparticles (ENPs) were not listed on any of the product labels.

There are a range of methods available to characterize the engineered nanoparticles used in the consumer products, including: scanning electron microscopy (SEM), transmission electron microscopy, laser scanning confocal microscopy, atomic force microscopy (AFM), as well as dynamic light scattering and small angle x-ray scattering techniques. For the characterization of sunscreens, TEM has been proven to be the best method; therefore, TEM was chosen for the characterization of the nanoparticles in the samples which were used in this study (Lorenz, 2010). Approximately, 0.05 grams of each sunscreen sample was diluted in 16 ml of methanol (99.8%). All the dispersions were sonicated to destroy the agglomerates formed by the particles to study the presence of ENPs in the products. The samples were kept overnight at room temperature. The images were then recorded using TEM which uses incoherently scattered electrons. Figures 8, 11, and 14 are images of the samples analyzed. For each sample at least 30 particles were analyzed and measured.

3.5.5 Manufacturing Process of the Sunscreen with octocrylene and avobenzone :

The manufacturing process of the sunscreen consists of mixing of ingredients in 5 parts. The process is discussed below:

Part A: Carbomer is dispersed in the water using vigorous agitation until the polymer is dispersed well and then Glycerin is added.

Part B: In a separate mixing reactor, Methyl Gluceth-20, PPG-20 methyl glucose ether, pentylene glycol, butylene glycol and ethyl alcohol are mixed until they are homogeneous. Then Part B is added to Part A with continuous mixing until both the phases are uniform.

Part C: In a separate mixing reactor, neopentyl glycol diethyl hexanoate and Sunscreen agent – octocrylene and avobenzene are mixed. To solubilize avobenzene, Part C is heated to about 40-45^{O} C and once it is done, it is allowed to cool below 40^{o}C. When it is cooled, Part C is added to the main batch with continued mixing.

Part D: Sodium hydroxide is added to the main batch with continued mixing.

Part E: DMDM hydantoin is added to the main batch with continued mixing(Lubrizol, 2008)

This product has a sun protection factor (SPF) of 25 which determined by the In Vitro testing. Other properties are (Lubrizol, 2008):

1. Viscosity: 6000 -8000 mPa.s
2. Appearance: Creamy off-white lotion
3. pH: 5.5-5.7

The processes were chosen from the GaBi commercial databases (ecoinvent and PE). The selected processes for building the model of Sunscreen with octocrylene and avobenzone as UV blocker are listed below:

Table 5: Sunscreen with organic chemical variant

Ingredients	**Weight %**	**Process**	**Source**
A.Deionised Water	25.02	**Water, ultrapure, at plant/GLO with US electricity**	Ecoinvent
Carbomer/Xantham gum	0.4	**Carboxy celluose, powder,at plant, RER**	Ecoinvent
Glycerin	20	**Glycerine, from palm oil, at esterification plant,MY[kg]**	Ecoinvent
B.Methyl gluceth-20	2.5	**Ethylene glycol dimethyl ether, at plant, RER**	Ecoinvent
PPG-20 Methyl glucose Ether	1.5	**Proplyene glycol, at plant, RER**	Ecoinvent
Proplyene glycol (Hydrolite)	2	**Proplyene glycol, at plant, RER**	Ecoinvent
Butylene glycol	2	**Butane-1,4 diol, at plant, RER**	Ecoinvent
Ethyl alcohol	25	**Ethanol, 97% in H_2O**	Ecoinvent

C. Neopentyl glycol diethylhexanoate	8	**Dipropylene Glycol**	PE
Avobenzone - butyl Methoxydibenzoylmethane	3	**Polyphenylene Oxide**	PE
Octocrylene	10	**MDI**	PE
Acrylates/ C10-30 Alkyl Acrylate Cross polymer	0.15	**polymethyl methaacrylate, beads, at plant, RER**	Ecoinvent
D. Sodium Hydroxide(18%)	0.18	**Sodium hydroxide, 50% in water, production mix, at plant, RER[kg]**	Ecoinvent
E. DMDM Hydantoin, Iodopropynyl Butylcarbamate	0.25	**Carbamate**	PE

3.5.6 Manufacturing process of the sunscreen with nano-titanium dioxide variant

The manufacturing process of the sunscreen consists mixing of ingredients in 4 parts. The process is described below:

Part A: Deionised water, disodium EDTA, hydroxypropyl methylcellulose, aminomethyl propanol, Butylene glycol, glycerin, methyl gluceth-20 are combined in the mixing reactor and are heated to 65^{o}C.

Part B: In a separate mixing reactor, combine diisopropyl adipate, cetyl ethylhexanoate, diisopropyl dimer dilinoleate and methyl glucose sesquistearate, heat to 65^{o}C. After the mixture is uniform acrylates are dispersed. The polymers will be slurry in the oil phase. Using rapid agitation Part B and Part A are mixed together to form an emulsion.

Part C: In the separate mixing reactor, part C ingredients and the sunscreen agent-titanium dioxide are mixed well. After mixing, the Part C is added to the main batch with moderate and continuous agitation

Part D: Propylene glycol and parabens are added to the main batch and mixed until uniform (Lubrizol, 2007).

This product has a sun protection factor (SPF) of 25 which is determined by In Vitro testing. Other properties are (Lubrizol, 2007):

1. Viscosity: 20,000 – 28000 mPa.s
2. Appearance: White, thick, creamy emulsion
3. pH: 6.7 – 7.0

The selected processes for building the model of the sunscreen with Nano-TiO_2 as the UV blocker in GaBi software are listed below:

Table 6: Sunscreen with nano-TiO2 variant

Ingredients	Weight%	Process	Source
A. Deionised Water	70	**Water, ultrapure, at plant/GLO with US electricity**	Ecoinvent
Disodium EDTA	0.05	**EDTA, ethylenediaminetetraacetic acid, at plant/RER WITH US ELECTRICITY U**	Ecoinvent
Hydroxypropyl Methyl Cellulose	0.1	**carboxymethyl cellulose, powder, at plant**	Ecoinvent
Aminomethyl Propanol	0.3	**2- Aminopropanol [Group NMVOC to air]**	PE International
Butylene Glycol	1	**butane-1,4-diol, at plant,RER**	Ecoinvent
Glycerine	2	**Glycerine, from palm oil, at esterification plant,MY[kg]**	Ecoinvent
Methyl Gluceth-20	2	**Ethylene glycol dimethyl ether, at plant, RER**	Ecoinvent
Cetyl hexanoate/Ester	2	**Esters of versatic acid, at plant**	Ecoinvent
Diisopropyl Dimer Dilinoleate/Ester	1	**Esters of versatic acid, at plant**	Ecoinvent
Methyl Glucose Sesquisterate/Ester	0.19	**Esters of versatic acid, at plant**	Ecoinvent
Acrylates\C10-30 alkyl acrylate	0.18	**polymethyl methacrylate, beads, at plant [polymers]**	Ecoinvent

crosspolymer			
Acrylates\C10-30 alkyl acrylate crosspolymer	0.18	**polymethyl methacrylate, beads, at plant [polymers]**	Ecoinvent
Nano Titanium Di-oxide	15	**Nano Titanium Di-oxide,at pilotplant**	Altairnano
Polyglyceryl	1	**Proplyene glycol, liquid, at plant**	Ecoinvent
Proplyene glycol	0.5	**Proplyene glycol, liquid, at plant**	Ecoinvent

3.5.7 Energy Calculations:

Energy requirements to a unit or a plant operation obeys first law of thermodynamics which states that "Enthalpy is conserved" or " In a thermodynamic process involving a closed system, the increment in the internal energy is equal to the difference between the heat accumulated by the system and the work done by it". For material streams enthalpy is calculated as:

$\Delta H = m * Cp * \Delta T$ ------------(1)

Where m is mass , C_p is the heat capacity, and ΔT is the difference in the temperature between the system and the ambient surroundings.

For material streams with mixture of compounds, the enthalpy is calculated as:

$\Delta H = \sum w * Cp * \Delta T$------------(2)

Where w is the weight fraction of each compound in the mixture, C_p is the heat capacity of each compound and ΔT is the difference between the temperature of the system and the ambient surroundings (Felder & Rousseau, 2000)

Energy requirements for the two manufacturing processes of the sunscreen are calculated from equation (2). The detailed calculations are shown in APPENDIX B. Although it has to be noted that the energy calculations from the above method does not account the energy losses occurred to the surroundings during the processing of sunscreen lotion.

CHAPTER 4

RESULTS AND DISCUSSIONS

Chapter 4, outlines the results obtained by modeling the Altair nano-TiO_2 production process, comparison of the cradle-to-gate impacts of two UV blocker alternatives i.e. nano-TiO_2 and conventional organic UV-blocker. Also discussed are the results obtained from the comparative impact study of the life cycle impacts of two sunscreens modeled in the GaBi software. Firstly, in the Chapter, the characterization results are discussed which was done to detect the nano-sized TiO_2 in the sunscreen lotions using Transmission Electron Microscope (TEM).

4.1 Characterization Results

All the three samples contained different shapes of titanium dioxide and zinc oxide particles. This analysis proved that the titanium dioxide particles in all the three samples were less than the size of 100nm (mostly in the range of 20nm-70nm). Although, the zinc oxide particles were greater than 100 nm of size. The summary of information of the results is shown in table 8.

This microscopy technique allowed to prove that these mineral sunscreens use ENPs with the shape and size varying considerably and these particles are present in the market and consumers are exposed to them. Manufacturing of these particles also makes them energy and resource intensive. Also, engineered nanoparticles are expensive as compared to their counter pigment particles (micro sized particles).

4.1.1 Characterization of Sample I:

The analysis of the images of TEM of sample I showed that it contained roundish particles of approximately of diameter 20-70nm and other bigger particles >100 nm of various shapes. The further analysis, with Energy Dispersive X-ray (EDX) revealed that the small particles were identified as Titanium dioxide and the larger particles were of ZnO. The images and the spectra of the sample I are shown in figure 8, 9 and 10.

4.1.2 Characterization of Sample II:

Using TEM analysis, sample II was found to contain rod shaped particles less than the 100 nm of size. The energy dispersive X-ray analysis (EDX) verified that these particles were of Titanium dioxide (TiO2). Because the samples were wet samples, the particles were still seen in agglomerated form, although ultrasonicator was used separate those particles. The images and the spectra of sample II are shown in figure 11, 12 and 13.

4.1.3 Characterization of Sample III:

The TEM analysis of sample III showed the presence needle shaped particles which were less than 100 nm in size and bigger particles of various other shapes which were greater than 100 nm in size. The Energy Dispersive X-ray analysis (EDX) further showed the smaller particles were of Titanium dioxide and the bigger particles were of ZnO. Being the wet samples, the particles existed in agglomerated form, after being separated by ultrasonicator. The images and spectra of sample III are shown in figure 13, 14 and 15.

The characterization technique, TEM, revealed the presence of nanoparticles [< 100 nm] being used in the sunscreen lotions, which was not mentioned on the product package. As the particles behave differently at this size than their bulk material and have energy intensive manufacturing processes it is important to consider, what potential and unintentional effects are being caused by them. For that purpose, transparency of the data and materials used in the products is an important factor to further study these nanoparticles.

4.2 Life Cycle Impact Study – TRACI 2.1

Life cycle impact assessment using TRACI 2.1 of the Altair nano-titanium dioxide production process are shown in figure 18 and 19. The impacts shown only represent the amount of damage caused by all the inputs to the process. In general, the impact assessment shows that steam generation and natural gas generation dominates the fossil fuel depletion category. The natural gas represents the largest energy input to the process. This is logical because the steam generation and the electricity generation, both are produced from burning the fossil fuels. Also, the whole process dominates the human toxicity and fossil fuel impact category the most, although the normalized scores are very low. If we are concerned of reducing the toxic chemicals or metals released from the process and reducing the fossil fuel use, the process should be modified such that the harmful chemicals or metals are recycled back or removed from the waste stream and are not released into the environment or some other innovation which reduces the release of these chemicals and metals. Also, reducing the dependency on the fossil fuels should be a priority.

To put this process in context with the conventional organic chemical UV-blockers, a comparison has been done on an equal mass basis, although the materials are used in different amounts in different sunscreens. Also, all the alternatives compared perform the same function i.e. UV-blockers in the sunscreen lotion. Within the fossil fuel category, the nano-titanium dioxide dominated the use of natural gas, crude oil and hard coal as compared to the conventional UV-blockers – octocrylene and avobenzone.

For the purpose of this thesis, on equal mass basis, the two sunscreens were then compared to study the impacts of the two types of UV-blockers on the product level. The two products are studied for their life cycle impacts. For both the sunscreens studied, Raw material production stage dominated all the other life cycle stages and made the impacts from other life cycle stages miniscule.

For the fossil fuel impact category, it was noticed that the sunscreen using the conventional organic UV-blockers dominated the use of natural gas and crude oil. It is because the production of other chemicals used in the formulation was also energy intensive. In comparison, the sunscreen using nano-titanium dioxide as UV-blocker showed less use of natural gas and crude oil. This is because, the production of other chemicals used in this formulation was less energy intensive.

The whole life cycle of both the sunscreens dominated the human toxicity and fossil fuel impact category. In the sunscreen, using organic chemicals as UV-blocker, the majority of the impacts came from the production of glycerine, ethanol, and avobenzone. In the nano- TiO_2 sunscreen variant, the majority of the impacts came from the production of the nano-TiO_2 particles. If we are going to use these nano-particles in the consumer products at this point of time, the other raw materials or components should be chosen, with minimum environmental impacts. The above studied sunscreen formulation is one example of that kind of scenario. Or improvement or optimization of these novel processes producing these nano-particles should be considered.

4.3 Uncertainty Assessment

Uncertainty was continually seen throughout this life cycle assessment, as it was largely unavoidable. Limitations on certainty were mainly due to the fact that specific data for the production of manufacturing process of nano-TiO_2 and the sunscreen lotions were not available in the literature and is therefore difficult to find. Also, the available data in the literature had many omissions and was not complete. Omissions include, data related to the electricity requirements for each unit process in nano-TiO_2 production and sunscreen manufacturing. Although, energy requirements were calculated theoretically by energy balance.

The uncertainty in the nano-TiO_2 production also came from the actual nanoparticles. Data is not available for these nanoparticles, for when and how they end up in the environment during the manufacturing of the particles. Similar case was observed for the manufacturing of the nanoparticles based product. Literature says, due to the size, shape and aging of these particles, they can behave differently as compared to their counter big particles. If in future the availability of that data proves that the nanoproduct has a larger impact than the conventional products, then it may not make sense to use these particles in the products.

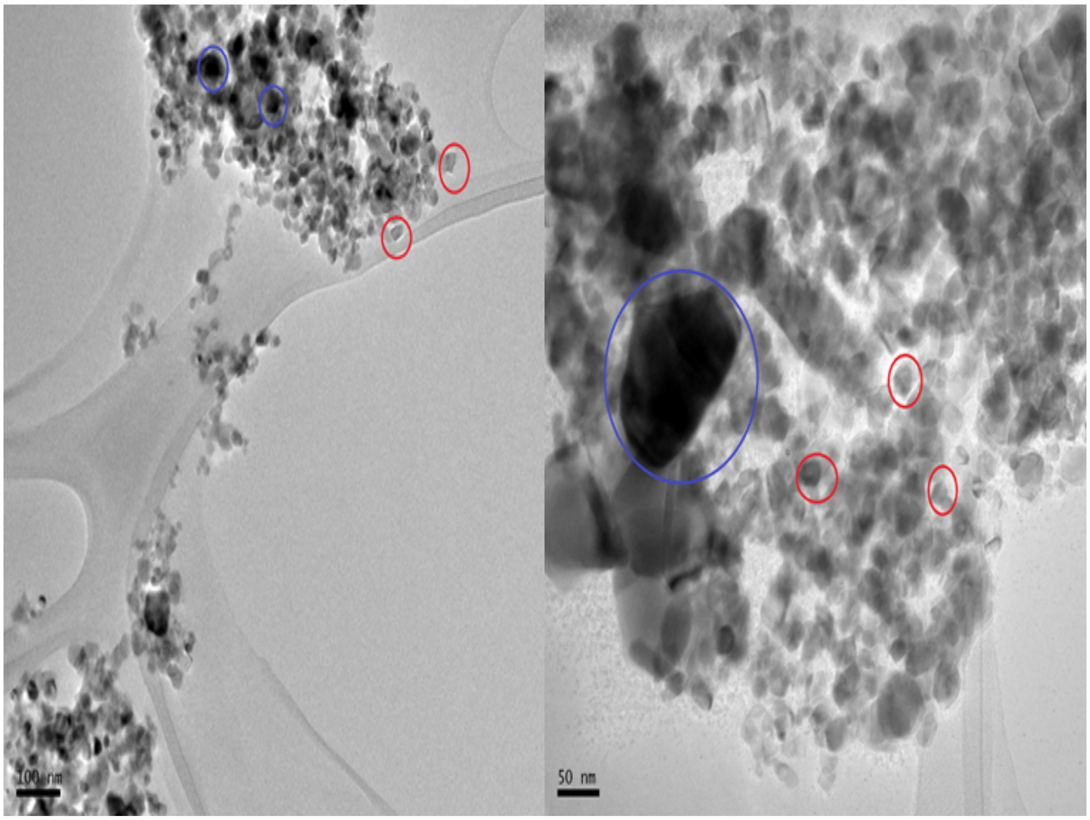
Other uncertainties were due to simple data gaps during modeling in GaBi. For example, data related to the ingredient production of the sunscreen. Proxy processes were used from the commercial databases in GaBi, where the data was not available for the actual chemical, also, the production processes used had geographical differences. Most of the data came from the European, Australian and Malaysian datasets. For electricity U.S. production dataset was used. A series of assumptions were made in an attempt to collect the necessary data (as dictated by the system boundary) while still preserving an acceptable level of quality.

Despite the large number of average data sources and necessary assumptions, the results in this life cycle assessment confidently represent the processes and impacts of an average sunscreen lotion sold in the market. The results can in fact represent most such sunscreen lotions, as insight gained through examination of patents, it indicates that most of these products are extremely similar in their basic ingredient makeup, and their proportions. A pedigree matrix is built to study the uncertainties and the data quality of the LCA study and the production process of nano-titanium dioxide. The pedigree matrix is shown in table 9 and 10.

Table 7: Size and shape of TiO2 particles detected in the sunscreens

Product	Sun protection factor (SPF)	Particle shape and Size observed of TiO_2	Elements detected by EDX
1.) Nature's gate Kids broad spectrum	20	Roundish (< 100nm)	Ti, Zn, Al, Si, C
2.) Banana Boat natural reflect	50	Rod shaped (<100 nm)	Zn, Ti, Al, Si, O, C
3.) Neutrogena Sensitive skin sunscreen	60	Needle shaped (<100nm)	S, Cl, Ca, Fe, Ti, Zn, Al, Fe, O

Figure 9: Sample I with SPF 20: The red circles represent TiO2 particles and blue circles represent ZnO particles



(a) (b)

Figure 10: Spectra of Figure (a)

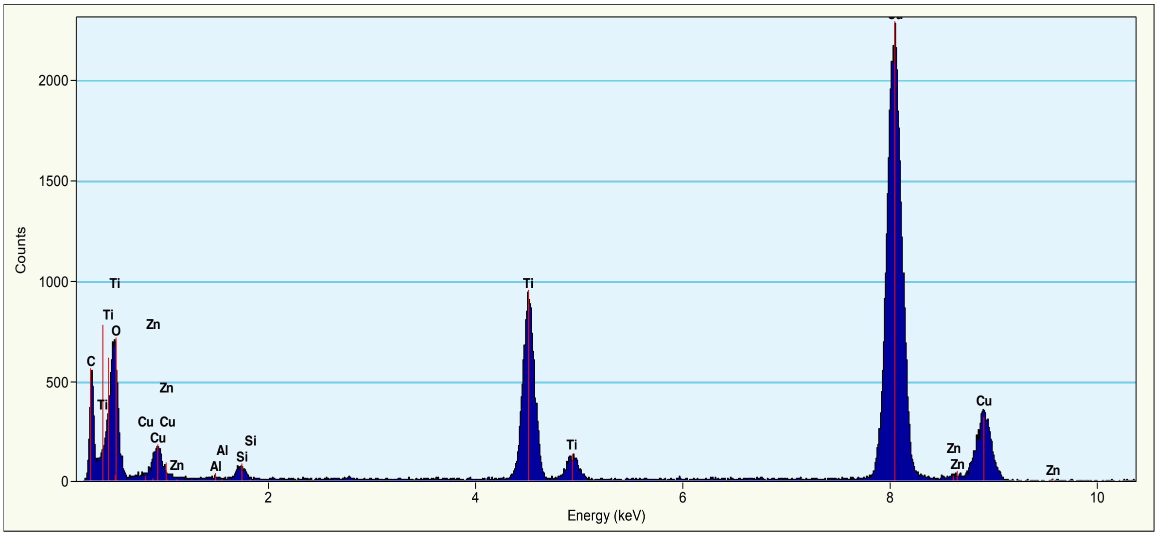


Figure 11: Spectra of Figure (b)

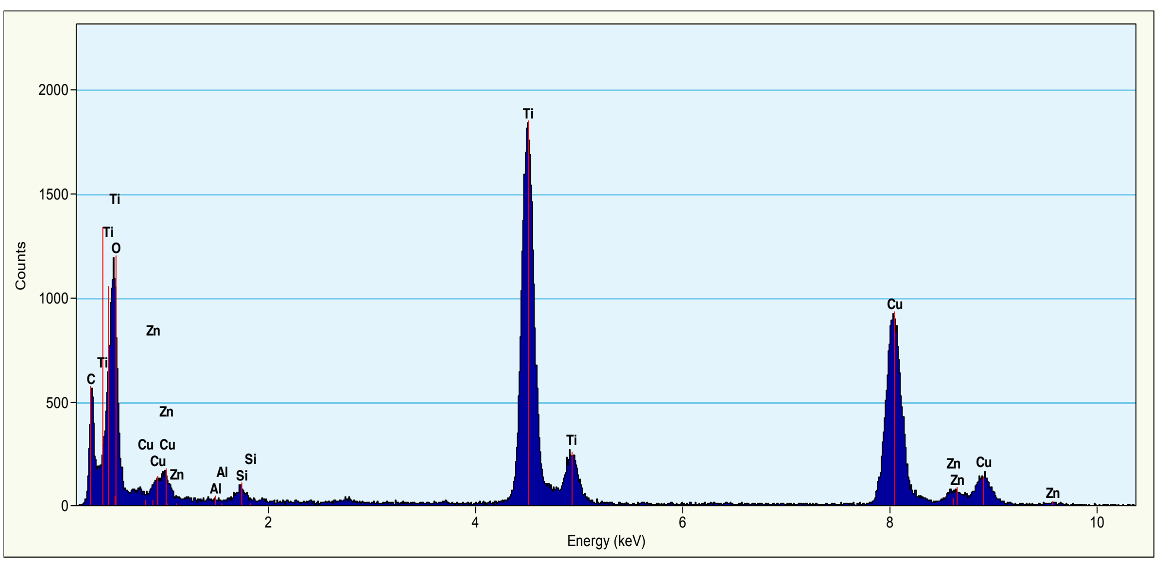
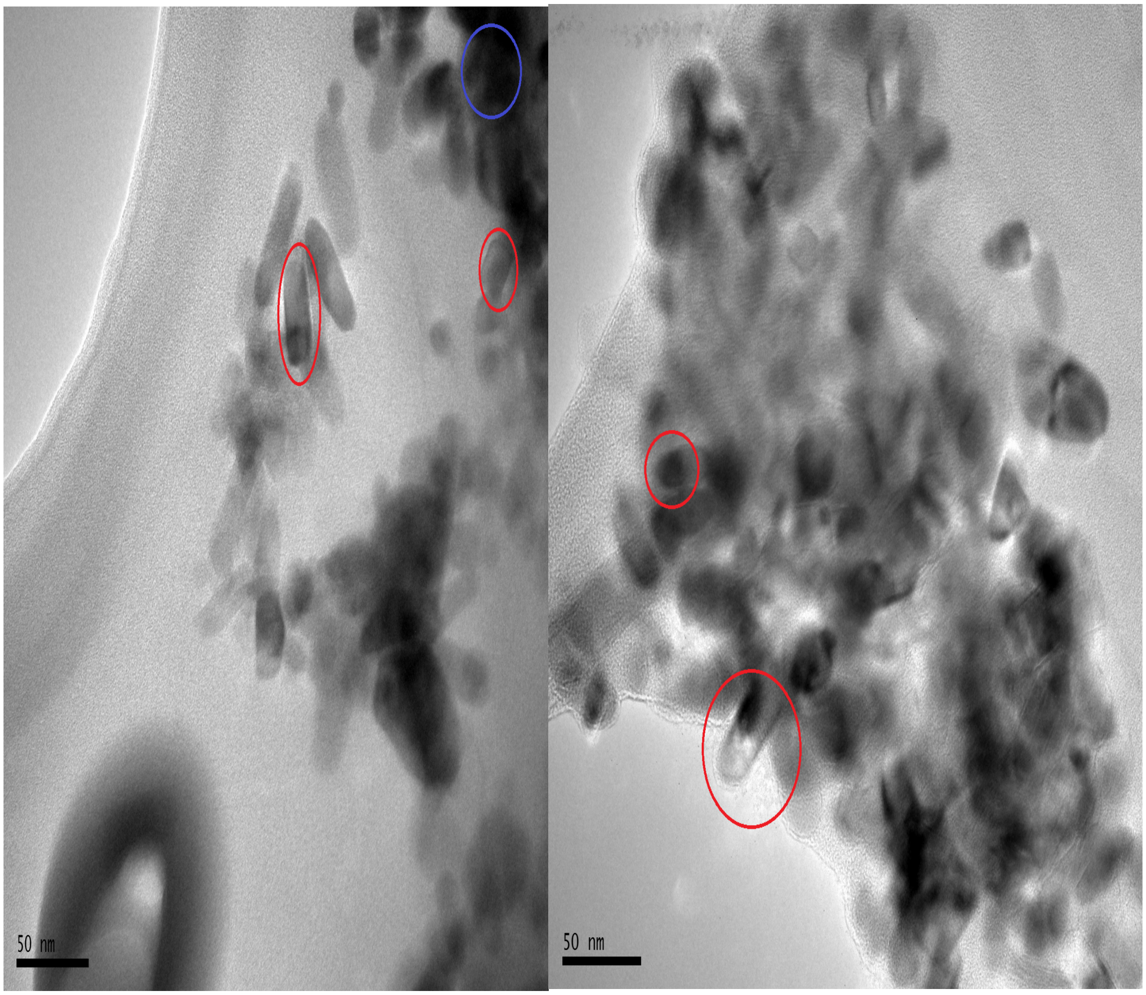


Figure 12: Sample II with SPF 50: The red circles represent TiO2 particles and blue circles represent ZnO particles



(a) **(b)**

Figure 13: Spectra of Figure (a)

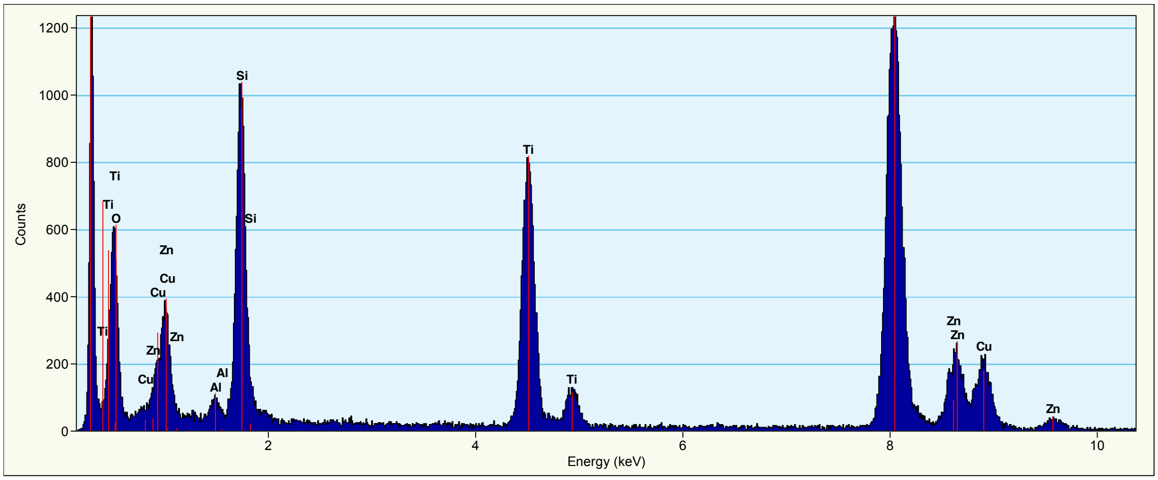


Figure 14: Spectra of Figure (b)

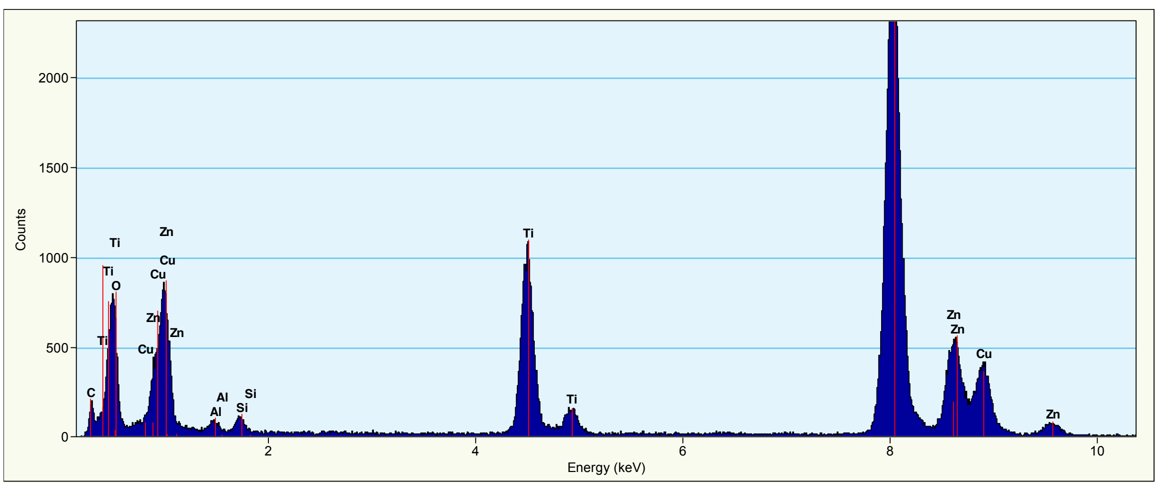


Figure 15: Sample III with SPF 60: The red circles represent TiO2 particles and blue circles ZnO particles

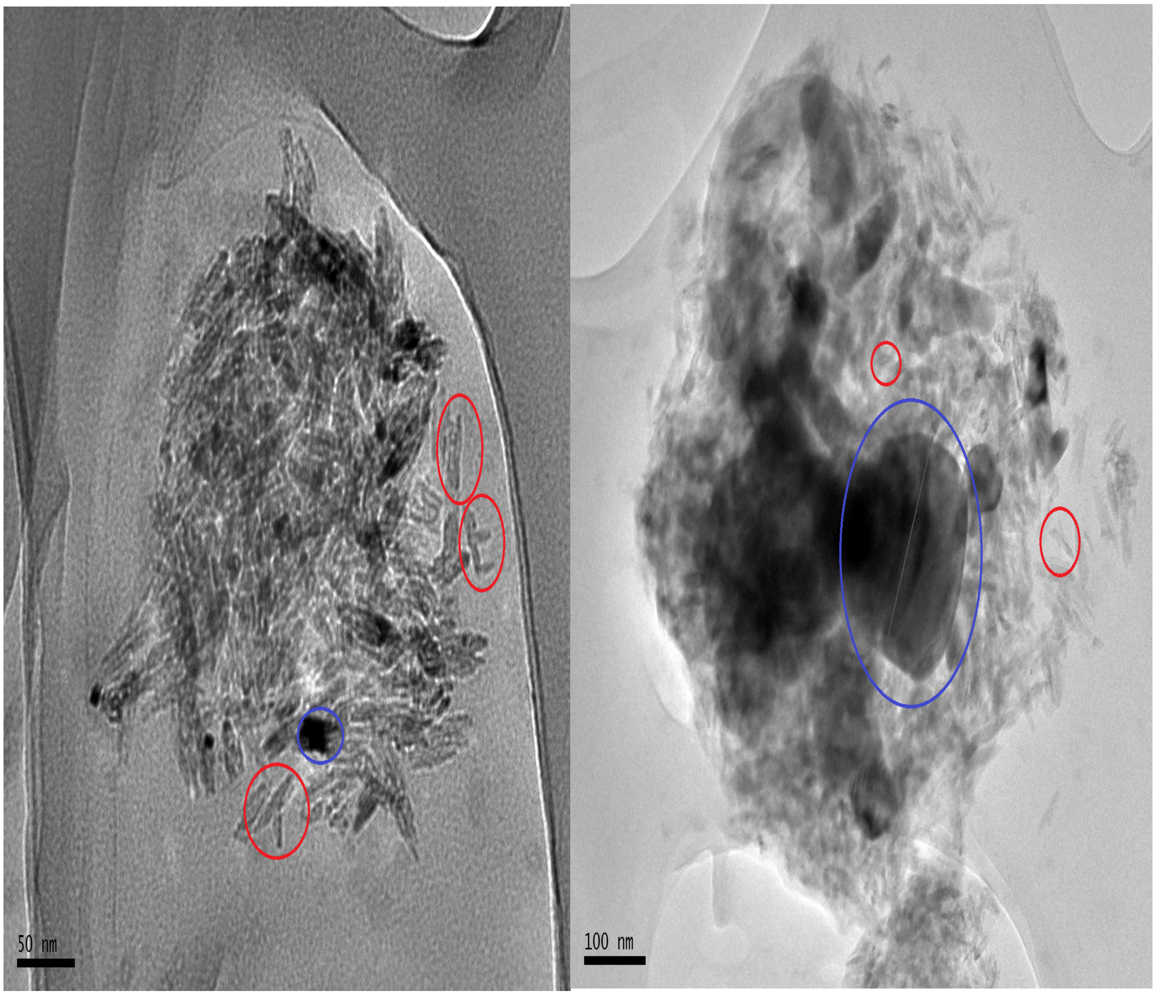


Figure 16: Spectra of Sample III in Figure (a)

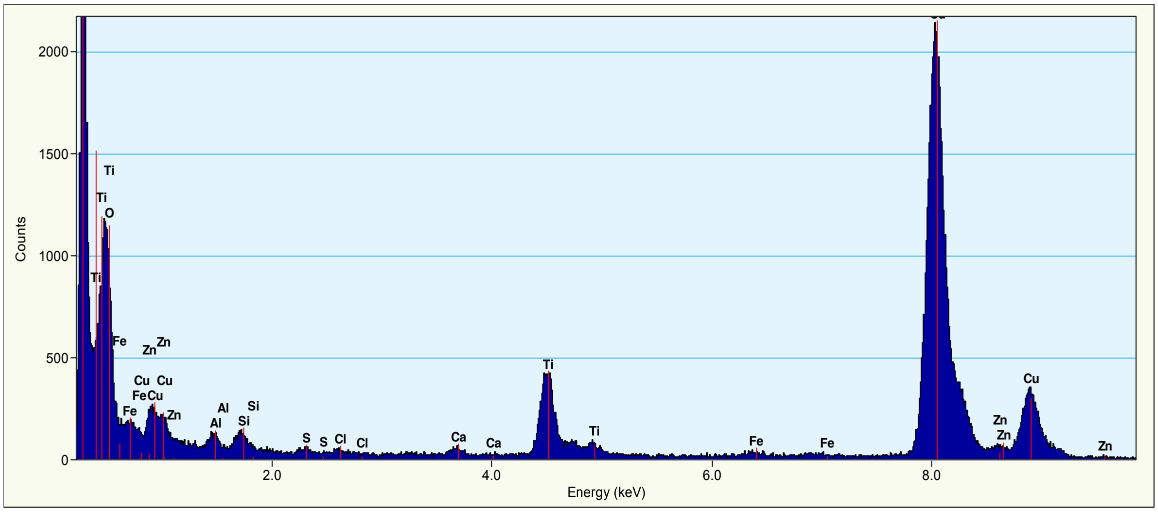


Figure17: Spectra of Sample III in Figure (b)

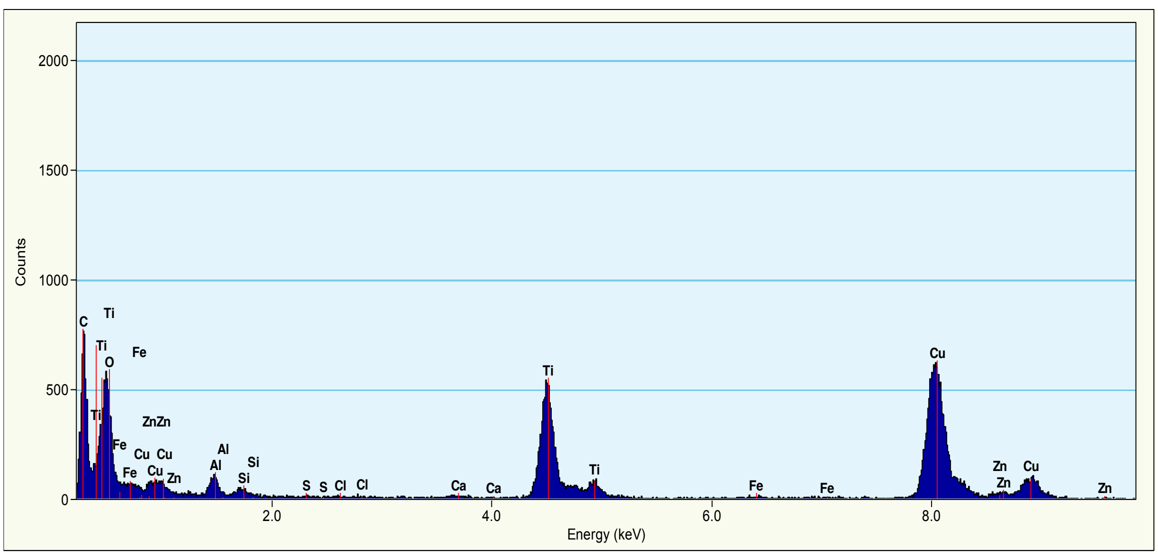


Figure 18: Energy losses for 1 kilogram of nano-TiO2 produced in terms of natural gas, crude oil and hard coal

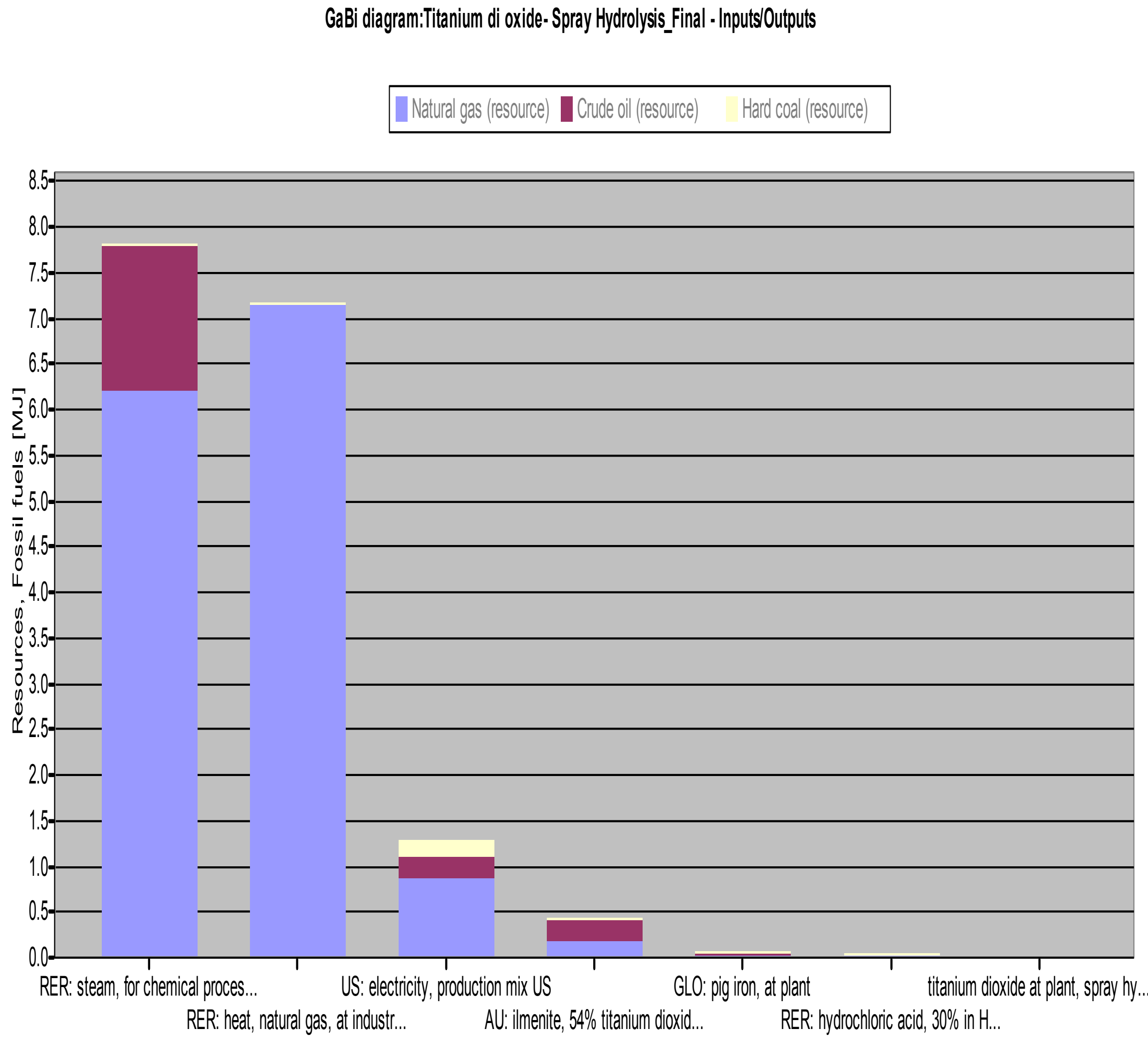


Figure 19: Normalized and weighted impacts of 1 kilogram of nano-TiO_2 production.

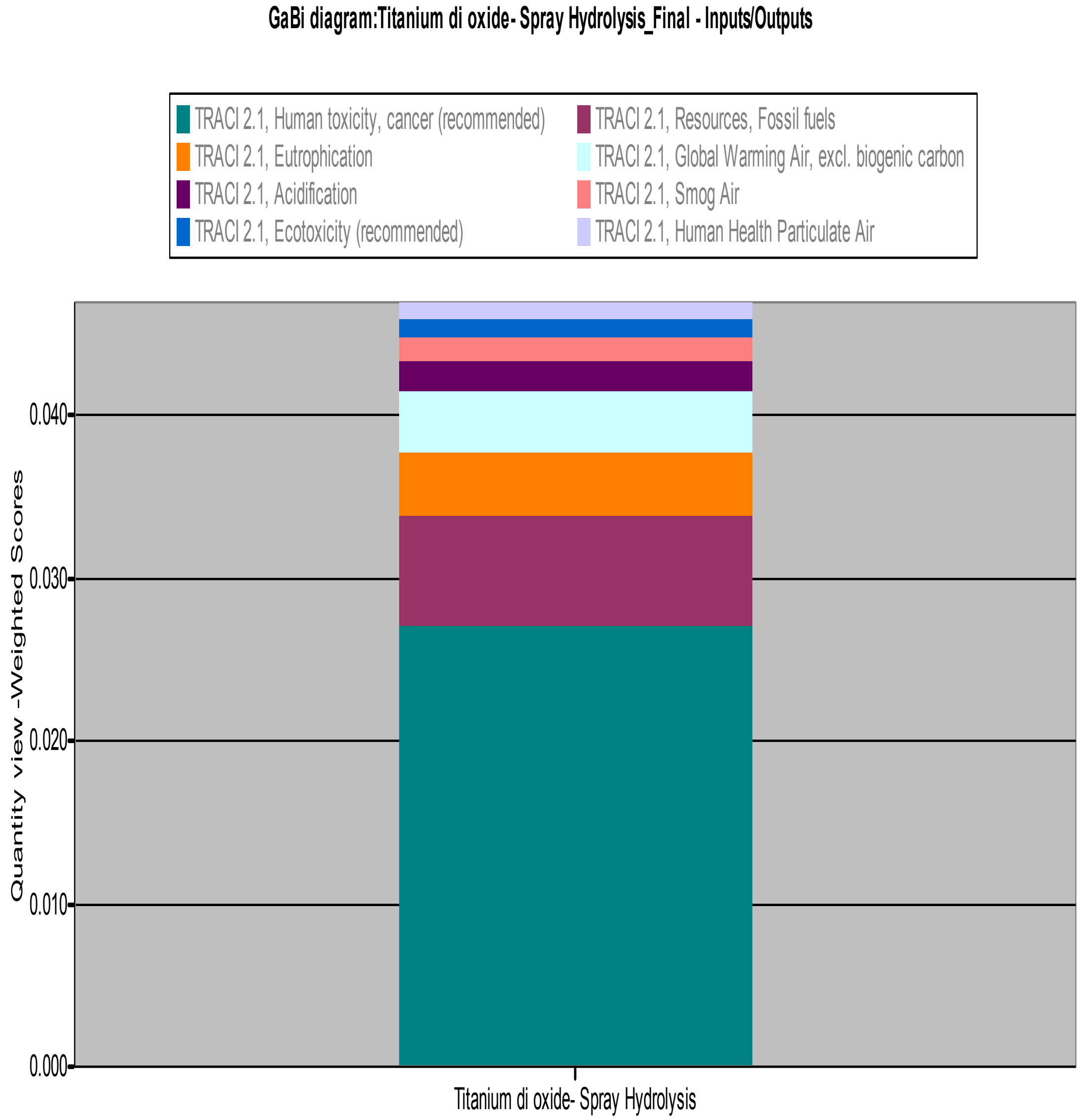


Figure 19: Comparison of energy use for nano-TiO2 to the conventional organic chemical UV-blockers (octocrylene and avobenzone) in terms of natural gas, crude oil and hard coal

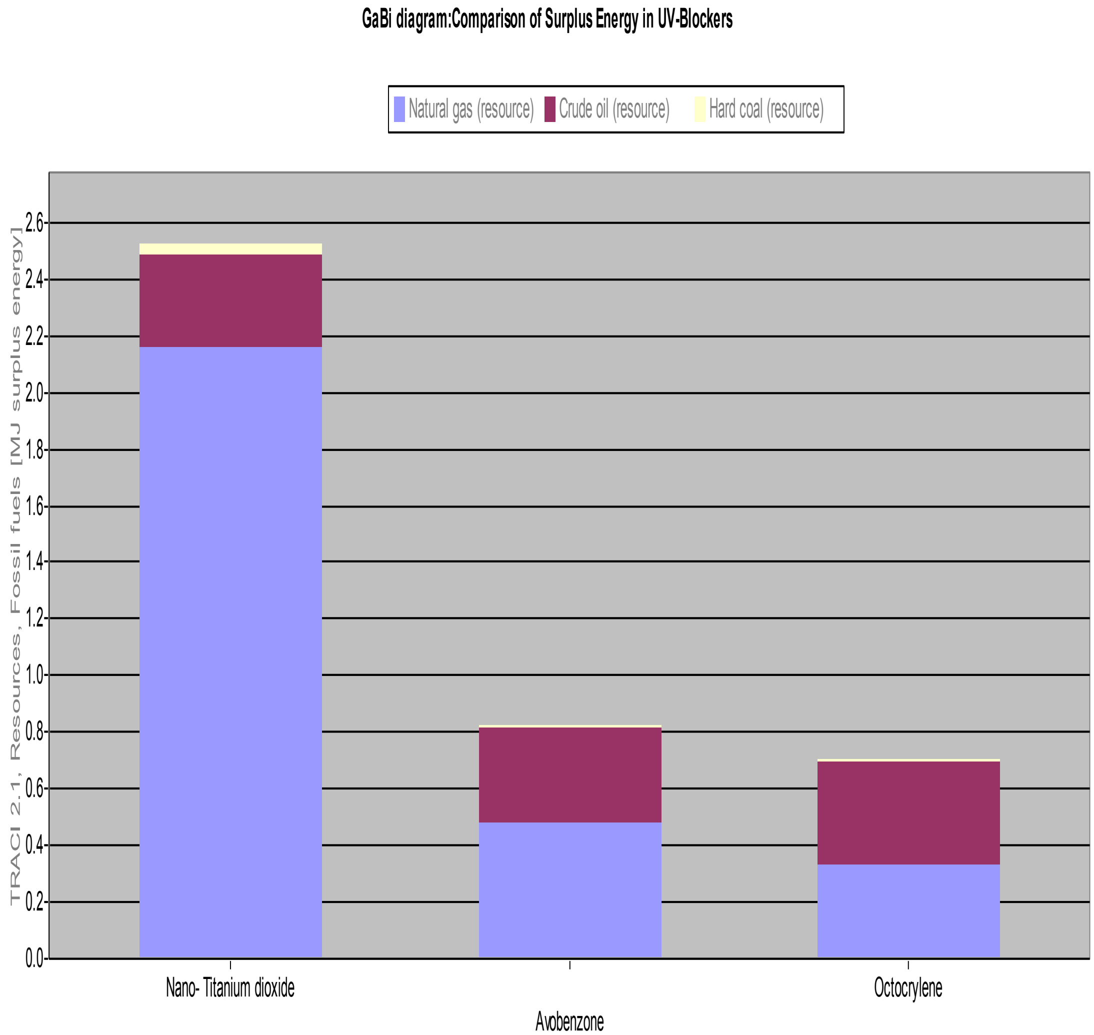


Figure 20: Comparison of impacts for the production of one kilogram of nano-TiO2, avobenzone and octocrylene.

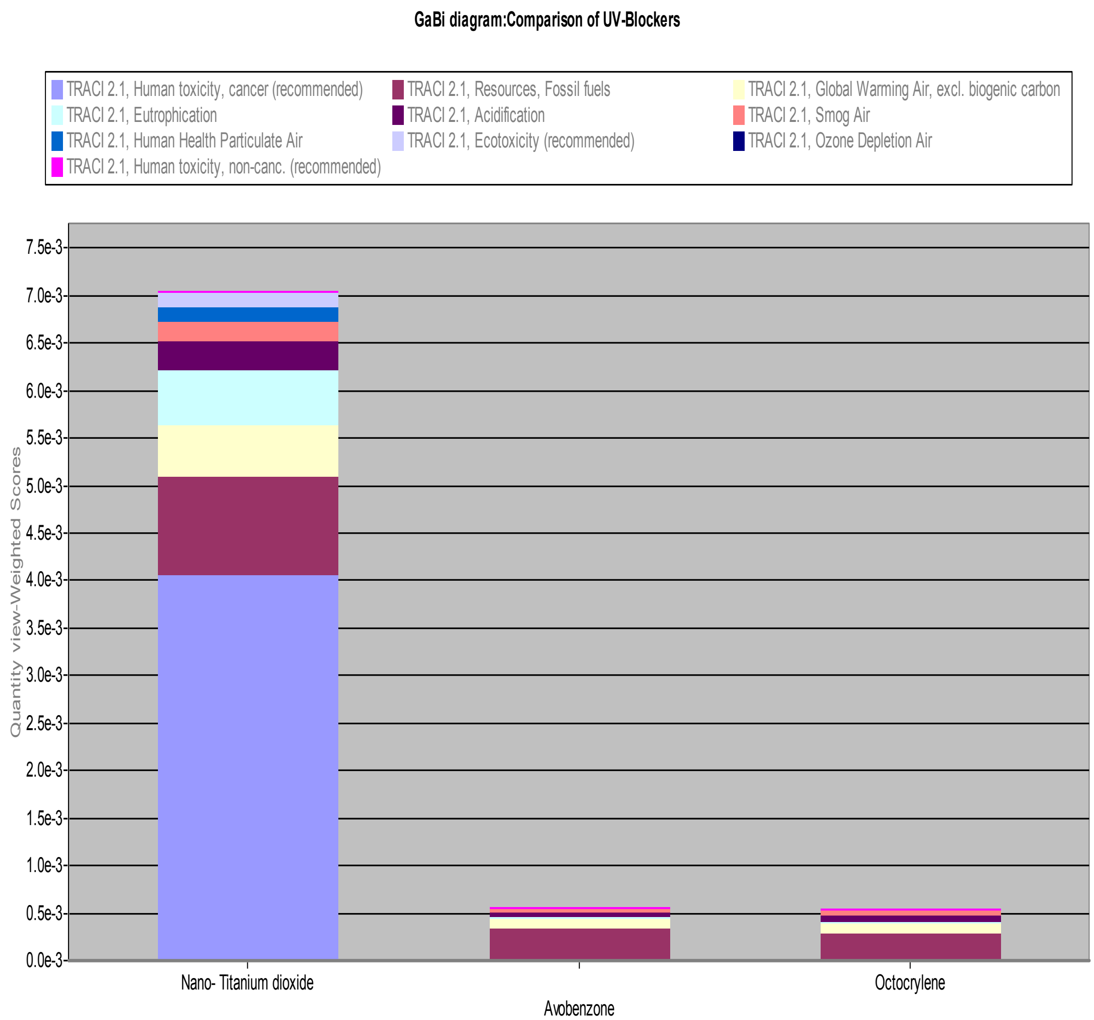


Figure 21: Comparison of energy losses in terms of natural gas, crude oil and hard coal for the production of one kilogram of organic chemical sunscreen variant versus nano-TiO_2 variant.

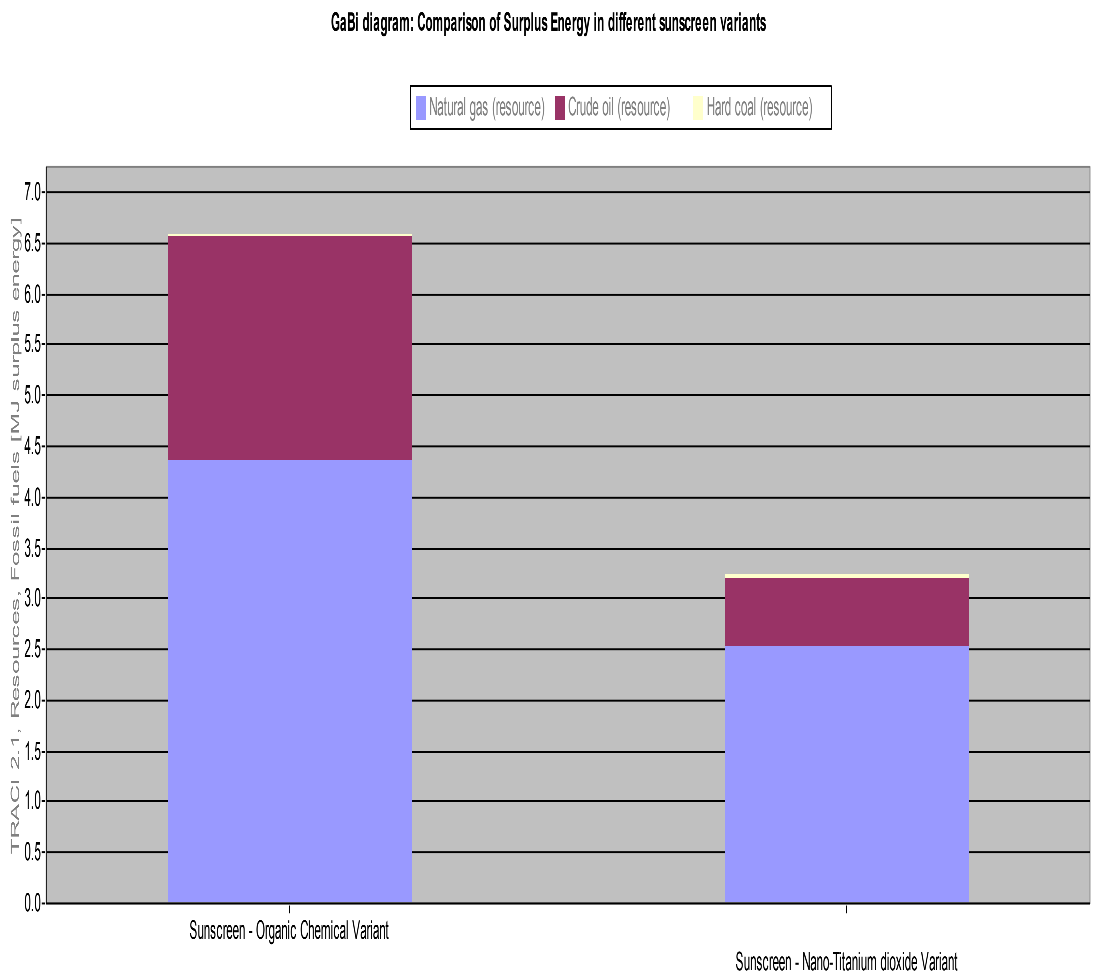


Figure 22: Comparison of impacts for the production of one kilogram of sunscreen lotion with organic chemical variant versus nano-TiO_2 variant

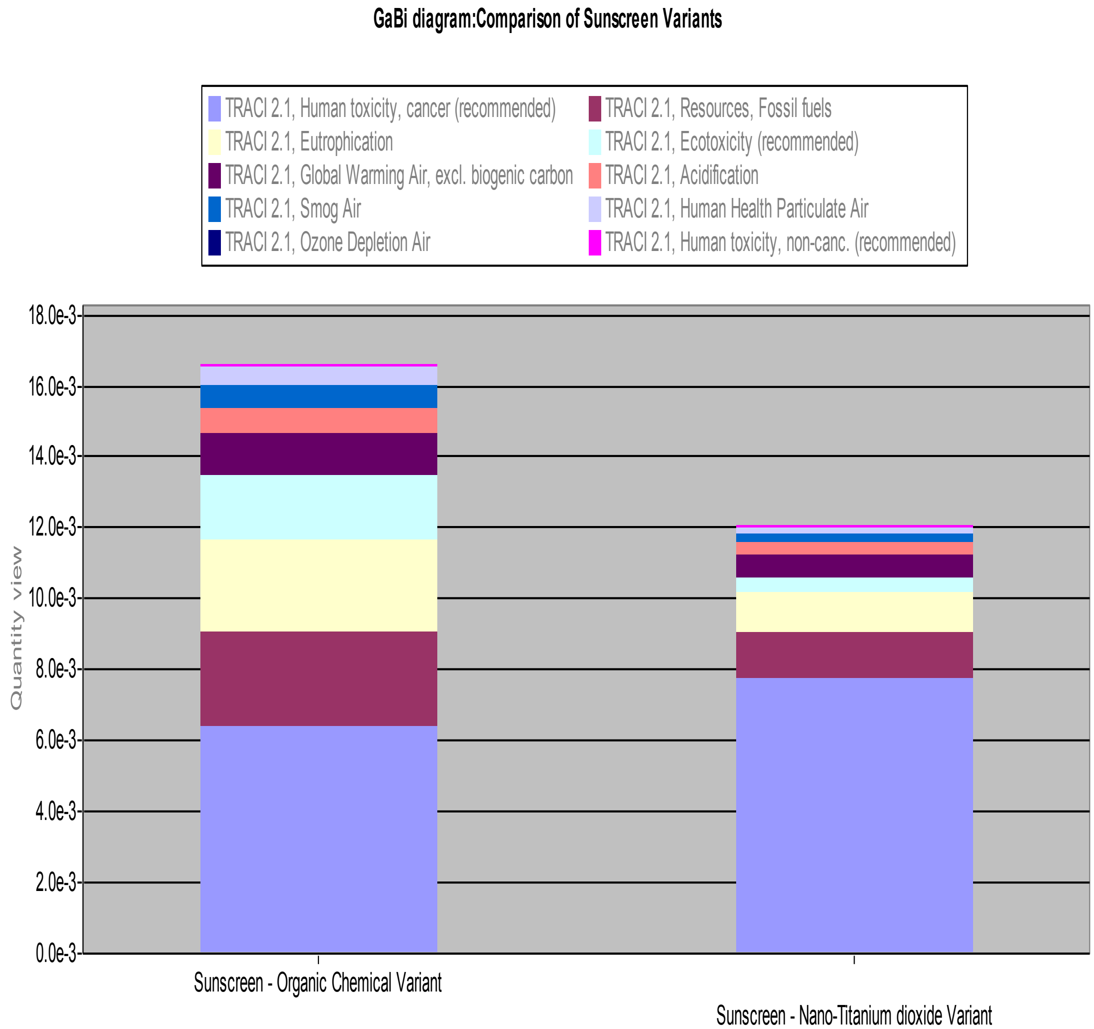


Table 8: Pedigree Matrix- Overall LCA

Indicator Score	1	2	3	4	5
Reliability of Source			The data found was for specific processes and qualified estimates were made for the processes which were not found, by the industrial experts.		
Completeness				Some of the data was out of date, and some of it used proxy processes. The data was representative, but was only found from the available sources. The majority of the data was obtained from the datasets available in GaBi and Patents available.	
Temporal Differences					Some of the data was recent, but much of it, on palm oil for example, was from a study undertaken

					from 1999 to 2003. Large portions of our data suffered this set back.
Geographical Differences			Most data was from Europe, using similar processes and subject to global market forces. Values are assumed to be similar to material production everywhere in the world.		
Further Technological differences		Processes described in the LCA match those studied. However, data was from different areas. Technology processes were normalized to the system studied as best they could be, though processes are very similar regardless. The impact loads were mostly accounted for using LCA methodology.			

Table 9: Pedigree Matrix for nano-TiO2 production process

Indicator Score	1	2	3	4	5
Reliability of Source	Verified data, information from public or other independent source				
Completeness				The data was representative, but was only found from the available Patents.	
Temporal Differences			The data was from less than 10 years of the difference.		Some of the data was recent, but much of it, on palm oil for example, was from a study undertaken from 1999 to 2003. Large portions of our data suffered this set back.
Geographical Differences		Data from the area under study.			

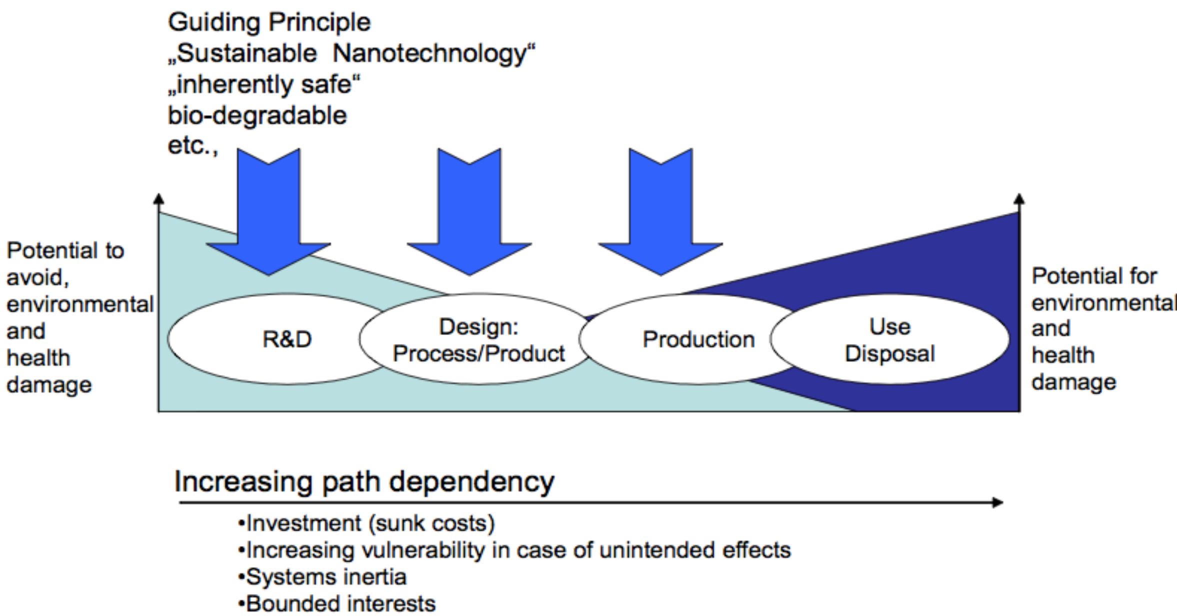
Further Technological differences		Data from processes and materials under study.			

CHAPTER-5

CONCLUSIONS AND FUTURE WORK

On the equal mass basis, the energy requirements and the impacts for producing nano-TiO_2 particles from Altair hydrochloride process are more as compared to the conventional organic chemical UV-blockers. Energy requirements and other impacts are similar to the chloride process for producing titanium dioxide which is the already existing commercial process. Steam production, ilmenite mining and natural gas production showed maximum energy losses in the Altair nano-TiO_2 production. The other major impact from the process is human toxicity which is due to the heavy metal emissions during the production of nano-TiO_2. Nano-TiO_2 is compared to the conventional organic chemical UV-blockers weighing the direct life cycle impacts of the two alternatives. Also, to study the comparison of the impacts at the product level, life cycle assessment of sunscreen lotion with nano-titanium dioxide as UV-blocker is done and is compared with the sunscreen lotion with avobenzone and octocrylene (conventional organic chemical UV blockers) as UV blockers. The sunscreen lotion with nano-titanium dioxide variant had lower life cycle impacts than the conventional organic chemical sunscreen variant. Although, most of the impacts came from nano-TiO_2 particles in the sunscreen, the other chemicals in the formulation did not contribute to much of the life cycle impacts. In the conventional organic chemical sunscreen most of the impacts came from glycerine, ethanol and avobenzone production. At the product level there are tradeoffs offs in few of the impacts categories, but overall the sunscreen with nano-titanium dioxide variant had lower impacts. The results of the LCA study demonstrate that various potential impacts for the upcoming new technology should be explored and studied for the fair comparison of different technologies. Previously, nanotechnology has been compared to their counter bulk material or other existing nanotechnology performing different functions. This LCA study is beneficial in giving the overview of comparison of materials performing the same function. It must also be pointed out that this approach can be used as a guiding principle for shaping the new technology towards future sustainability. Further it can be also be used as a part of product design to avoid the potential adverse effects of nanotechnology on environment and humans during the production, use and disposal of these materials. Following diagram shows the path dependency of any new technology (Steinfeldt, Petschow, & Haum, 2004):

Figure 23: Path Dependency of any new technology



Quelle: Haum et al. 2004

For the more clear and fair comparison, the data is needed at detailed unit process level for both raw material processing stage and product manufacturing stage. Studies should also be performed for relevant formulations in each industry, which are incorporating nanoparticles in their products. There is a need to study these nanoparticles according to their size and shape (Tyner, Wokovich, Godar, Doub, & Sadrich, 2011) and how each of them behaves in the environment throughout their life cycle, especially the behavior of these particles at end-of-life which is the least unexplored area.

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APPENDIX A

SUMMARY OF PRODUCTS USED FOR CHARACTERIZATION OF NANO-TITANIUM DIOXIDE

1.) Product Name: Kids broad spectrum mineral sunscreen, Nature's Gate

Information on Package: SPF 20, water resistant, free of fragrances, parabens, phthalates and oxybenzone. Apply liberally and evenly 15 minutes before sun exposure.

Ingredients:

Active Ingredients: Titanium dioxide 8.3%, Zinc oxide 2.0%

Inactive Ingredients: allantoin, aloe barbadensis leaf juice, altheaea offinalis (marshmallow) root extract, bisabolol, butyrospermum parkii butter, calendula officinalis flower extract, caprylic/capric triglyceride, carthamus tinctorius seed oil, cetearyl alcohol, cetearyl wheat straw glycosides, chamomilla recutita flower extract, dehydroxantham gum, diisopropyl adipate, dimethicone, ethylhexylglycerin, Euterpe olercea fruit extract, glycerin, glyceryl stearate, glyceryl undecylenate, hydrastis Canadensis extract, phenoxyethanol, polysorbate 80, propylheptyl caprylate, prunus armeniaca kernel oil, stearic acid, stearyl alcohol, triethoxycaprylysilane, viola tricolor extract, water.

1.) **Product Name**: Natural reflect sunscreen lotion, Banana Boat

Information on Package: SPF 50+, Active ingredients sourced from 100% natural minerals, paraben and PABA free, water resistant, oxybenzone-free, hypoallergenic and fragrance free.

Ingredients:

Active Ingredients : Titanium di-oxide 3.6%, Zinc oxide 4.0%

Inactive Ingredients: Water, caprylic/capric triglyceride, octyldodecyl citrate crosspolymer, butyloctyl salicylate, cetyl PEG/PPG-10 dimethicone, lauryl PEG-8 dimethicone, ozokerite, ethylhexyl methoxycrylene, C30-38 olefin/isopropyl maleate copolymer, sodium chloride, dimethicone, caprylyl glycol, PEG-8, alumina, glycerin, sodium citrate, tocopheryl acetate, aloe barbadensis leaf juice, phenoxyethanol

2.) **Product Name**: Sensitive Skin Sunscreen, Neutrogena

Information on Package: SPF 60, 100% naturally sourced sunscreen ingredients, fragrance free, water resistant

Ingredients:

Active Ingredients: Titanium Dioxide 4.9% , Zinc Oxide 4.7%

Inactive Ingredients: Alumina, arachidylalcohol, arachidyl glucoside, ascorbic acid, beeswax, behenyl alcohol,benzyl alcohol, BHT, bisabolol, butylene glycol, butyloctyl salicylate, cetyl dimethicone, dimethicone, dimethicone PEG-8 laurate, dipotassium glycyrrhizate, disodium EDTA, ethylhexylglycerin, glyceryl stearate, hydroxyl-ethyl acrylate, isohexadecane, methicone, methylisothiazolinone, pantothenic acid, PEG-100 stearate, PEG-8, polyaminopropyl biguanide, polyhydroxystearic acid, polymethyl metharylate, polysorbate 60, retinyl palmitate, silica, stearic acid, styrene/acrylates copolymer, tocopheryl acetate, triethoxycaprylylsilane, trimethylsiloxysilicate, trisiloxane, water, xanthan gum.

APPENDIX B

INPUT ENERGY CALCULATIONS

SUNSCREEN – NANO-TITANIUM DIOXIDE VARIANT

	m (mass in grams)	Cp (J/g K)	T in K	weight fraction(w)	Energy = w*Cp*T (J)
Deionised Water	700	4.18	40	0.7	117.04
Disodium EDTA	0.5	20.069	40	0.0005	0.40138
Hydroxypropyl Methyl Cellulose	1	4.5	40	0.001	0.18
Aminomethyl Propanol	3	2.68	40	0.003	0.3216
Butylene Glycol	10	2.24	40	0.01	0.896
Glycerine	20	2.377	40	0.02	1.9016
Methyl Gluceth-20	20	1.78	40	0.02	1.424
Diisopropyl Adipate	40	1.16	40	0.04	1.856
Cetyl hexanoate/Ester	20	2.16	40	0.02	1.728
Diisopropyl Dimer Dilinoleate/Ester	10	2.16	40	0.01	0.864
Methyl Glucose Sesquisterate/Ester	1.9	2.16	40	0.0019	0.16416
Acrylates\C10-30 alkyl acrylate crosspolymer	1.8	1.27	40	0.0018	0.09144
Acrylates\C10-30 alkyl acrylate crosspolymer	1.8	1.27	40	0.0018	0.09144
Nano Titanium Di-oxide	150	0.15	40	0.15	0.9
Polyglyceryl	10	2.24	40	0.01	0.896
Proplyene glycol	5	2.51	40	0.005	0.502
Parabens	5		40	0.005	0
	1000				
				Total Energy (J)	82.26936858

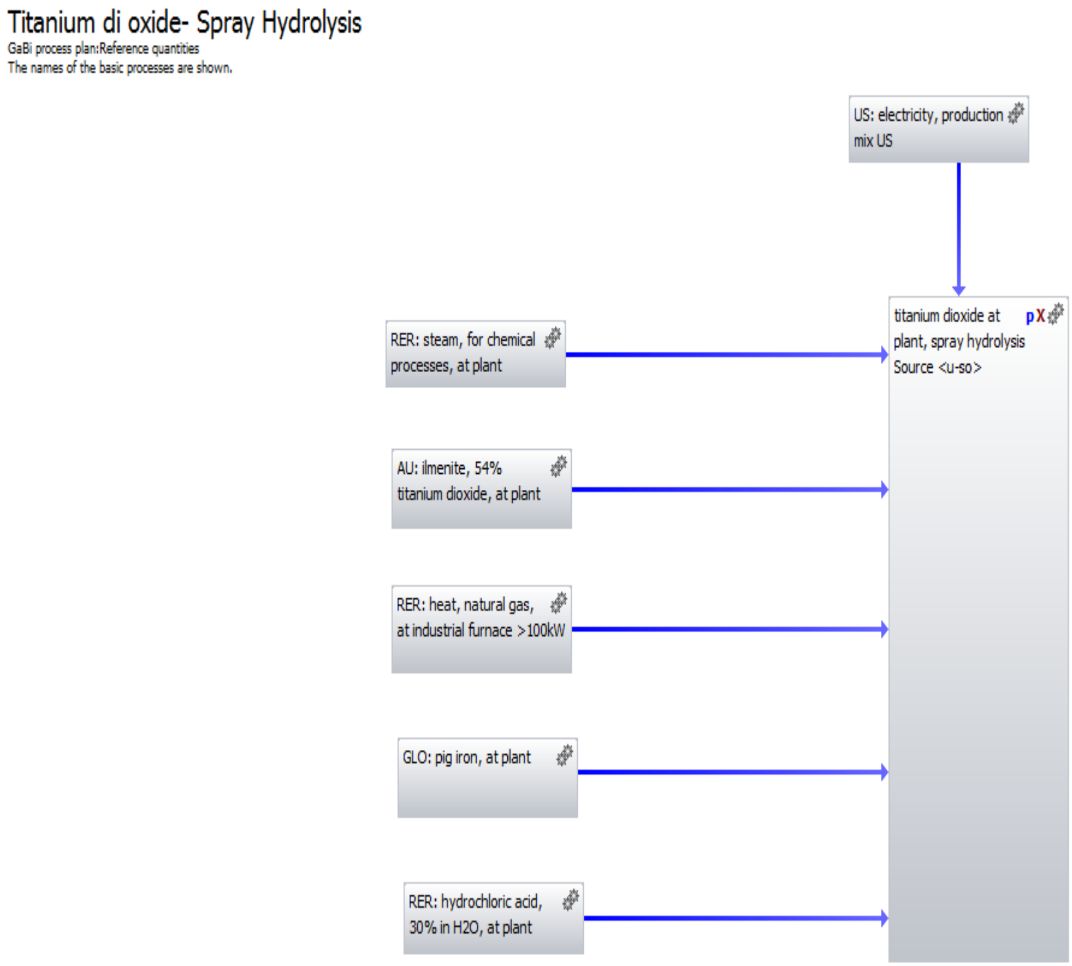
SUNSCREEN – OCTOCRYLENE AND AVOBENZONE VARIANT

	m(mass in grams)	Cp (J/g K)	T in K	weight fraction (w)	Energy = w*Cp*T(J)
A.Deionised Water	250.2	4.18	20	0.2502	20.91672
Carbomer/Xantham gum	4	4.5	20	0.004	0.36
Glycerin	200	2.377	20	0.2	9.508
B.Methyl Gluceth-20	25	1.78	20	0.025	0.89
PPG-20 Methyl Glucose Ether	15	2.51	20	0.015	0.753
Proplyene Glycol(Hydrolite)	20	2.51	20	0.02	1.004
Butylene Glycol	20	2.24	20	0.02	0.896
Ethyl Alcohol	250	2.46	20	0.25	12.3
C. Neopentyl Glycol Diethylhexanoate	80	2.18	20	0.08	3.488
Avobenzone - Butyl Methoxydibenzoylmethane	30	1.2	20	0.03	0.72
Octocrylene	100	1.38	20	0.1	2.76
Acrylates/ C10-30 Alkyl Acrylate Crosspolymer	1.5	1.27	20	0.0015	0.0381
D. Sodium Hydroxide(18%)	1.8	28.23	20	0.0018	1.01628
E. DMDM Hydantoin, Iodopropynyl Butylcarbamate	2.5		20	0.0025	0
	1000				
				Total Energy (J)	54.6501

APPENDIX C

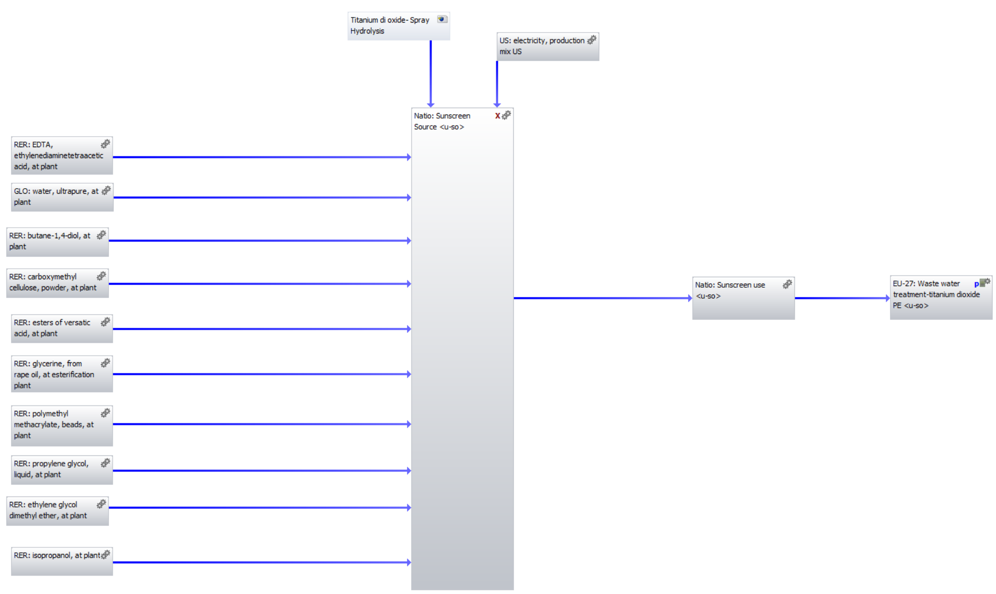
GABI MODELING

TITANIUM DI OXIDE – SPRAY HYDROLYSIS PROCESS



SUNSCREEN- TITANIUM DI OXIDE AS UV BLOCKER

Sunscreen - Titanium di oxide as UV blocker
GaBi process plan:Reference quantities
The names of the basic processes are shown.



SUNSCREEN – ORGANIC CHEMICAL AS UV BLOCKER