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LIFE CYCLE ASSESSMENT AS A TOOL FOR GREEN CHEMISTRY: APPLICATION TO KRAFT PULP INDUSTRIAL WASTEWATER TREATMENT BY DIFFERENT ADVANCED OXIDATION PROCESSES

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Abstract

Life Cycle Assessment (LCA) is used to evaluate a chemical process from an environmental point of view. The objective is to assess its usefulness as a tool for Green Chemistry (GC). In order to show the benefits of the tool, it is applied to compare different Advanced Oxidation Processes (AOPs) applied for the treatment of kraft mill bleaching wastewaters containing organic halogens. The treatments considered are photocatalysis (PhC), fenton and photo-fenton reactions (FPhF), the coupling of these two processes (PhC+FPhF), photocatalysis in combination with hydrogen peroxide (PhC+H2O2), ozonation (O3), and ozonation in the presence of UVA light (O3+UVA). These processes are assessed under three scenarios concerning the energy source used: electricity from the grid, electricity produced by co-generation in the mill, and solar energy. The results show that using solar energy instead of grid electricity reduces the impact more than 90% for all AOPs, but with the available data it is not clear which of the treatments has the least environmental impact if solar energy is used. Producing electricity by co-generation in the kraft mill reduces the impact for all AOPs about 50% as compared to grid electricity. If grid electricity or co-generation electricity is used, the preferable AOP is PhC+FPhF, and it is not clear if the worst options are PhC, O3 or O3+UVA due to uncertainty in the data used for ozone-based treatments. The economic costs of the AOPs are also estimated, showing that environmental impact is proportional to cost. It can be concluded that LCA seems to be a valuable tool for GC, because it takes into account and quantifies all the life cycle stages and discusses a diversity of impact categories.

Keywords: Life Cycle Assessment, Green Chemistry, Advanced Oxidation Processes, photocatalysis, fenton and photo-fenton, ozonation, co-generation, solar energy.

1. PURPOSE

The aim of the present work is to apply Life Cycle Assessment (LCA) to a chemical reaction in order to assess the suitability of this tool for environmental evaluation of chemical products and chemical processes. In order to show the benefits of the tool, it is applied in a case study that compares different Advanced Oxidation Processes (AOPs) applied to treat kraft pulp mill wastewaters.

Therefore, two objectives can be identified:

- A general objective is to assess the usefulness of the LCA methodology to be applied in Green Chemistry (GC), thus contributing to its acceptance as a tool for environmental assessment in this area.

- A specific objective is to apply LCA to a chemical process, prior to its implementation at industrial scale, so that preliminary environmental information can be obtained. The analysed process is the advanced oxidation of industrial pulp bleaching effluents, using different techniques: photocatalysis, Fenton and photo-Fenton, ozonation, and some combinations of these processes.

2. *INTRODUCTION*

This chapter introduces Green Chemistry (GC) and Life Cycle Assessment (LCA), as well as the possible connection between these two approaches.

2.1. Green Chemistry (GC)

In this chapter, the concept of Green Chemistry, its background as well as its applications are briefly described.

2.1.1. Definition

Introduced in the early 1990's, Green Chemistry is an approach to addressing the environmental consequences of products or processes at the design stage (Anastas & Lankey, 2000). A new but straightforward method, Green Chemistry is defined as:

"The use of chemistry for pollution prevention by means of a proper design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances" (Anastas & Warner, 1998).

For the purposes of this definition, the use of the term "chemistry" is used in its formal definition as applying to the structure and transformation of all matter, making the applicability extremely broad. It should be noted that since the consequences of energy generation and use are directly and inextricably linked to the materials used to generate, capture, store, and transport it, energy concerns are inherently addressed by the above definition. Therefore, the methods and techniques of Green Chemistry address these issues at the design stage, and at the most fundamental level, i.e. the molecular level, dealing with the intrinsic rather than the circumstantial properties of a product or process (Anastas & Lankey, 2000).

Another clarification in the above definition is the term hazardous. The hazards in this definition include, but are not limited to, toxicity, physical hazards, (*eg* explosions, fires), global climate change, and resource depletion (see the 12 principles in chapter 2.1.3).

During the introduction of pollution prevention as a way of achieving environmental goals, Green Chemistry was immediately recognized as a tool for decreasing waste and emissions at the source. It was also recognized as a powerful tool for sustainable technology and industrial ecology. Green Chemistry differs from historical approaches to environmental protection in several ways (Anastas & Lankey, 2001) :

- It addresses hazard rather than exposure
- It is economically driven rather than economically draining
- It is non - regulatory
- It prevents problems before they occur through avoidance approaches
- It considers the full life cycle impacts at the design stage

2.1.2. GC background

In the United States, the Pollution Prevention Act (PPA) of 1990 stablished source reduction as the highest priority in solving environmental problems (Anastas & Kirchhoff, 2002). Shortly after the passage of the PPA it was recognized that a variety of disciplines needed to be involved in source reduction. This recognition extended to chemists, the designers of molecular structures and transformations. In 1991, the Office of Pollution Prevention and Toxics in the U.S. Environmental Protection Agency (EPA) launched the first research initiative of the Green Chemistry Program, the Alternative Synthetic Pathways Research Solicitation. In 1993, the EPA program officially adopted the name "U.S. Green Chemistry Program", which has served until today as a focal point for major activities in the U.S., such as the Presidential Green Chemistry Challenge Awards and the Annual Green Chemistry and Engineering Conference.

In the first half of the 1990's, both Italy [1] and the United Kingdom [2] launched major initiatives in Green Chemistry, establishing research and education programs in Green Chemistry. During the last half of the decade, Japan organized the Green and Sustainable Chemistry Network (GSCN) [3]. Nowadays, Japan Italy, the U.K., Australia, and other nations have adopted Green Chemistry awards.

The first books, papers, and symposia on the subject were introduced in the 1990's, and the inaugural edition of the journal *Green Chemistry*, sponsored by the Royal Society of Chemistry, appeared in 1999[4]. Since the early 1990's, Green Chemistry has grown internationally. Major research, education, and outreach initiatives have been established around the globe (Anastas & Kirchhoff, 2002).

2.1.3. The twelve principles

The design of environmentally benign products and processes may be guided by the 12 Principles of Green Chemistry (Anastas & Warner, 1998), listed below. These principles are a categorization of the fundamental approaches taken to achieve the goal of pollution

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[1] http://www.helios.unive.it/inca

[2] http://www.chemsoc.org/networks/gcn

[3] http://www.gscn.net/

[4] http://www.rsc.org/is/journals/current/green/greenpub.htm

prevention, and have been used as guidelines and design criteria by molecular scientists (Anastas & Kirchhoff, 2002).

1. **Prevention**: It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom economy**: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less hazardous chemical syntheses**: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing safer chemicals**: Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. **Safer solvents and auxiliaries**: The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Design for energy efficiency**: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of renewable feedstocks**: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce derivatives**: Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for degradation**: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time analysis for pollution prevention**: Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.
12. **Inherently safer chemistry for accident prevention**: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

As it has been shown, Green Chemistry offers an interesting framework for chemists and engineers to design “environmentally friendly” processes and products; the twelve principles are useful as guidelines. However, they don’t allow for a quantitative assessment of the environmental improvements achieved by applying them, therefore tools are needed in order to do this. In the present study Life Cycle Assessment (LCA) is suggested to be the adequate tool for this purpose, because it takes into account all the steps of the whole life of the chemical product or process and considers different environmental impacts; its usefulness is tested in the present study through the application to the environmental assessment of a chemical process.

2.2. Life Cycle Assessment (LCA)

LCA is introduced in this chapter, with a brief definition, background, and describing the methodology.

2.2.1. Definition

LCA is an environmental management tool increasingly used to predict and compare the environmental impacts of a product or service, "from cradle to grave". The International Standards Organisation (ISO) has defined LCA as:

"A technique for assessing the environmental aspects and potential impacts associated with a product by:

- *Compiling an inventory of relevant inputs and outputs of a product system,*
- *Evaluating the potential environmental impacts associated with those inputs and outputs,*
- *interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study"* (ISO 14.040).

The technique examines every stage of the life cycle, from the winning of the raw materials, through manufacture, distribution, use, possible re-use/recycling and then final disposal. For each stage, the inputs (in terms of raw materials and energy) and outputs (in terms of emissions to air, water, soil, and solid waste) are calculated, and these are aggregated over the Life Cycle. These inputs and outputs are then converted into their effects on the environment, i.e. their environmental impacts. The sum of these environmental impacts then represents the overall environmental effect of the Life Cycle of the product or service. Conducting LCAs for alternative products allows comparison of their overall environmental impacts.

2.2.2. LCA background

The origins of the LCA methodology can be traced to the late 1960's (Miettinen & Hamalainen, 1997). Initial studies were simple and generally restricted to calculating energy requirements and solid waste. During the oil crisis of the early 1970's, extensive energy studies based on Life Cycle Inventories (LCI) were performed for a range of industrial systems (Fava & Page, 1992). By the end of the 1980's, numerous studies using LCA had been performed, mainly by private companies in Sweden, Switzerland and the USA (Huppes, 1996; Udo de Haes, 1993). However, these studies were performed using different methods and without a common theoretical framework.

Since 1990, attempts have been made to develop and standardise the LCA methodology under the coordination of the Society of Environmental Toxicology and Chemistry (SETAC) (Udo de Haes, 1993). In 1993 SETAC published a "Code of Practice", which presents general principles and a framework for the conduct, review, presentation and use of LCA findings. An international standard for LCA put together by the International Standards Organisation has recently emerged (Box 1). Azapagic (1999) has reviewed aspects of the ISO standards, and compared them with the SETAC methodology, finding that both are similar. The main difference is the interpretation stage, where ISO includes further analysis and sensitivity studies.

Box 1. The ISO 14.040 series on LCA.

- ISO 14.040 Environmental Management – Life Cycle Assessment – Principles and Framework (ISO 1997).
- ISO 14.041 Environmental Management – Life Cycle Assessment – Goal and Scope Definition and Inventory Analysis (ISO 1998).
- ISO 14.042 Environmental Management – Life Cycle Assessment – Life Cycle Impact Assessment (ISO/FDIS, 1999).
- ISO 14.043 Environmental Management – Life Cycle Assessment – Life Cycle Interpretation (ISO 1999).

Source: Mc Dougall et al., 2001.

2.2.3. Methodology

The ISO 14.040 standard determines four basic stages for LCA studies, graphically represented in Figure 1, and briefly described below.

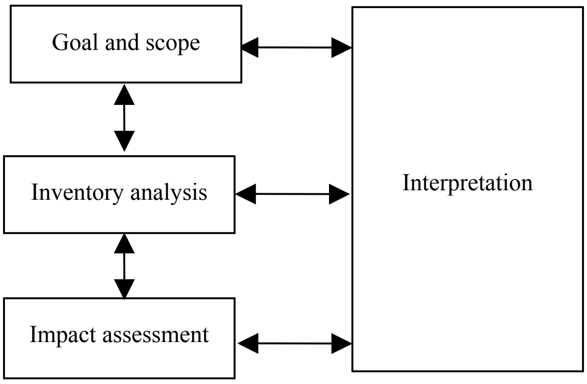

Figure 1. Stages in a LCA study. Source: ISO 14.040

2.2.3.1. Goal and scope

This is the first stage of the study and probably the most important, since the elements defined here, such as purpose, scope, and main hypothesis considered are the key of the study. This is an interactive stage, so if during the development of the study new information or data is found, it may be advisable to make changes in this stage.

In first place, the goal of the study is defined, as well as the reasons that have lead to its realization, the kind of decisions that will be made from the results obtained, and if these will be of internal use (for a company, for instance) or external (to inform the general public or an institution).

Secondly, the scope of the study is defined. Usually this implies defining the system, its boundaries (conceptual, geographical and temporal), the quality of the data used, the main hypothesis and *a priori* limitations. A key issue in the scope is the definition of the functional unit. This is the unit of the product or service whose environmental impacts will be assessed or compared. It is often expressed in terms of amount of product, but should really be related to the amount of product needed to perform a given function.

2.2.3.2. Inventory analysis

The inventory analysis is a technical process of collecting data, in order to quantify the inputs and outputs of the system, as defined in the scope. Energy and raw materials consumed, emissions to air, water, soil, and solid waste produced by the system are calculated for the entire life cycle of the product or service.

In order to make this analysis easier, the system under study is split up in several subsystems or processes (Figure 2), and the data obtained is grouped in different categories in a LCI table.

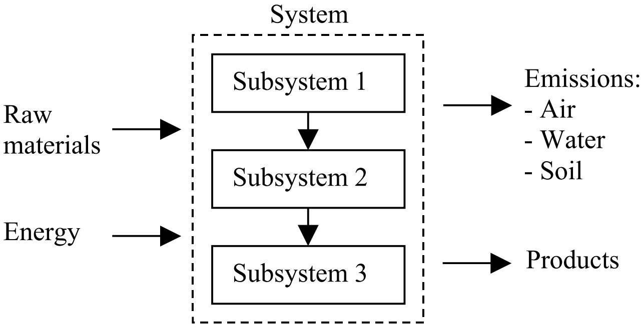

Figure 2. Schematic diagram of a system. Inputs and outputs are the elements to be determined in the inventory analysis. Source: Fullana & Puig, 1997.

2.2.3.3. Impact assessment

Life Cycle Impact Assessment (LCIA) is a process to identify and characterise the potential effects produced in the environment by the system under study. The starting point for LCIA is the information obtained in the inventory stage, so the quality of the data obtained is a key issue for this assessment. LCIA is considered to consist of four steps that are briefly described below.

The first step is Classification, in which the data originated in the inventory analysis are grouped in different categories, according to the environmental impacts they are expected to contribute.

The second step, called Characterisation, consists of weighting the different substances contributing to the same environmental impact. Thus, for every impact category included in LCIA, an aggregated result is obtained, in a given unit of measure.

The third step is Normalisation, which involves relating the characterised data to a broader data set or situation, for example, relating SO_x emissions to a country's total SO_x emissions.

The last step is Weighting, where the results for the different impact categories are converted into scores, by using numerical factors based on values. This is the most subjective stage of an LCA and is based on value judgements and is not scientific. For instance, a panel of experts or public could be formed to weight the impact categories. The advantage of this stage is that different criteria (impact categories) are converted to a numerical score of environmental impact, thus making it easier to make decisions. However, a lot of information is lost, and reality is simplified.

2.2.3.4. Interpretation

This is the last stage of the LCA, where the results obtained are presented in a synthetic way, presenting the critical sources of impact and the options to reduce these impacts. Interpretation involves a review of all the stages in the LCA process, in order to check the consistency of the assumptions and the data quality, in relation to the goal and scope of the study.

2.2.4. Benefits and limitations of the life cycle approach

Life Cycle Assessment is an inclusive tool. All necessary inputs and emissions in many stages and operations of the life cycle are considered to be within the system boundaries. This includes not only inputs and emissions for production, distribution, use and disposal, but also indirect inputs and emissions – such as from the initial production of the energy used – regardless of when or where they occur. If real environmental improvements are to be made by changes in the product or service, it is important not to cause greater environmental deteriorations at another time or place in the Life Cycle.

LCA offers the prospect of mapping the energy and material flows as well as the resources, solid wastes, and emissions of the total system, i.e. it provides a "system map" that sets the stage for a holistic approach.

The power of LCA is that it expands the debate on environmental concerns beyond a single issue, and attempts to address a broad range of environmental issues, by using a quantitative methodology, thus providing an objective basis for decision making.

Unfortunately, LCA is not able to assess the actual environmental effects of the system. The ISO 14.042 standard, dealing with Life Cycle Impact Assessment, specially cautions that LCA does not predict actual impacts or assess safety, risks, or whether thresholds are exceeded. The actual environmental effects of emissions will depend on when, where and how they are released into the environment, and other assessment tools must be utilised. For example, an aggregated emission released in one event from one source, will have a very different effect than releasing it continuously over years from many diffuse sources.

Clearly no single tool can do everything, so a combination of complementary tools is needed for overall environmental management. A summary of the most common tools or approaches is shown in Table 1, summarizing their characteristics and highlighting their strengths and weaknesses.

Table 1. Tools for environmental management.

Tool	Main characteristics	Advantages/disadvantages
Environmental Impact Assessment	Used to identify the environmental and socio-economic effects of one economic activity, usually at a specific location and at one point in time (UNEP, 1996).	**A**: Legally required. Detailed. Site and time specific. **D**: Usually qualitative. Little success in mitigating overall impacts. Not life-cycle based
Risk Assessment	Involves the estimation and evaluation of risk to the environment caused by a particular activity or exposure (Burgess & Brennan, 2001). The impacts may be on humans, aspects of flora or fauna, water, land, etc.	**A**: Quantitative. Assesses safety. Site and time specific. **D**: Not life-cycle based.
Cost-benefit Analysis	An economic value is estimated for any loss of environmental quality (termed an externality) not accounted for in within normal market pricing structures (Burgess & Brennan, 2001).	**A**: Monetary values easily understood. **D**: Uncertainty and complexity assessing externality value.
Corporate Environmental Performance	Framework provided by ISO 14.031, for environmental performance evaluation based on environmental indicators, and operational performance indicators (Chambers et al., 2000).	**A**: Illustrates material and energy intensity of production and services. **D**: Not life-cycle based.
Material Intensity per Unit Service (MIPS)	Approach to material accounting, combining life cycle analysis and material accounting, to determine the overall mass transformed for a given process (Chambers et al., 2000).	**A**: Quantitative. Life cycle based. **D**: Assumes same ecological impact for all materials.
Ecological Footprint	Estimates resource use of a population, region, or process in surface units. Takes into account: built-up, agricultural, pasture, forest, CO_2 absorption land, and sea (Chambers et al., 2000).	**A:** Easily understood. Quantitative. **D:** Used mainly to assess regional sustainability. Difficult to include other categories than CO_2 in process assessment.
Life Cycle Assessment	Takes into account all inputs (energy, resources) and outputs (emissions, waste) through the entire life cycle of a product or process, expressing them as potential environmental impacts.	**A**: Life-cycle based. Quantitative. Expresses environmental impacts. Detailed. **D**: Large quantity of data needed. Environmental impacts are only potential and not real.

2.3. Why combine LCA and GC?

In the recent years several approaches or tools have been developed for environmental management for different purposes, as it has been shown in Table 1. The purpose of this chapter is to focus on the potential suitability of LCA to assess the “greenness” or the degree of sustainability of chemical products and processes.

An essential aspect of Green Chemistry is that it can facilitate environmental improvements at every stage of the life cycle of the product or process (Anastas and Lankey, 2000), as can be seen in Figure 3. If one or more of these improvements are to be assessed quantitatively, LCA can be an adequate tool, allowing not only the assessment of the consequences of these improvements at the stages they are made, but at all of them.

As it has been already mentioned, Green Chemistry offers twelve principles as practical guidelines for chemists and engineers. However, these principles are qualitative. If the implementation of one or more of these principles is to be carried out in a given process or product, which one should be a priority? or, is it possible that adopting one principle may be detrimental to another?. By using LCA, these questions can be answered, since the "hotspots" in the life cycle are highlighted, and the effects in different environmental impacts can be assessed.

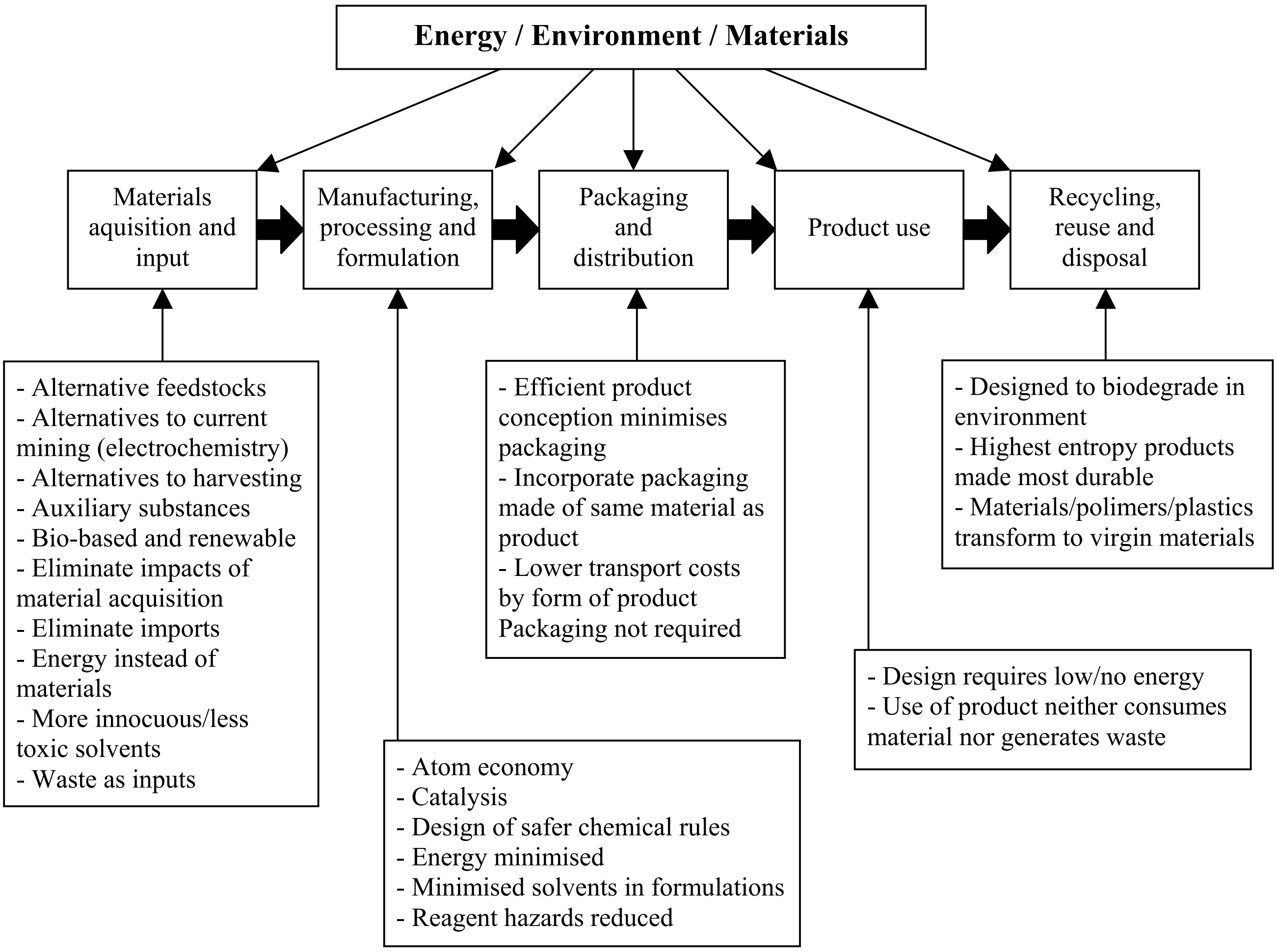

Figure 3. Summary diagram showing how specific innovations in pollution prevention can be achieved at each stage of the Life Cycle. Source: Anastas & Lankey, 2000.

A practical case study to assess the "cleanliness" of a chemical reaction by means of LCA has been carried out by Domènech et al. (2002), comparing two different routes for maleic anhydride production (Figure 4, Table 2).

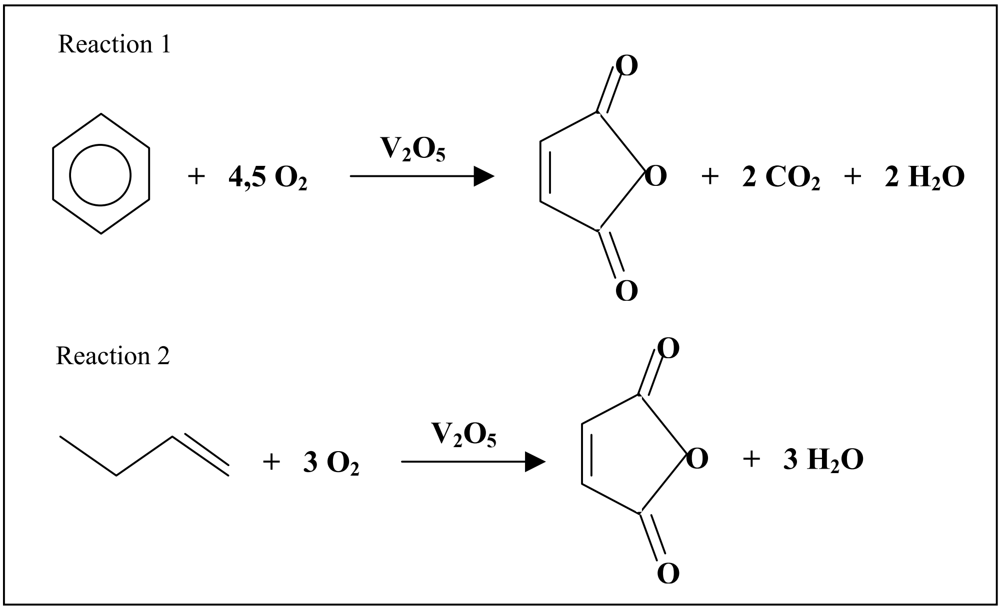

Figure 4. Two alternative pathways for maleic anhydride production. Source: Domènech et al., 2002.

Table 2. Environmental comparison of the different maleic anhydride production pathways.

Reaction	Description	Atom efficiency (%)			LCA Results (%) *					
		C	O	H	GWP	AP	EP	OFP	EC	SWP
1	Production of maleic anhydride using benzene as feedstock	67	33	33	100	100	100	100	100	100
2	Production of maleic anhydride using butene as feedstock	100	50	25	8	73	66	62	68	91

GWP: Global Warming Potential; AP: Acidification Potential; EP: Eutrophication Potential; OFP: Oxidant Formation Potential; Energy Consumption; SWP: Solid Waste production.
*** Relative values. Reaction 1 constitutes 100% impact.**
Source: Domènech et al., 2002.

As can be seen from the data in Table 2, the butene route for maleic acid production shows a lower environmental impact with regard to the benzene route, decreasing from 9% in SWP to 92% in GWP. The results of this case study reinforce the atom economy principle, and the authors conclude that LCA seems to be a valuable tool to evaluate, from an environmental point of view, a better way to obtain a chemical product.

3. LCA APPLICATION TO AOPs

In this chapter LCA is applied to AOPs used to treat paper pulp industrial wastewaters, in order to assess and compare them from an environmental point of view.

3.1. Goal

As it has been stated in chapter 1, the objective of this LCA case study is to compare different emerging technologies for advanced oxidation of industrial wastewaters from the kraft pulp industry. The assessed technologies are: photocatalysis, Fenton and photo-Fenton, ozonation, and some combinations of these processes.

The general purpose is to contribute to the acceptance of LCA as a tool for "green" design of chemical products and processes, by showing the kind of information that the tool is able to provide in a practical application. Since part of the data used is derived from laboratory experiments, the extrapolation of the results to industrial scale is limited. However, this preliminary assessment may highlight the critical sources of environmental impact in the process life cycle, and the areas where improvements should be made when implementing these techniques to a larger scale.

3.2. Scope

The scope of the study introduces and describes the system under study, and the different elements needed to perform the LCA, such as the function and functional unit, the system boundaries, or the data used, among others.

3.2.1. Pulp industry and water pollution

The pulp and paper industry has historically been considered a major consumer of natural resources (wood) and energy (fossil fuels, electricity), including water, and a significant contributor to pollutant discharges to the environment (EIPPCB, 2000). An overview of the kraft pulp process is presented in Figure 5, whereas Figure 6 shows the mass and energy flows of environmental relevance in the process.

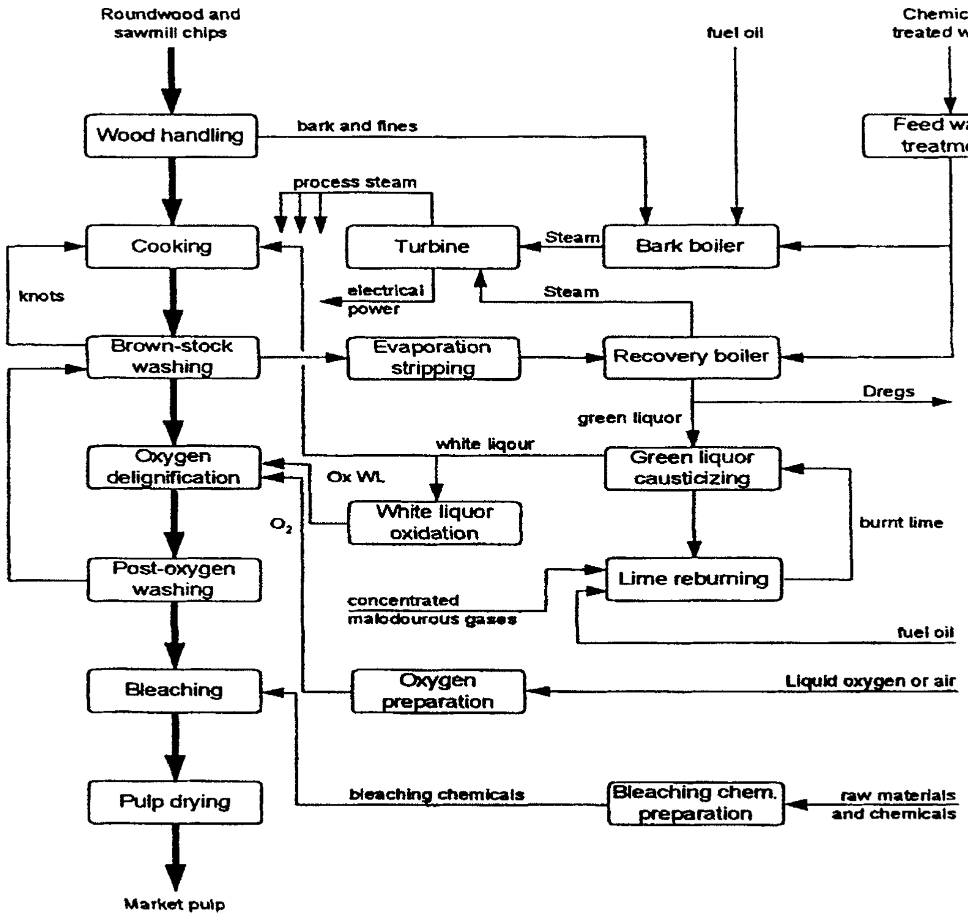

Figure 5. Overview of the processes in a kraft pulp mill. Source: SEPA, 1997.

Using the criteria of fresh water consumption and the volume of wastewater discharged, the pulp and paper industry is considered one of the most polluting among all industrial sectors (Balcioglu and Arslan, 1998).

The sulphate or kraft process is the most applied production method of chemical pulping, accounting for ca. 80% of world pulp production. In Western Europe kraft pulp accounts for approximately 40% of the whole production of 38 million tonnes in 2001 (EIPPCB, 2000; CEPI, 2002). The kraft process is normally used to obtain cellulosic pulps, containing around 10% of the original lignin (Pérez, 2001). The pulp obtained from the kraft process quite often follows a bleaching sequence, thus obtaining bleached kraft pulp.

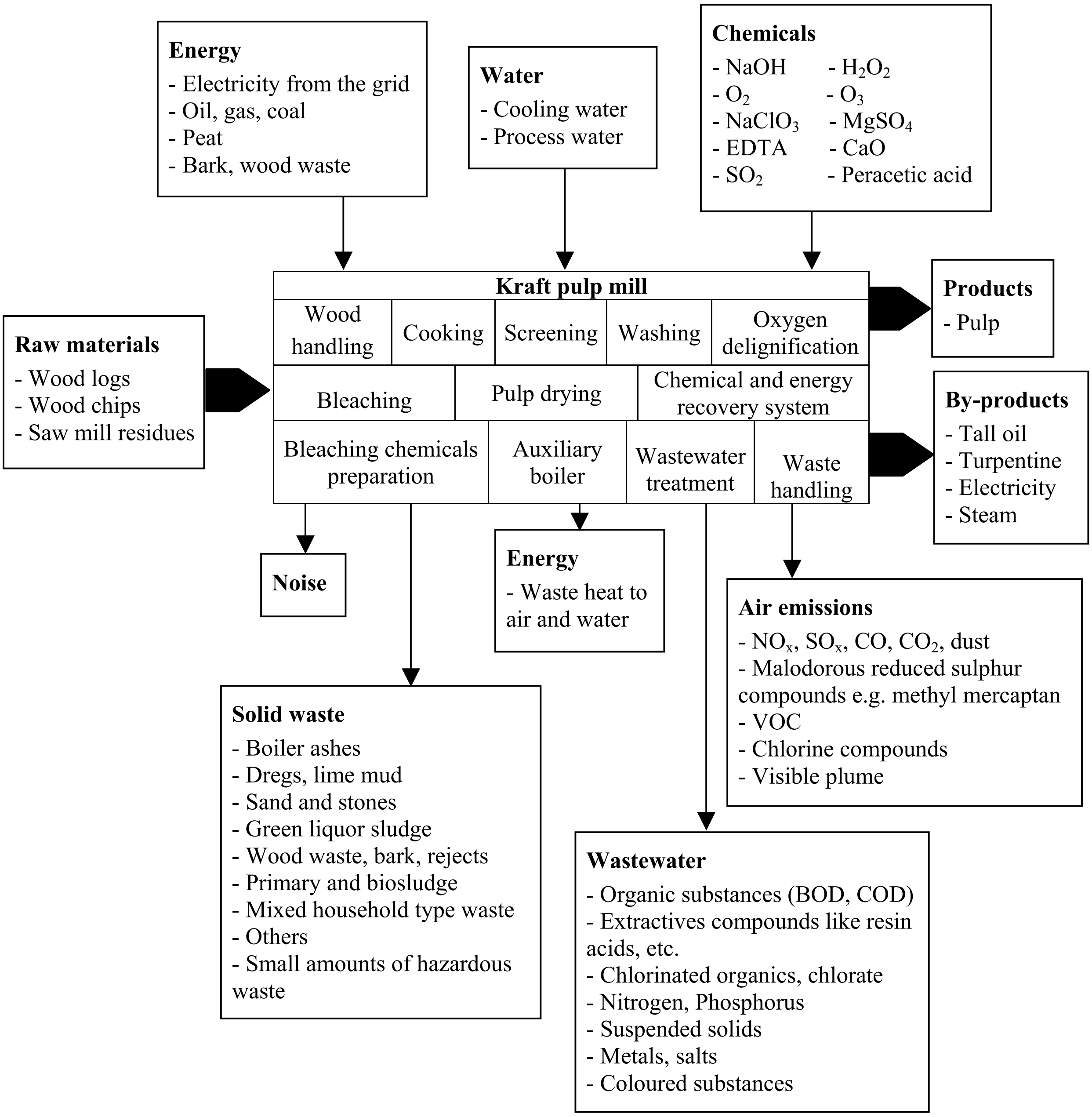

Figure 6. Inputs and outputs of environmental relevance in a kraft pulp mill. Source: EIPPCB, 2000.

Currently, the most relevant environmental problem in the cellulose pulp industry is related to the effluents discharged from the pulp bleaching process (Rodríguez et al., 1998). In this process, pulp is bleached in sequences of successive stages, usually four to five. The most common used chemicals are chlorine dioxide, oxygen, ozone and peroxide. Lately, peracetic acid has been also used as bleaching chemical (EIPPCB, 2000), and recently, chlorine and hypochlorite have been phased out as primary bleaching chemicals, as a result of the public concern about the potential hazard of adsorbable organic halogens (AOX) such as dioxins and furanes, detected in bleaching plant effluents discharged into the aquatic environment.

AOX like chlorophenols and polyphenolic compounds are important contaminants and they are difficult to eliminate by conventional wastewater treatment processes. Due to their stability and bioaccumulative nature, they remain in the environment for long periods. They are highly toxic and carcinogenic; consequently, they are ranked high among pollutants and their formation has to be avoided or at least they have to be removed before releasing wastewater into natural streams.

Although elemental chlorine bleaching sequences have been removed in pulp mills, the alternative chemical most widely used is chlorine dioxide, which still enables the formation of organic chlorine compounds, giving a typical value of 2 kg AOX per tonne of pulp for a conventional bleaching sequence D(EOP)DED[5] (EIPPCB, 2000). As a consequence, the pulp and paper industry is facing more stringent regulations on the quality of effluent discharges allowed to enter into the receiving waters, and most specially from the bleach pulp mills. The possible strategies to comply with these regulations are:

- Application of Total Chlorine Free (TCF) bleaching sequences, using ozone, oxygen, or peracetic acid.
- Application of Elemental Chlorine Free (ECF) bleaching sequences with modifications such as extended cooking or oxygen delignification.
- Treatment of wastewaters by physical-chemical processing, AOPs.

3.2.2. Advanced oxidation processes (AOPs)

The AOPs are included among the more accepted techniques for wastewater treatment (Hoffmann et al., 1995; Bauer & Fallmann, 1997; Balcioglu & Arslan, 1998; Andreozzi et al., 1999; Chen & Ray, 1999). The AOPs are used to cause the pollutants to be completely mineralised without a waste stream being formed, whereby these technologies are more interesting than accumulation and concentration techniques.

Traditionally, AOP technologies are those which are based on the *in situ* formation of hydroxyl radicals ($OH\cdot$) by means of different reacting systems (Bauer & Fallmann, 1997; Andreozzi et al., 1999; Yeber et al., 1999; Pérez et al., 2001; Torrades et al., 2001). The hydroxyl radical is an extraordinarily reactive species, with a strong oxidative nature: E^o = 2,8 V vs. NHE, being much greater than other common oxidants: Ozone 2,08 V, hydrogen

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[5] “D” means chlorine dioxide; “E” means extraction; “O” means oxygen; “P” means peroxide.

peroxide 1,78 V, chlorine 1,36 V, chlorine dioxide 1,27 V, oxygen 1,23 V, etc.), being able to completely transform organic carbon to CO_2.

Among the most extensively known AOPs are (Pérez, 2001):

- Heterogeneous photocatalytic oxidation
- Ozonation reactions and ozonation coupled with heterogeneous or homogeneous photocatalysis
- H_2O_2/UV systems
- Fenton and photo-Fenton reactions

The fundamentals of these groups of AOPs are briefly described in the next sections.

3.2.2.1. Photocatalysis

Heterogeneous photocatalysis is based on the production of electron-hole pairs (eq. 1) by illumination with light of band gap energy (λ < 380 nm for TiO_2) of a semiconductor powder dispersed in an aqueous medium.

$$TiO_2 + h\nu \rightarrow h_{bv}^{+} + e_{bc}^{-} \qquad (1)$$

These charge carriers migrate to the surface of the particles and react with adsorbed species of suitable redox potential. The main reactions of this process are summarized in eqs. 2-4 (Pérez et al., 2002):

$$h_{bv}^{+} + H_2O_{ads} \rightarrow OH^{\cdot} + H^{+} \qquad (2)$$

$$h_{bv}^{+} + OH^{-}_{ads} \rightarrow OH^{\cdot} \qquad (3)$$

$$e_{bc}^{-} + O_2 \rightarrow O_2^{-} \qquad (4)$$

Despite photocatalysis has been shown to be adequate for the degradation of a wide variety of compounds, the process is only efficient for rather dilute effluents, and involves consumption of a large amount of energy (Hoffmann et al., 1995; Legrini et al., 1993). Many research groups try to enhance the process by adding reagents with different chemical roles such as H_2O_2, O_3, Fe(II), and Fe(III) (Sánchez et al., 1996; Dionysiou et al., 2000).

3.2.2.2. Ozonation

The application of ozone in wastewater treatment is a well-known technique and research field (Sánchez et al., 1998; Tanaka et al., 1996; Klare et al., 1999; Mao et al., 1995). The mechanism of organic matter oxidation by O_3 has been carefully studied by Hoigné and colleagues (Hoigné et al., 1985, 1988; Staehelin et al., 1985). Ozone could react with the organic load present in the wastewater in two ways:

- Direct reaction with the O_3 molecule
- Indirect reaction with OH radicals produced after O_3 degradation.

The decomposition of the O_3 molecule can be achieved in several ways: at basic pH, under UV irradiation, and using additives such as Fe (II), etc. The yield of OH radicals, calculated by Hoigné et al., is 0,65 molecules of OH· for every molecule of ozone decomposed. Since the oxidative power of the OH radical (2,8 V vs. NHE) is higher than the oxidative power of ozone (2,08 V vs. NHE), O_3 is a more efficient oxidant when the experimental conditions favour its degradation to OH·. The mechanism of O_3 decomposition in the presence of UV light has been studied by Peyton et al., (1987).

Ozone in conjunction with UV light, is a tool used today in the decontamination of drinking water as well as for the treatment of strongly contaminated wastewaters. Nevertheless, there is little accurate data on the ozonation of micropollutants (Pérez, 2001).

3.2.2.3. Fenton and photo-Fenton reactions

The Fenton reaction is a combination of Fe(II) and H_2O_2 with production of OH·, and is a well known technique of organic matter degradation that has been object of increasing interest in research studies in recent years (Peyton, 1990; Chamarro et al., 2001; Pérez et al, 2001). The generally accepted reaction for OH· formation is:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\cdot \qquad (5)$$

If H_2O_2 is in excess, it can react with Fe(III) species to regenerate Fe(II) (Fenton-like reaction):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH_2^\cdot + H^+ \qquad (6)$$
$$Fe^{3+} + HO_2^\cdot \rightarrow Fe^{2+} + O_2 + H^+ \qquad (7)$$

Thus Fe(II) can be considered a catalyst in the process of OH· generation. Furthermore, the incidence of UV-Vis light can enhance the recovery of Fe^{2+} through the photo-Fenton process:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^\cdot \qquad (8)$$

The use of Fenton reagent as an oxidant for wastewater treatment is attractive due to the fact that (Pérez, 2001):

- Iron is a highly abundant and non-toxic element. Iron is the second most abundant metal and the fourth most abundant element in the Earth's crust where it is found as ferrous or ferric ions.

- Hydrogen peroxide is easy to handle and environmentally benign.

- Photo-Fenton reaction could be performed under solar irradiation, which is a very promising, low-cost treatment.

3.2.3. Experimental

There has not been specific experimental work for the purpose of carrying out the present LCA. Instead, data from previous studies has been used. These studies are briefly introduced below.

3.2.3.1. Background

The Chemistry Dept. of UAB and the Chemistry Engineering Dept. of UPC in Terrassa have been working together for several years in the field of wastewater treatment using AOPs (Pérez et al., 2001; Torrades et al., 2001). In March 2002 a paper was published (Pérez et al., 2002), in which several options for pulp bleaching effluent treatment were assessed from an economic point of view, after laboratory scale experiments.

The results of the study allowed the identification of cheap and expensive options for TOC removal in pulp mill effluents, as well as synergies and cost decrease derived from the combination of treatments. However, the idea arose that a full assessment of these AOPs should include environmental information. As a consequence, the LCA methodology was chosen as the adequate tool to complement the previous economic assessment.

Being so, the mentioned work constitutes the starting point of the present LCA, and has been used as a main source of information. For this reason, a brief description of the experimental work is made below.

3.2.3.2. Methodology and results

The effluents used in the study were the aqueous refuse of the chlorination step of the bleaching sequence (D_{20} C_{80}) (E(O)) D_1 D_2 applied to Kraft paper pulp of Eucalyptus Globulus (90%) and Eucalyptus Grandis (10%), which was supplied by a north-east Spanish paper manufacturer. In order to reduce the level of organic contaminants, hydrolisis of the wastewaters with $Ca(OH)_2$ (pH 12, 1 h) followed by acidification (pH 3) was carried out. The composition of the wastewater entering the AOP after hydrolysis can be seen in Table 3.

Table 3. Initial characterisation of the bleaching kraft mill effluent after hydrolysis pretreatment.

Parameter	Value
pH	10,6
TOC (mg/dm^3)	441
COD (mg/dm^3 O_2)	1.384
Color (mg/dm^3 Pt)	197

Source: Pérez et al., 2002.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm^3 capacity. The reaction mixture inside the cell, consisting of 100 cm^3 of organic effluent and the precise amount of reagents, was continuously stirred with a magnetic bar. The temperature was kept at 25° C and the duration of the experiment was 180 minutes.

A 6 W Philips black-light fluorescent lamp was used as light source. The intensity of the incident light inside the photoreactor was 1,38x10^{-9} einstein/s.

Ozone was produced by a Sander Labor Ozonisator 301.7, fed with pure oxygen. The resulting ozone and oxygen mixture was immediately bubbled through the bleaching effluent. A working current of 1 A and a pressure of 0,5 bar were used. An ozonised oxygen flow rate of 330 cm^3/min (1,5 g O_3/h) was employed to ensure saturation of the system.

Several treatment options were assessed (Table 4, Figure 7), most of them being combinations of processes, and different reagent doses were tried. TOC was used as indicator of organic pollutant removal. In this Table, only the percentage of initial TOC removed is shown, as this is the main parameter of interest for the present LCA. Further information can be found in Pérez et al. (2002).

Table 4. List of AOP treatments included in the experiments and %TOC removal achieved after 180 minutes.

Treatment	% TOC removal
Photocatalysis 1 g/dm^3 TiO$_2$ 2 g/dm^3 TiO$_2$ 6 g/dm^3 TiO$_2$	 8 15 16
Photocatalysis + H$_2$O$_2$ 10 ppm H$_2$O$_2$ 100 ppm H$_2$O$_2$ 500 ppm H$_2$O$_2$	 14 17 21
Photocatalysis + H$_2$O$_2$ + 20 ppm Fe^{2+} 10 ppm H$_2$O$_2$ 100 ppm H$_2$O$_2$ 500 ppm H$_2$O$_2$	 18 20 30
Fenton and Photo-fenton (20 ppm Fe^{2+} + 500 ppm H$_2$O$_2$)	30
Ozonation	48
Ozonation + UVA	69
Ozonation / Photocatalysis (2 g/litre TiO$_2$) *	38
Photocatalysis (2 g/litre TiO$_2$) / Ozonation **	40

*** 1 h Ozone followed by 2 h Photocatalysis.**
**** 1 h Photocatalysis followed by 2 h Ozone.**

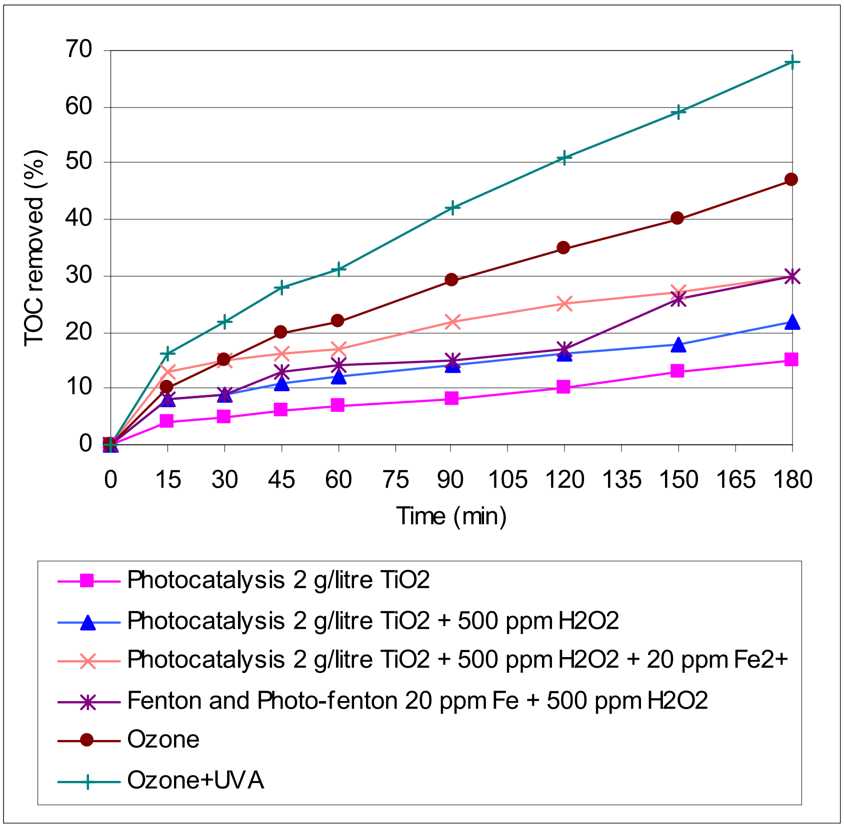

Figure 7. TOC removal vs. time in the experiments carried out with the bleaching kraft pulp mill wastewater (treatments not included in the LCA are omitted). Source: Pérez et al. (2002).

3.2.4. Treatments included in the LCA

Not all treatments included in Pérez et al. (2002) have been considered in the LCA. Inclusion and exclusion criteria are presented and discussed below:

- In those techniques involving several H_2O_2 doses, only the highest-dose case has been included, as the TOC removal achieved was higher.
- In photocatalysis using only TiO_2, only the 2 g/litre dose has been included, since this is the more cost-effective one. It is also the dose chosen in the other photocatalytic treatments.
- The combinations of ozone and photocatalysis have been excluded, because they are incompatible with the functional unit defined (see section 3.2.6.). The reason is that these treatments are designed by setting a reaction time (1 hour) for one of the technologies, and leaving the remaining time (2 hours) for the other technology. Nevertheless, the functional unit sets the minimum TOC to remove (15%), which implies a specific reaction time for each treatment depending on its rate. Therefore, the approach of setting a reaction time is not valid.

In this way, 6 different treatments are included in the LCA. In Table 5, the different treatments considered are summarized, along with the acronyms used from now on in the study.

Table 5. AOP treatments included in the LCA and acronyms assigned.

Treatment	Acronym
Photocatalysis (2g/litre TiO_2)	PhC
Photocatalysis (2g/litre TiO_2 + 500 ppm H_2O_2)	PhC+H2O2
Photocatalysis (2g/litre TiO_2 + 500 ppm H_2O_2 + 20 ppm Fe)	PhC+FPhF
Fenton and photo-Fenton (500 ppm H_2O_2 + 20 ppm Fe)	FPhF
Ozonation	O3
Ozonation + UVA	O3+UVA

3.2.5. System function

At industrial scale, the AOPs could be used as a pretreatment for wastewater. This would be useful to increase the biodegradability of the organic content in the water before entering a biological treatment stage. On the other hand, the AOP could be placed after the biological stage, thus allowing the remaining persistent pollutants to be destroyed before discharging the water into the aquatic recipient.

Each of these options can be identified as different functions (pre-treatment/post-treatment). However, since this case study is derived mainly from laboratory scale data, it is not possible to anticipate the configuration of a large scale application. As a consequence, the function of the system has been defined in a wide way sense as:

Degradation of the persistent organic load in a kraft pulp mill effluent.

3.2.6. Functional unit

As it has been stated in section 3.2.3. the starting point for this LCA is the series of experiments carried out by Pérez et al. (2002). Therefore, the hypothesis, methodology as well as the results obtained in that work have to be taken into account in order to define the functional unit, that is, the unit of service whose environmental impacts will be assessed and which will be the basis to compare the different AOP technologies.

The main problem to define the functional unit arises from the different TOC removal efficiencies achieved by the different treatments included in the experiments. This implies that two possible ways of defining the functional unit can be discarded:

- **A certain volume of wastewater entering the system**: for instance, one cubic meter of wastewater. If different treatments achieve different TOC removal efficiencies, the purified water would have different quality in each case, thus leading to an incomparability in terms of the final product obtained.

- **A certain quantity of pollutants destroyed**: for instance one kg of TOC removed from the wastewater. In this case, as TOC removal efficiencies are different, the volume of water needed to achieve the same weight of pollutant removed would be different, thus leading to an incomparability in terms of volume of water treated and discharged. However, this approach was the one chosen in Pérez et al. (2002) to compare the economic costs of the AOPs.

The approach taken in the present study has defined the functional unit on the basis of the same volume treated (1 m^3) and the same amount of pollutants destroyed. In order to do this, a TOC removal threshold has to be defined that can be accomplished by all the AOPs compared. The minimum TOC removal achieved by all the treatments included, as can be seen in Table 4, is 15%, which corresponds to heterogeneous photocatalysis with a TiO_2 load of 2 g/litre. Then, the functional unit is defined as:

Removal of 15% TOC from 1 m^3 kraft pulp mill wastewater as shown in Table 3.

It could be argued that 15% pollution removal is a very low threshold. In a full-scale plant, probably this wouldn't be enough to comply with legislation. However, it must be borne in mind that this is a preliminary assessment carried out from laboratory data. We are more concerned about making a fair comparison of AOPs than about the significance with regard to a hypothetical full-scale plant.

3.2.7. Scenarios considered

Three scenarios have been considered, affecting one of the key points in the study: the energy sources used to run the AOPs.

3.2.7.1. Baseline: grid electricity

In the baseline scenario, it is considered that the energy source used to run either the UVA lamp or the ozonisator is electricity coming from the grid. This scenario is intended not to be representative of the pulp and paper industry, but of a general application of the AOPs to industrial wastewater treatment, where the main source of energy is electricity purchased from the grid.

3.2.7.2. Co-generation of heat and power (CHP)

First scenario is representative of the industry in general, where usually electricity is purchased from the grid. This, however, is not very representative of the pulp and paper industry, where co-generation of heat and power (CHP) allows pulp and paper mills to be almost self-sufficient in energy terms. Co-generation in this context is defined as the simultaneous generation of electrical energy and thermal energy (steam) (Neill and Gunter, ltd., 1999). Co-generation plants raise the conversion efficiency of fuel use from around 30% to 80% or more, thus increasing substantially energy efficiency.

In this second scenario, the energy source used to run either the UVA lamp or the ozonisator is considered to be electricity coming from co-generation in a kraft pulp mill.

3.2.7.3. Solar light

Most of the AOPs have shown to be more effective by using a lamp as light source; however, this leads to an important economic and environmental problem, caused by the electrical demand.

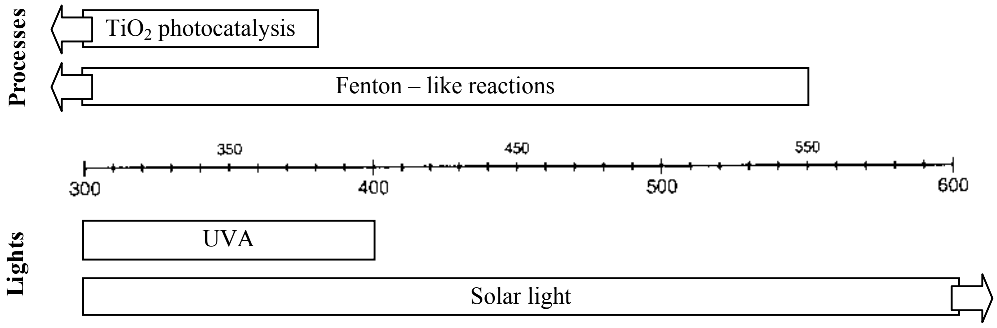

Figure 8. Wavelength intervals (nm) of different light sources used and the more appropriated intervals for some of the AOPs studied.

As can be seen in Figure 8, solar energy can provide photons with the wavelength required for these processes. Actually, solar energy has a higher intensity in the UVA region than the lamp used in the experiments (5-6 mW/cm^2 for sunlight, 0,13 mW/cm^2 for the lamp), and it constitutes a renewable, cheap and clean energy source, which is already being used for this purpose in pilot plants (Figure 9). For this reason, in the third scenario it has been considered that sunlight is the only energy source to run the photo-assisted AOPs. This implies, however, that ozonation either in the dark or in the presence of light is excluded from this scenario, since ozone has to be produced using electricity.

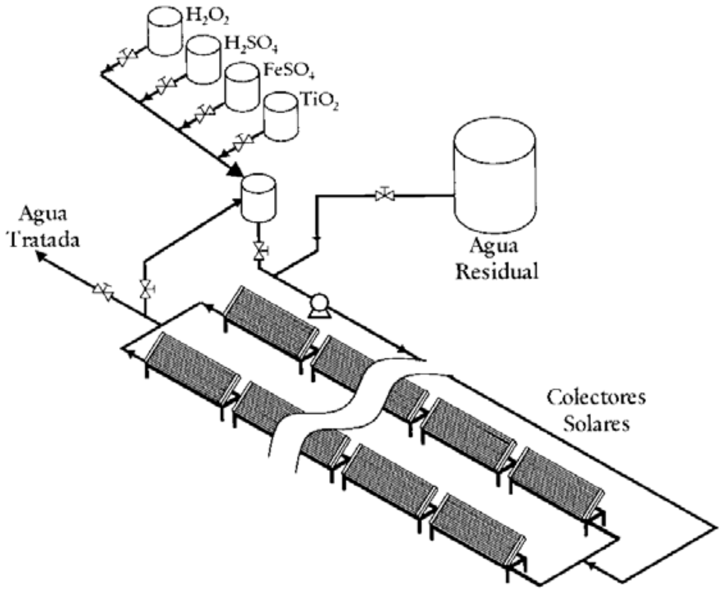

Figure 9. Diagram of a solar photocatalytic wastewater treatment plant. Source: PSA.

3.2.8. System boundaries

In this section, all processes (both included and excluded) considered in the study are identified, as well as the reasons for their inclusion or exclusion. A general flow diagram showing the system-boundaries is presented in Figure 10.

3.2.8.1. Excluded processes

- Infrastructure and equipment for the different treatments are not included in the LCA, since most of these technologies are nowadays hardly applied at full scale and data is therefore nonexistent. Infrastructure and equipment used in the laboratory is not considered to be representative.

- The biological stage, either before or after applying the AOPs, is excluded. As discussed in 3.2.5., with regard to biological treatment, AOPs can be used as a post-treatment to comply with AOX emission limits, but also as a pre-treatment to increase the biodegradability of the wastewater. None of these configurations have been chosen as the most representative, and therefore biological treatment has been excluded. Furthermore, as the study focuses in AOPs, the functional unit has been defined in such a way that processes placed before and after the AOP can be excluded, as they are constant for all treatments.

- Physical-chemical pre-treatments and post-treatments are excluded, as they are also constant for all treatments. In particular, this applies for: alkaline hydrolysis (pre-treatment), acidification (pre-treatment), and neutralization (post-treatment).

- The environmental effects of the 85% TOC not removed (375 g/m^3) from the water are not taken into account, for several reasons:

  Firstly, because in a full-scale application, all or almost all this recalcitrant TOC in the water would be removed, and so the environmental effects derived. In fact, setting as functional unit the removal of only 15% TOC is not really representative of a real plant, but it is the only way to fairly compare the different treatments with the available data.

  Secondly, the same TOC content is present in the effluents of all treatments, so it is not a relevant aspect for the comparison, and can be excluded from the system.

  Even if it was to be taken into account, there is no analytical data from the experiments concerning the content of single organohalogens or other toxic substances in the effluent, as the only monitoring parameter was TOC. This is a too general parameter to estimate the actual toxicity in the water.

- CO$_2$ emissions produced by the mineralization of TOC (242 g CO$_2$/m^3 assuming 100% mineralization of the 15% TOC removed) are not taken into account. In the present application, TOC in the wastewater comes from a biogenic source (wood), therefore these emissions are compensated by the uptake of CO$_2$ through photosynthesis (see section 3.4.1.1).

3.2.8.2. Included processes

- Production of electricity consumed by the different AOPs. This sub-system comprises extraction of resources, transport, and electricity production.

- Production of chemicals, meaning the catalytic and stoichiometric reagents consumed by the AOPs. This sub-system comprises extraction of resources, transport, production of the different chemicals, and transport to the wastewater treatment plant.

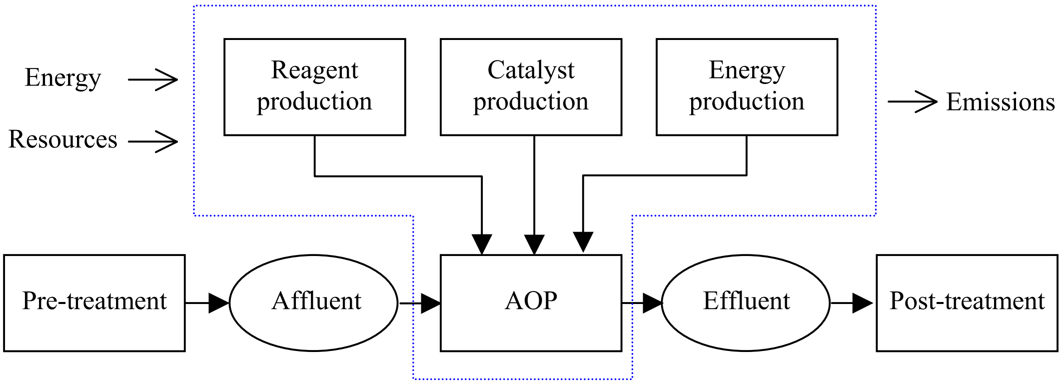

Figure 10. General flow diagram and system boundaries.

3.2.9. Main hypothesis and limitations

The main hypothesis considered and the limitations which have to be borne in mind are presented and briefly discussed below.

- TOC is used as indicator of water pollution removal in all treatments. Ideally, toxicity should be the monitoring parameter, since toxic effects of persistent organic substances are the main reason to apply AOPs to wastewater. However, TOC seems to be a reasonable approximation, as it measures the organic content in solution. Furthermore, since all treatments are based in the generation of the same oxidant agent (OH radical), it is expectable that similar intermediates and final reaction products are produced.

- Stoichiometric reagents are assumed to be lost after 15% TOC removal. As reagent consumption is calculated from the applied dose (ppm), the problem is that the same consumption would be assigned either to a system removing 90% TOC or to another removing 15%, as it is the case in the present study.

- Catalysts are also assumed to be lost after 15% TOC removal, unless there is a specific catalyst recovery stage considered after treatment.

- The catalyst recovery stage has been considered in all treatments involving the use of TiO_2. This is justified by the fact that the catalyst dose is quite high in the case of TiO_2 (2g/litre) as compared to Fe (II) (20 ppm). If TiO_2 was not recovered this would have noticeable consequences in operation costs. This is not the case with Fe (II), so there seems to be no reason for recovery of this chemical. However, in those treatments involving the use of both catalysts, it is assumed that both are recovered, because in spite of TiO_2 being the target catalyst, the recovery stage considered (see 3.3.2.) also works for Fe recovery.

- Although experiments were performed using a Fe (II) source, in particular Fe_2SO_4, it has not been possible to find inventory data for the production of this chemical. Instead, $FeCl_3$, which is a Fe (III) salt, has been used due to the availability of LCI data. It is assumed that Fe (III) works similarly to Fe (II), since in the presence of light and under the experimental conditions tested, Fe (III) is readily reduced to Fe(II).

- The catalyst content in the effluent (i.e. the fraction of Fe and Ti which is not recovered) is not considered to have any harmful effects in the aquatic environment.

- $FeCl_3$, H_2O_2, and O_2 are chemicals of wide consumption in industrial processes, and are assumed to be produced in Spain. The transport distance to deliver them from the factories to the wastewater treatment plant is assumed to be 100 km, travelled by a 16 tonnes truck.

- Transport of the main raw material for TiO_2 production, ilmenite, is assumed to be first by ship, and the distance assumed is 5.000 km. This figure would be higher if ilmenite was imported from Australia, or USA, but shorter if it comes from Norway. Also a road transport to the TiO_2 production plant is considered, assuming 500 km, and a 40 tonnes truck. For distribution of TiO_2 the location of the supplier, Degussa, is considered. The plant is located in Frankfurt, Germany. The distance considered from this point to Spain is 1500 km, travelled by a 40 tonnes truck. Furthermore, a local distribution distance is also considered, from the local dealer in Spain to the wastewater treatment plant. The same distance of 100 km, as discussed for the other chemicals, is considered.

- One of the key parameters in the study is the time needed by each treatment to reach 15% TOC removal. This is directly dependent on the reaction kinetics of each AOP. As can be seen in Figure 7, all treatments follow a similar pattern: a higher TOC removal rate the first minutes, followed by a lower rate. There is, however, some experimental uncertainty, being the clearest example the Fenton and photo-Fenton curve, which shows almost a plateau during the second hour of treatment. We have attributed this plateau not to the process but to the uncertainty already mentioned, thus suggesting that in this period of time the real slope is slightly higher. For this reason, in order to calculate the time needed by this treatment to reach 15% TOC removal, instead of the 90 minutes calculated from the graphic, a decrease to 75 minutes is assumed.

- One of the most important limitations of this study arises from the laboratory scale at which the process parameters were measured. Laboratory reactors and equipment neither are optimized, nor show scale-economies. The clearest case is ozonation, one of the few AOPs commonly applied in water treatment, and from which full-scale data is available. An industrial ozonisator uses about 10-15 kWh/kg O_3 produced (EIPPCB, 2000), whereas the consumption reported for the laboratory ozonisator is about 150 kWh/kg O_3, one order of magnitude above. As a baseline case, the laboratory data has been used in the study. Nevertheless, this shift in scale for ozonation will be discussed in the interpretation phase as a sensitivity analysis.

3.2.10. Data collection and data quality

The data used in this LCA comes from several sources, and therefore, the quality is different in each case. As the quality of the final results directly depends on the input data, some issues, such as the validity and the reliability of the data have to be discussed.

In this section, however, only a general overview of the data quality is presented in Table 6. In the corresponding sections of the inventory, every sub-system as well as the data sources and quality are discussed in detail.

Table 6. Summary of sources and quality of the data used in the LCA.

Topic	Sources	Geography	Age
ENERGY			
Electricity (spanish mix)	Local data concerning contribution of the different technologies to electricity production in Spain (IDAE, 2002). Total aggregated inventory of the different production technologies (coal, gas, nuclear, hydro, fuel) from the BUWAL 250 database (Habersatter, 1996).	Local	<=7 y.
Electricity (co-generation)	Data on emissions for co-generation in kraft pulp mills, using black liquor, bark, and oil as fuels. Several sources are used, such as databases (Habersatter, 1991,1996) and literature concerning pulp and paper processing (see section 3.3.1.6.)	International	<=8 y.
Solar light	No data needed. Solar energy doesn't produce any environmental impact.	-	-
Energy consumption by the AOPs	Experimental data from Pérez et al. (2002).	Local	<1 y.
CHEMICAL PRODUCTS			
TiO_2	Data on emissions and consumption of raw and auxiliary materials from Huizinga et al. (1993). Environmental impact of raw and auxiliary materials mainly from the BUWAL 250 database (Habersatter, 1996).	Europe	<=10 y.
H_2O_2	Data from CEFIC, calculated using the methodology from Boustead (1999). Total aggregated inventory.	Europe	8 y.
$FeCl_3$	Incomplete data from the IVAM database, including energy consumption, and stoichiometric amounts of steel and HCl. Production of these materials from the BUWAL 250 database (Habersatter, 1996).	Europe	<=7 y.
O_2	Oxygen production data from the BUWAL 250 database (Habersatter, 1996)	Europe	7 y.
Chemical products consumption by the AOPs	Experimental data from Pérez et al. (2002).	Local	<1 y.
TRANSPORTS			
Truck 16 tonnes	Data on fuel consumption and emissions from the BUWAL 250 database (Habersatter, 1996).	Europe	7 y.
Truck 40 tonnes	Data on fuel consumption and emissions from the BUWAL 250 database (Habersatter, 1996).	Europe	7 y.
Sea transport	Data on fuel consumption and emissions from the BUWAL 250 database (Habersatter, 1996).	Europe	7 y.

3.2.11. Multiple processes (allocation)

Multiple processes are those from which two or more products are obtained. For these multiple processes, a solution has to be found by either avoiding multiple processes by dividing the process into sub-processes or by enlarging the system under investigation so that the co-products are also involved, or by allocation, which means to divide the inputs and outputs among the products.

3.2.11.1. Co-generation in the kraft pulp mill

In the present LCA the problem of allocation appears when dealing with electricity produced by means of co-generation. Kraft pulp mills use internal waste products (such as black liquor and bark) and other fuels to produce both steam and electricity, whereas the system under study only consumes electricity. In the calculations, the inputs and outputs have been partitioned between steam and electricity using energy as a basis. This means that the emissions and other environmental burdens are allocated to the total energy output, regardless the type of energy produced (electricity or steam). For instance, given a CHP plant, production of 1 MJ steam has the same impact than production of 1 MJ electricity; the higher the total energy output, the lower the environmental impact per unit energy produced.

As mentioned above, another fact related to co-generation, is that most of the fuels used to produce energy in the mill are waste: black liquor from the cooking process, and bark. In the calculations, the environmental impact of obtaining these materials is considered zero, as the impact is not allocated to them, but to the produced pulp.

3.2.11.2. Energy and chemicals for the AOPs

The following allocation rules have been used to calculate energy and chemicals consumption by the different AOPs:

- Electricity consumption for UVA irradiaton has been calculated on the basis of time required to reach 15% TOC reduction and the lamp power.

- Electricity consumption for O_3 production has been allocated on the basis of time required to reach 15% TOC reduction and the parameters of the ozonisator (voltage and current intensity).

- O_2 consumption for O_3 production has been calculated on the basis of time required to reach 15% TOC reduction and the parameters of the ozonisator (O_2 flow).

- $FeCl_3$, TiO_2, and H_2O_2 consumption is calculated from the dose applied in each treatment (in ppm or g/litre).

As can be seen, energy and O_2 are time-dependent inputs, whereas the remaining chemical products are volume-dependent inputs. Time-dependency is preferable for the calculations, since TOC reduction is time-dependent (see Figure 7). Allocating inputs on the basis of volume of treated water has the problem that a system removing 90% of the TOC would be allocated the same amount of chemicals than another system treating the same amount of water but only removing 30% TOC. This problem is avoided in the present LCA by setting the amount of TOC to be removed by all treatments, but this leads to the hypothesis that the chemicals are assumed to be lost after 15% TOC removal (see section 3.2.9.).

3.2.11.3. Other processes

Allocation rules are also used for the calculation of LCIs of chemical products that are consumed directly or indirectly by the system, such as chlorine, oxygen or sulphuric acid. However, as the inventory data is taken from the literature or from databases, the allocation rules are already applied.

3.3. Inventory analysis

In the inventory analysis, data is collected and inputs and outputs are attributed to the processes. Data aggregation finally results in a list of all environmental inputs and outputs in the product system, namely, the inventory table. In this chapter the sub-systems and their environmental relevant data are summarized in 3.3.1. whereas the consumptions for each treatment are presented in 3.3.2. Finally, in 3.3.3. a summary table is shown for each scenario.

3.3.1. Sub-systems

The following subsystems are considered:

- TiO_2 production and delivery
- H_2O_2 production and delivery
- $FeCl_3$ production and delivery
- O_2 (for O_3 production) production and delivery
- Production of electricity in Spain
- Production of electricity from co-generation in the kraft pulp mill.
- Solar energy

3.3.1.1. Titanium dioxide (TiO_2)

Titanium is the ninth most abundant element on the earth's crust. Mineral sources for titanium are rutile, ilmenite, and leucoxene. However, the principal titanium mineral is ilmenite ($FeTiO_3$), which is found in either alluvial sands or hard-rock deposits. The principal use of TiO_2 is as paint filler. The whiteness and high refractive index of TiO_2 is unequaled for whitening paints, paper, rubber, plastics, and other materials (Grayson et al., 1981). Nevertheless, TiO_2 consumed in our system is used as a catalyst (Degussa p-25).

Figure 11. A titanium mine in California (USA). Source: http://pangea.stanford.edu/~kurt/kurt-where-mining.html

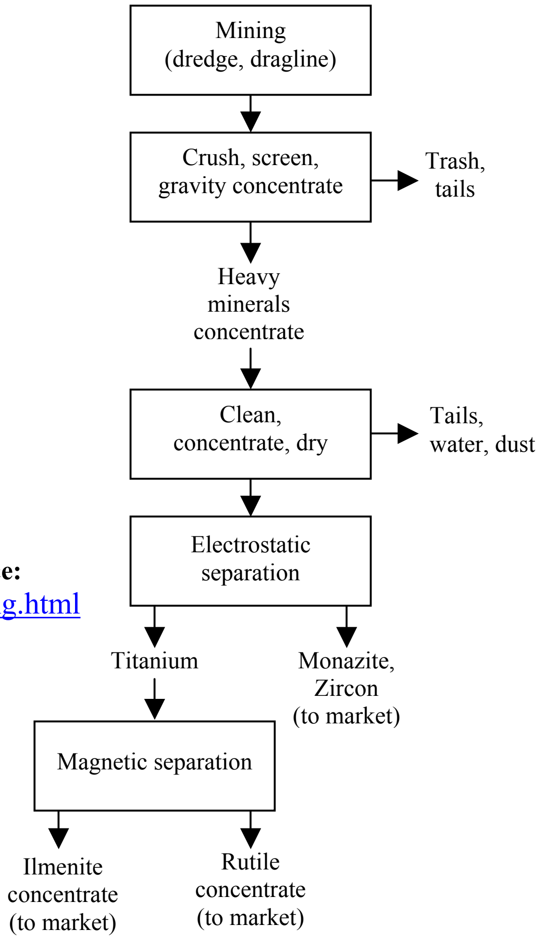

Figure 12. Typical processes and products of a titanium beach-sand mining and beneficiating operation. Source: Grayson et al., 1981.

Ilmenite is mined by the open-pit method (Figures 12 and 13), mainly in Australia, South Africa, Canada, USA, and Norway (USGS, 2001). A dredge is often used for the recovery of titanium-mineral placer deposits. Gravity spirals are used for wet separation of heavy minerals, while magnetic and high tension separation circuits are used to separate the heavy mineral constituents. Ilmenite is often beneficiated to produce synthetic rutile and titaniferous slag.

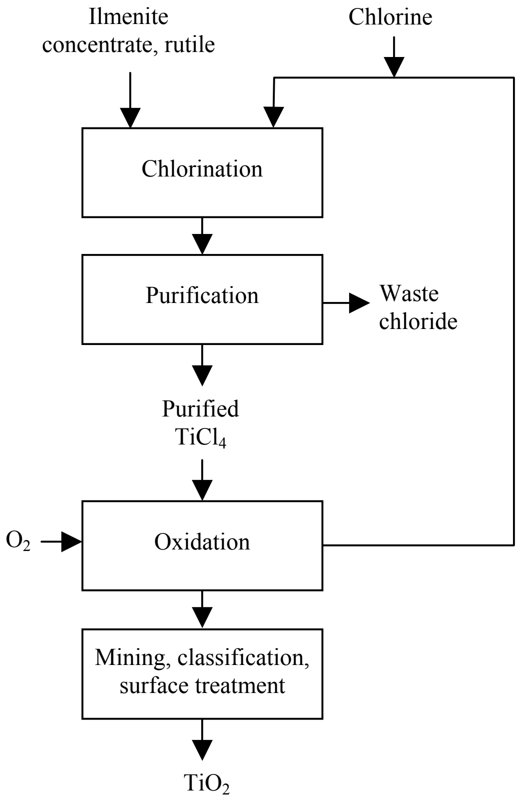

Figure 13. The chloride process for TiO_2 production. Source: Grayson et al., 1981.

TiO_2 production can be carried out by two routes: the sulphate process or the chloride process. Here only the latter is described, since it is the process used by the TiO_2 catalyst supplier in the experimental work, Degussa.

In the chloride process (Figure 13), ilmenite or rutile is conducted to chlorinating equipment where it forms a sludge bed in the air current. Crushed coke is fed into the process in order to increase the temperature. When the temperature is approximately 1000 ºC the air current is replaced by chlorine which causes the formation of titanium tetrachloride vapour. Titanium tetrachloride coagulates and crystallises during cooling. Combustion produces pure titanium dioxide and chlorine cycled into the chlorinating equipment or stored for re-use.

The environmental burdens of TiO_2 production have been inventoried according to different sources:

- Consumption of ilmenite concentrate, auxiliary materials (oxygen, coke and chlorine), as well as process emissions and waste produced in the chloride process have been collected from Huizinga et al. (1993), except for CO_2 emissions. A figure of 3 kg CO_2/kg TiO_2 has been considered, which added to the remaining emissions from ilmenite and auxiliary materials production gives a figure of 4,4 kg CO_2/kg TiO_2 produced, in accordance with the figures reported by Häkinnen et al. (1999) for the overall LCI of this product, in the range of 4,1-5,9 kg CO_2/kg TiO_2.

- Environmental burdens of mining and concentrating ilmenite have been collected from IVAM database (IVAM lca data 2.0). These data is originally from iron ore mining, but is considered to be representative since in these ilmenite ores magnetite (Fe_3O_4) is also separated from ilmenite deposits by magnetic methods.

- Transport of the main raw material, ilmenite, is assumed to be first by ship, and the distance assumed is 5.000 km. This figure would be higher if ilmenite was imported from Australia, or the USA, but shorter if it comes from Norway. Data from energy consumption (0,093 MJ light oil/tkm) in the transport process is from BUWAL (1996). Also a road transport to the TiO_2 production plant is considered, assuming 500 km, and a 40 tonnes truck, using also data from the BUWAL database (Habersatter, 1996).

- Chlorine and oxygen production data has been collected from the BUWAL 250 database (Habersatter, 1996). For oxygen production, the european mix for electricity production has been substituted by the spanish mix (see 3.3.1.5.).

- Coke production data has been collected from Annema et al. (1992), including coal mining and process emissions.

- For TiO_2 the supplier in Europe, Degussa, is located in Frankfurt, Germany. The distance considered from this point to Spain is 1500 km, travelled by a 40 tonnes truck. Furthermore, a local distribution distance of 100 km is also considered, from the local dealer in Spain to the wastewater treatment plant, using a 16 tonnes truck.

In Table 7 the disaggregated inventory table[6] for TiO_2 production is shown. The corresponding inventory tables for the auxiliary materials and the overall aggregated inventory table[7] for TiO_2 can be found in appendix 1.

The unit used to quantify the transport processes is the “tonne km”, abbreviated as tkm. This unit is obtained multiplying the amount of material transported by the overall distance travelled.

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[6] In a disaggregated inventory table inputs from the technosphere (manufactured products) to the system are shown.

[7] In an aggregated inventory table only elementary flows (from nature or to nature) are shown.

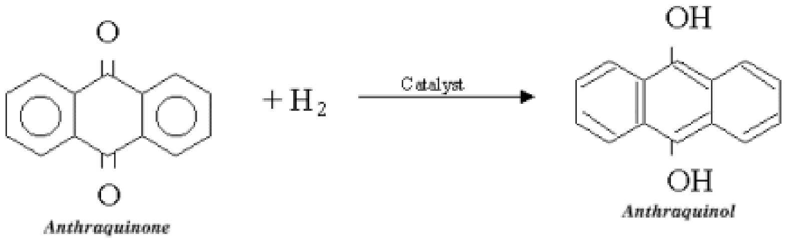
Table 7. disaggregated inventory table for TiO_2 production. (distribution not included).

INPUTS			
Inputs from technosphere			
Ilmenite Concentrate	2,0	kg	Raw material
Sea transport	10,0	tkm	Ilmenite transport
Road transport 40 t	1,0	tkm	
Chlorine	0,9	kg	Auxiliary materials
Oxygen	0,2	kg	
Coke	0,2	kg	
OUTPUTS			
Outputs to nature			
Emissions to air			
Dust	1,3	g	Chloride production process
Cl2	27,0	mg	
HCl	0,2	g	
SOx	13,3	g	
CO	0,2	g	
NOx	2,2	g	
CO2	3,0	kg	Assumed.
Emissions to water			
Cr (III)	44,0	mg	Chloride production process
V	90,0	mg	
Zn	22,0	mg	
Cu	7,0	mg	
Pb	7,0	mg	
Al	0,3	g	
TiO2	0,1	g	
Fe	22,2	g	
Mg	1,3	g	
Hg	20,0	μg	
Cd	9,0	μg	
SS	0,8	g	
Outputs to technosphere			
Waste			
Waste (not inert)	0,3	kg	Chloride production process
Chemical Waste	0,1	kg	
Products			
TiO2	1,0	kg	

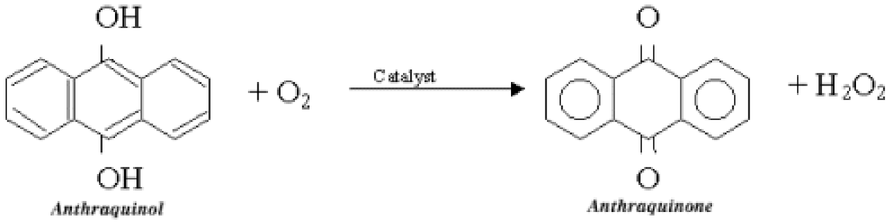
3.3.1.2. Hydrogen peroxide (H_2O_2)

Hydrogen peroxide (H_2O_2) is a chemical product used mainly as a bleaching agent, but also as a disinfectant/deodorising, oxidising agent, and propellant (Ashford, 2001).

The most widely applied production method is based on the autoxidation of an anthraquinone (Grayson et al., 1981). In this process (Figure 14), a reaction mixture containing a carrier solvent and anthraquinones (usually 2-ethyl or 2-pentyl-anthraquinone) is reduced catalytically to the corresponding anthraquinol (or anthrahydroquinone, eq. 9).



(9)



(10)

The anthraquinone is usually called the reaction carrier or working material, whereas the anthraquinone-solvent mixture is called the working solution. The working solution containing the anthrahydroquinone is separated from the hydrogenation catalyst and aerated with an oxigen containing gas, usually air, to reform the anthraquinone and simultaneously produce hydrogen peroxide (eq. 10).

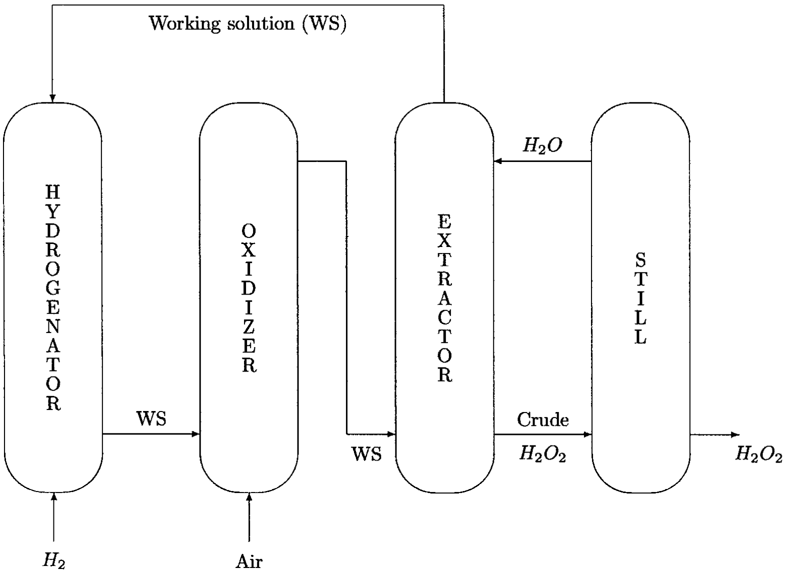


Figure 14. Hydrogen peroxide process (Riedfl-Pfleiderer process). Source: Grayson et al., 1981.

Inventory data for H_2O_2 production has been collected from CEFIC[8]. The data sources used to calculate the LCI are listed below, and further information on the methodology can be found in Boustead (1999).

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[8] www.cefic.org/sector/peroxy/ecohydro/1.htm

- Information on the production of hydrogen peroxide was supplied by nine plants (year 1995) in Belgium, Finland, France, Germany, Italy, Spain, Sweden and the United Kingdom. Most of these producers manufactured their own hydrogen using the reformer process but some use some electrolytic hydrogen. Information on the production of alkyl anthraquinone was provided by the principal producer in Europe.

- Information on some chemical intermediates were derived from earlier work carried out for CEFIC and APME.

- Information on the production of fuels and energy have been derived from the reports of the International Energy Agency (1995, 1995b, 1995c).

- Data for supporting operations and transport have been obtained from other manufacturers and operators.

- The transport distance to deliver H_2O_2 from the factory to the wastewater treatment plant is assumed to be 100 km, travelled by a 16 tonnes truck. Data from energy consumption (2,88 MJ diesel fuel/tkm) in the transport process is taken from BUWAL (1996). The product is assumed to be commercialised aqueous diluted to 50% by weight. This has to be taken into account in the transport process, since the weight transported is doubled.

The gross or cumulative energy associated with the production of purified hydrogen is 23 MJ/kg. Total aggregated inventory is shown in Appendix 1. CO_2 emissions from biomass have been segregated (CO_2-re[9]), and substances quantified as <1 mg have been excluded.

3.3.1.3. Ferric chloride ($FeCl_3$)

Ferric chloride ($FeCl_3$), is a solid composed of dark, hexagonal crystals. Much chlorine from chemical processes is converted to ferric chloride, which is then used for the manufacture of salts, pigments, pharmaceuticals, dyes, for photoengraving, preparation of catalysts, and waste and sewage treatment (Grayson et al., 1981).

$FeCl_3$ may be prepared from iron and Cl_2 in a flow system at 350 ºC or from Fe_2O_3 and HCl in a flow system at up to 1000 ºC. According to KIWA data included in the IVAM LCA database, the main raw material for $FeCl_3$ production is steel.

Iron and steel production involves, as first step, the iron ore extraction in the form of hematite (Fe_2O_3) or magnetite (Fe_3O_4), either in open pits or underground, and its beneficiation consists on crushing, screening, washing, or grinding followed by magnetic separation or flotation. Although these concentrates are of acceptable chemical quality, they

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[9] CO_2-re meaning carbon dioxide from a renewable source (biomass).

must be agglomerated into a coarser form before they can be used in the furnaces. This process is called sintering, in which the material is mixed with lime and coke and passed through a flame chamber, where the product sinters together. The obtained clinker-like material is cooled and screened, and it is ready for dispatch to the blast furnace (CRC for waste management and pollution control ltd., 1998).

The blast furnace is essentially a large chemical reactor into which are charged iron ore, coke, and limestone. As the iron ore descends through the furnace, it is reduced to iron (eq. 11). The main product of the blast furnace is hot metal or pig iron.

$$FeO + C \longrightarrow Fe + CO \tag{11}$$

Pig iron generally is refined to make steel or it may be used to make iron castings. Steel is produced in the basic oxygen furnace (BOS), where 280 tonne-capacity vessels (Figure 15) are filled with scrap metal and pig iron, and a lance blowing pure oxygen is lowered in, causing temperature to reach 1700 ºC, melting the scrap, lowering the carbon content of the molten iron, and helping to remove impurities. The liquid steel obtained must be cast into a standard shape so that it can be rolled, to give a greater toughness, shock resistance, and tensile strength (CRC for waste management and pollution control ltd., 1998).

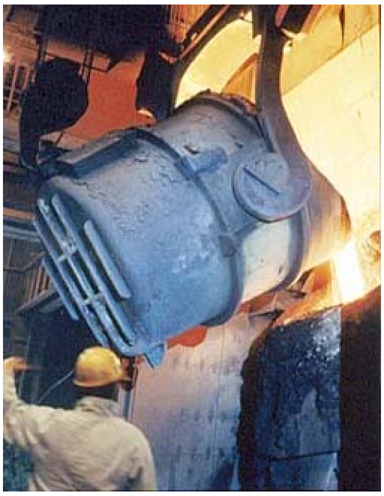

Figure 15. Basic oxygen furnace being charged with molten iron.
Source: http://www.usx.com/corp/media/photos.htm

The other raw material for $FeCl_3$ production is hydrogen chloride (HCl), which can be produced industrially by mixing NaCl and H_2SO_4 (eq. 12); from NaCl, SO_2, air and water vapor; by controlled combination of the elements, or as by product of the synthesis of chlorinated hydrocarbons.

$$2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + HCl \tag{12}$$

As mentioned before, inventory data for $FeCl_3$ production is derived from KIWA Water Research. These data, however, are not very complete; only the stoichiometric amounts of steel and hydrogen chloride, as well as an electric consumption are included. For the production of raw materials and energy the following assumptions were made:

- Production of steel has been collected from the BUWAL 250 database (Habersatter, 1996). The inventory includes emissions from raw material production, energy production, production of semimanufactures and auxiliary materials, transports and the production process, from 80% iron ore and 20% scrap. The system model is based on the production of packaging steel in Germany.

- Production of HCl is also collected from the BUWAL 250 database, which includes production from NaCl and sulphuric acid (eq. 12).

- For the electric energy consumed in HCl manufacture the spanish mix for electricity production has been used.

- The transport distance to deliver $FeCl_3$ from the factory to the wastewater treatment plant is assumed to be 100 km, travelled by a 16 tonnes truck. Data from energy consumption (2,88 MJ diesel fuel/tkm) in the transport process is taken from BUWAL (1996). According to KIWA data, the product is commercialised aqueous diluted to 40% by weight. This has to be taken into account in the transport process.

In Table 8 the disaggregated inventory table for $FeCl_3$ is shown. The corresponding inventory tables for the auxiliary materials and the overall aggregated inventory table for $FeCl_3$ is shown in appendix 1.

Table 8. disaggregated inventory table for $FeCl_3$ production. (distribution not included).

INPUTS			
Inputs from nature			
Water	600	g	
Inputs from technosphere			
Steel	138	g	Raw materials
HCl	123	g	
Electricity (spanish mix)	0,14	kWh	Process energy
OUTPUTS			
Outputs to technosphere			
Products			
FeCl3 (40%)	1	kg	

3.3.1.4. Oxygen (O_2) for ozone production

Ozone can be produced either from dry air or from pure (commercial) oxygen. Since the ozonisator used in the laboratory experiments works with pure oxygen, this is the option chosen in the LCA.

Oxygen constitutes 21% of the earth's atmosphere. Its main applications are steelmaking (see 3.3.1.3.), medicine, and in metallurgy for welding and cutting metals. Commercial O_2 is produced by the fractionation of air in units where it is cleaned, dried, compressed, and refrigerated until it partially liquefies. It is then distilled into its components, mainly nitrogen oxygen and argon (Grayson et al., 1981). The oxygen gas is distributed as a compressed gas in high pressure cylinders.

Data for production of oxygen includes only the energy consumption of the process, since no process emissions occur nor is any waste produced:

- In the BUWAL 250 database (Habersatter, 1996) the energy consumption is quoted at 0,5 kWh electricity/kg O_2 produced.
- O_2 is assumed to be produced in Spain, therefore the spanish electricity mix is used (see 3.3.1.5.).
- The transport distance to deliver O_2 from the factory to the wastewater treatment plant is assumed to be 100 km, travelled by a 16 tonnes truck. Data from energy consumption (2,88 MJ diesel fuel/tkm) in the transport process is collected from the BUWAL database (Habersatter, 1996).

The corresponding aggregated inventory table for O_2 production is shown in appendix 1.

3.3.1.5. Electricity from the grid - scenario 1

Electricity is produced in Spain using several technologies, which are summarised in Table 9. In this Table also the contribution of each technology to total production in 2001 is shown. This mix of electricity production has been used in the scenario 1 as the energy source to run the AOPs.

Table 9. Technology mix for electricity production in Spain.

Technology	%
Coal	30,4
Natural gas	9,7
Hydropower	16,5
Nuclear	27,0
Oil	10,4
Others (renewable)	6,0

Source: IDAE, 2002.

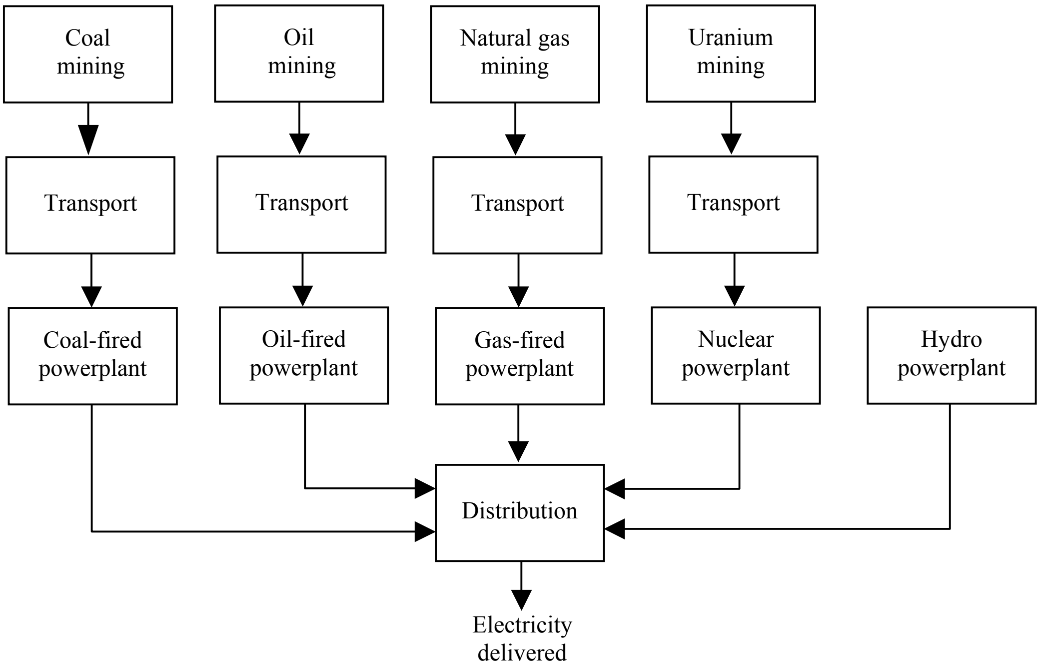

Figure 16. Processes involved in electricity production in Spain.

The environmental burdens of producing this mix of electricity has been calculated from the BUWAL database (Habersatter, 1996), which includes an inventory table for each technology. The following assumptions are made in this model:

- Generation of electricity (medium voltage) is based on the higher heating value of the fuels, and grid losses are accounted for.

- The system includes the production of primary energy resources and the processing and transport of the primary sources.

- The environmental impacts from infrastructure and capital goods are excluded.

- Renewable energy sources (except hydraulic), such as solar photovoltaic, wind power, and others, which account for 6% of total production of electricity in 2001, are not included in the database, and therefore this 6% is given zero impact.

The aggregated inventory table for the spanish mix of electricity, as a result of the contribution of each technology, is shown in appendix 1.

3.3.1.6. Electricity from co-generation - scenario 2

As it has been stated before, kraft pulp mills are almost self sufficient in energy terms, since only around 50% of the incoming wood is incorporated in the final product (market pulp), whereas the remaining 50%, constituted by black liquor and bark, is used in the plant to produce both electricity and process heat. This simultaneous production of electrical and thermal energy is called co-generation.

The main fuel in a kraft pulp mill is the so-called black liquor. In the cooking process, the fibres are liberated, dissolving the lignin and part of the hemicellulose in the cooking chemical solution (white liquor), which contains sodium hydroxide and sodium sulphide as active chemicals. The residue from this process, a solution containing the lignin and hemicellulose fraction, as well as the spent chemicals, constitutes the black liquor. This residue is used in a chemical and energy recovery system (Figure 17) aimed at recovering the inorganic pulping chemicals to be re-used, and at destructing the dissolved organic material and recovering its energy content.

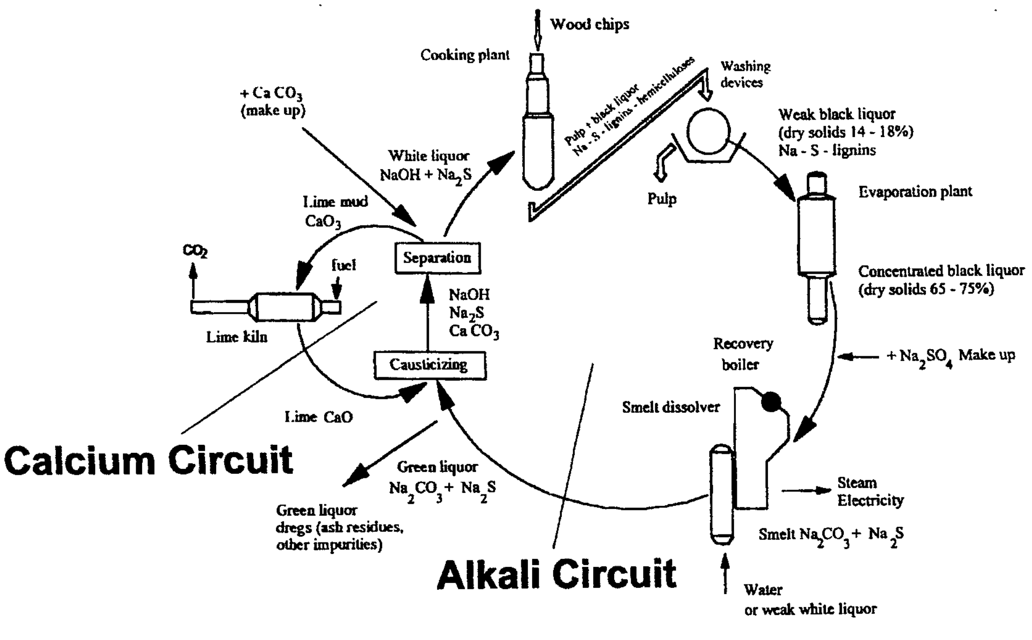

Figure 17. Recovery cycles of chemicals for a kraft mill. Source: EIPPCB, 2000.

Black liquor from pulp washing normally has a dissolved solids content of 14-18%, which has to be increased before the liquor can be burnt. The liquor is concentrated in a multi-effect evaporation plant to a dry-solids content of 65-75% and introduced in the boiler. In a conventional recovery boiler there is an oxidizing zone in the upper part and a reducing zone in the lower part (Figure 18). In the latter, a smelt consisting mainly of sodium sulphide and sodium carbonate is formed. These reduction reactions consume part of the energy released by combustion of the organic fraction in the oxidizing zone.

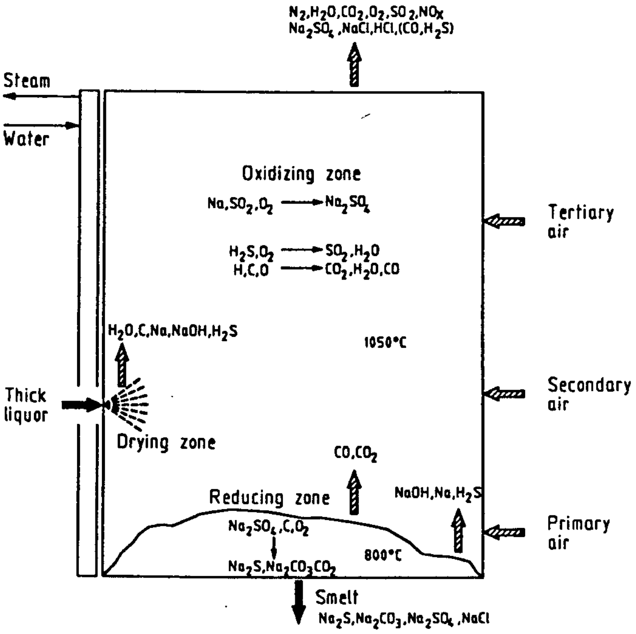

Figure 18. Some conceptual chemical reactions in a recovery boiler. Source: EIPPCB, 2000.

The second fuel in importance in a kraft mill is bark. This waste material is generated by debarking of the incoming wood. Debarking can be carried out either by the wet or the dry process, although the former is being phased out, because it uses and pollutes water, and creates bark with a lower energy content.

Figure 19 shows a typical energy system in a kraft pulp mill. In such a system, Boilers are used to generate steam at high pressures and temperatures; the high quality steam is delivered to turbines that utilize it to generate electricity. The steam, in passing through the turbine, loses temperature and pressure, and is finally used in the process.

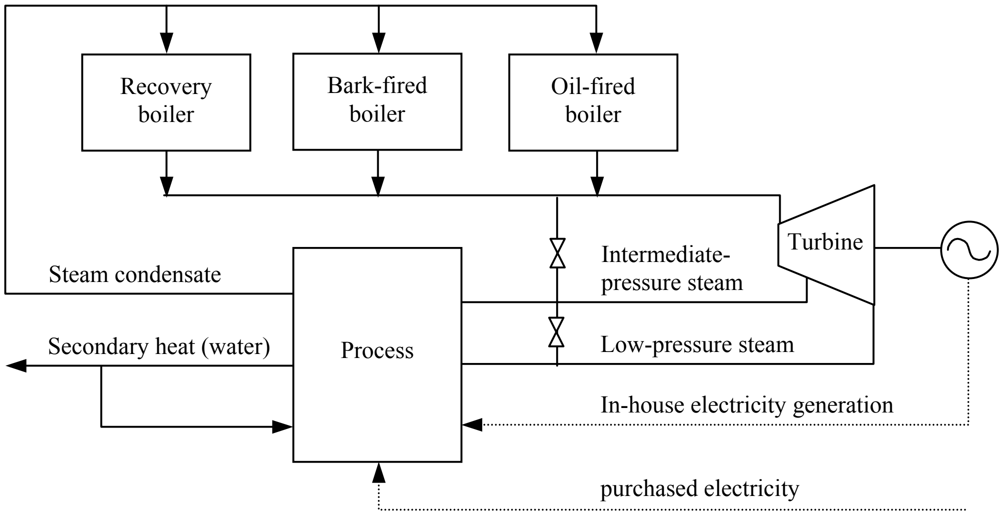

Figure 19. Typical energy system in a kraft pulp mill. Source: Smook, 1990.

The inventory of kraft mill electricity produced by co-generation has been developed specifically for the present study, as these data have not been found neither in databases nor in literature. Some hypothesis and allocation rules have already been discussed in sections 3.2.9. and 3.2.11. The detailed data sources and hypothesis considered in order to build the LCI are presented below:

- The energy profile of the plant has been collected from a kraft mill in Pontevedra, Spain, as shown in Table 10 (García, E., personal communication). The mill is absolutely self-sufficient in energy terms, therefore purchased electricity is set to zero.

Table 10. Energy sources considered for the kraft pulp mill.

Fuel	%
Black liquor	65
Bark	30
Oil	5
Total	100

Source: ENCE.

- As it has been discussed in section 3.2.11., environmental burdens related to co-generation have been allocated equally to the steam and electricity produced, using energy as a basis. In this approach, the environmental impact of producing 1MJ steam is the same as compared to producing 1 MJ of electricity. Another allocation rule to keep in mind is that fuel production is only included in the case of oil, while for black liquor and bark it is not included, as these materials are waste from pulp production.

- The CHP plant considered is a back-pressure turbine with intemediate steam tapping. The energy efficiency is about 80%.

- The calorific value for the different fuels are 15 MJ/kg dry solids in black liquor (Gullichsen & Fogelholm, 2000) and 10 MJ/kg bark in fresh weight (Brkich et al., 1999), and 42 MJ/kg for oil (Habersatter, 1996).

- Data for oil has been collected from the BUWAL 250 database (Habersatter, 1996). Includes detailed emission data on heat production from heavy oil in Europe, including production and transport of primary energy sources, excluding the infrastructure of the energy systems.

- Data on emissions related to black liquor and bark combustion have been calculated independently from different sources, mainly european, that are summarized below:

  EIPPCB (2000) includes recent data on SO_x , NO_x , and dust emissions for recovery boilers and bark boilers per ADt[10] produced.

  NGGIC (2000) includes average CO_2, CO, NO_x, CH_4, N_2O, and NMVOC emissions per MJ biomass burnt.

  BUWAL 132 database (Habersatter, 1991) also includes average dust, CO_2, CO, SO_2, NO_x, N_2O, and NMVOC emissions per MJ biomass burnt, and also overall dust, SO_2, CO, SO_2, NO_x, H_2S and mercaptan emissions per ADt produced.

  Adams et al. (1997) includes ranges of emissions for PAHs and metals in recovery boilers.

  Someshwar & Jain (1995) includes average data on HCl emissions per ADt from 15 kraft recovery boilers in Finland.

- Some emissions from recovery boilers are quantified per ADt. In order to express them per MJ of useful energy produced in the CHP plant, it has been assumed that 1,7 tonnes of black liquor solids (HHV 15 MJ/kg) are produced per ADt.

- The kraft mill is assumed to have an electrostatic precipitator (ESP) as the only pollution removal device.

Taking into account all these assumptions, the following consumptions are attributable to producing one kWh in a kraft mill:

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[10] Air dry tonne, with a 90% solids content.

- 0,225 MJ heavy oil.
- 2,93 MJ or 0,195 kg black liquor solids, attributable to 0,115 kg product pulp.
- 1,35 MJ bark, or 0,135 kg bark.

Resource consumption and emissions related to these amounts of materials can be found in the appendixs: in appendix 1 the aggregated inventory table is shown, while in appendix 2 detailed data on emissions from recovery boilers and bark boilers is shown.

3.3.1.7. Solar light - scenario 3

Solar energy is directly consumed in scenario 3 by photocatalytic processes and fenton like reactions (photo-assisted AOPs). This energy is completely clean, therefore zero environmental impact is considered.

3.3.2. Treatments

In this section every treatment is first briefly described, and energy and chemicals consumed are quantified; for the AOPs fundamentals, however, refer to section 3.2.2.

3.3.2.1. Photocatalysis (PhC)

In heterogeneous photocatalysis, a TiO_2 powder is added to the wastewater, and the mixture is irradiated with an UVA lamp. Once the treatment is finished, the catalyst has to be recovered. This is done in a separate tank, where the colloidal suspension is stored. By addition of a base, the pH of the suspension is displaced to attain the zero charge point (pH 7), in such a way to eliminate the forces of repulsion, and allowing the catalyst to be settled (Blanco et al., 2001). The supernatant is removed, and the catalyst is reused.

TiO_2 consumption is 2g/litre wastewater, and it is assumed that 95% of the catalyst is recovered (Malato, S. personal communication), whereas the remaining 5% is lost. The time needed to reach 15% TOC removal in 0,1 litres wastewater is 3 hours. The UVA lamp power is 6 W. Therefore the inputs per functional unit are:

- ⇒ 100 g TiO_2
- ⇒ 180 kWh for UVA irradiation

3.3.2.2. Fenton and photo-Fenton (FPhF)

In Fenton and photo-Fenton reactions, Fe (II) and H_2O_2 are added to the wastewater, and the mixture is irradiated with an UVA lamp. Once the treatment is finished, the effluent is discharged and the catalyst is considered not to be recovered.

H_2O_2 consumption is 500 ppm, being commercialized as 50% aqueous solution. Fe (II) consumption is 20 ppm. As discussed in section 3.2.9, in the calculations a Fe (III) source, $FeCl_3$ 40%, is considered. The time needed to reach 15% TOC removal in 0,1 litres wastewater is 1,25 hours. The UVA lamp power is 6 W. Therefore the inputs per functional unit are:

- ⇒ 1 kg H_2O_2 50%
- ⇒ 145 g $FeCl_3$ 40%
- ⇒ 75 kWh for UVA irradiation

3.3.2.3. Photocatalysis + H_2O_2 (PhC+H2O2)

In this case, H_2O_2 is used to improve heterogeneous photocatalysis. In this way, H_2O_2 is added along with TiO_2 powder to the wastewater, and the mixture is irradiated with an UVA lamp. Once the treatment is finished, the catalyst has to be recovered. The recovery stage, however, has already been described in section 3.3.2.1.

The concentration of H_2O_2 is 500 ppm, being commercialized as 50% aqueous solution. The TiO_2 load is 2g/litre wastewater, and it is assumed that 95% of the catalyst is recovered (Malato, S. personal communication), whereas the remaining 5% is lost. The time needed to reach 15% TOC removal in 0,1 litres wastewater is 1,75 hours. The UVA lamp power is 6 W. Therefore the inputs per functional unit are:

- ⇒ 1 kg H_2O_2 50%
- ⇒ 100 g TiO_2
- ⇒ 105 kWh for UVA irradiation

3.3.2.4. Photocatalysis + Fenton and photo–Fenton (PhC+FPhF)

This treatment is aimed at determining synergistic effects between these two processes. Fe (II), H_2O_2 , and TiO_2 powder are added to the wastewater, and the mixture is irradiated with an UVA lamp. Once the treatment is finished, TiO_2 catalyst has to be recovered. This recovery stage has already been described in secion 3.3.2.1. As discussed in 3.2.9, although the target catalyst is TiO_2, the recovery process also works for Fe (II), which is precipitated in the form of hydroxides, settled, and reused.

H_2O_2 consumption is 500 ppm, being commercialized as 50% aqueous solution. Fe (II) consumption is 20 ppm. As discussed in section 3.2.9, in the calculations a Fe (III) source, $FeCl_3$ 40%, is considered. TiO_2 load is 2g/litre wastewater. For both catalysts 95% is assumed to be recovered (Malato, S. personal communication), whereas the remaining 5% is lost. The time needed to reach 15% TOC removal in 0,1 litres wastewater is 0,5 hours. The UVA lamp power is 6 W. Therefore the inputs per functional unit are:

- ⇒ 1 kg H_2O_2 50%
- ⇒ 100 g TiO_2
- ⇒ 7 g $FeCl_3$ 40%
- ⇒ 30 kWh for UVA irradiation

3.3.2.5. Ozonation (O3)

In the ozonation treatment, wastewater is bubbled until saturation with a gas mixture containing oxygen and ozone, which is obtained from an ozonisator fed with pure oxygen. When the treatment is finished, the effluent is discharged.

The oxygen flow-rate through the ozonisator is 19,8 litres/hour, with a pressure of 0,5 bar. Assuming 298 ºK, the flow-rate is 81 g O_2/hour. The working current is 1 A, and the voltage 220 V, therefore the ozonisator power is 220 W. Finally, the time needed to reach 15% TOC in 0,1 litres wastewater is 0,5 hours. From these data the inputs to the system per functional unit are:

- ⇒ 405 kg O_2 for ozone production
- ⇒ 1.100 kWh electricity for ozone production

3.3.2.6. Ozonation + UVA (O3+UVA)

In this treatment the wastewater is simultaneously irradiated with UVA light, and bubbled until saturation with a gas mixture containing oxygen and ozone, which is obtained from an ozonisator fed with pure oxygen. When the treatment is finished, the effluent is discharged.

The oxygen flow-rate through the ozonisator is 19,8 litres/hour, with a pressure of 0,5 bar. Assuming 298 ºK, the flow-rate is 81 g O_2/hour. The working current is 1 A, and the voltage is 220 V, therefore the ozonisator power is 220 W. The UVA lamp power is 6 W. Finally, the time needed to reach 15% TOC in 0,1 litres wastewater is 0,25 hours. From these data the inputs to the system per functional unit are:

- ⇒ 203 kg O_2 for ozone production
- ⇒ 550 kWh electricity for ozone production
- ⇒ 15 kWh electricity for UVA irradiation

3.3.3. Summary tables

The following Tables contain a summary of the inputs to every treatment. First and second scenario includes all treatments, whereas third scenario excludes those treatments involving ozonation. For every chemical product, distribution by truck (either 16 or 40 tonnes payload) from the factory to the wastewater plant is quantified as tkm. The overall aggregated inventory table for every treatment can be found in appendix 1.

Table 11. Summary of energy and chemicals consumption per functional unit in scenario 1.

Inputs	Treatments					
	PhC	FPhF	PhC+H2O2	PhC+FPhF	O3	O3+UVA
Grid electricity (kWh)	180	75	105	30	1.100	565
TiO_2 (kg)	0,1		0,1	0,1		
Truck 40 t (tkm)	0,15		0,15	0,15		
Truck 16 t (tkm)	0,01		0,01	0,01		
$FeCl_3$ 40% (kg)		0,145		0,007		
Truck 16 t (tkm)		0,0145		0,0007		
H_2O_2 50% (kg)		1	1	1		
Truck 16 t (tkm)		0,1	0,1	0,1		
O_2 (kg)					405	203
Truck 16 t (tkm)					40,5	20,3

Table 12. Summary of energy and chemicals consumption per functional unit in scenario 2.

Inputs	Treatments					
	PhC	FPhF	PhC+H2O2	PhC+FPhF	O3	O3+UVA
Co-generation electricity (kWh)	180	75	105	30	1.100	565
TiO_2 (kg)	0,1		0,1	0,1		
Truck 40 t (tkm)	0,15		0,15	0,15		
Truck 16 t (tkm)	0,01		0,01	0,01		
$FeCl_3$ 40% (kg)		0,145		0,007		
Truck 16 t (tkm)		0,0145		0,0007		
H_2O_2 50% (kg)		1	1	1		
Truck 16 t (tkm)		0,1	0,1	0,1		
O_2 (kg)					405	203
Truck 16 t (tkm)					40,5	20,3

Table 13. Summary of energy and chemicals consumption per functional unit in scenario 3.

Inputs	Treatments			
	PhC	FPhF	PhC+H2O2	PhC+FPhF
TiO_2 (kg)	0,1		0,1	0,1
Truck 40 t (tkm)	0,15		0,15	0,15
Truck 16 t (tkm)	0,01		0,01	0,01
$FeCl_3$ 40% (kg)		0,145		0,007
Truck 16 t (tkm)		0,0145		0,0007
H_2O_2 50% (kg)		1	1	1
Truck 16 t (tkm)		0,1	0,1	0,1

3.4. Life Cycle Impact Assessment

The aim of LCIA is to determine the potential environmental impacts of a product system by using category indicators derived from LCI results. The LCIA phase provides information for the interpretation phase (ISO 1999).

In the present study the following elements of LCIA, have been carried out:

- Selection of impact categories, impact indicators and models
- Assignment of LCI results (classification)
- Calculation of category indicator results (characterisation)
- Normalisation

3.4.1. Selection and definition of impact categories

Over the last decades a large number of impact category models have been developed (Udo de Haes et al. 1999), such as for:

- Extraction of (a)biotic resources
- Land use
- Global Warming
- Stratospheric Ozone Depletion
- Human Toxicity and Eco-toxicity
- Photochemical Oxidant Creation
- Acidification
- Nutrification

This list summarizes the most commonly accepted and applied impact categories. The first two impact categories are input-related, while the latter ones are output-related. In the present study all these impact categories have been included, except land use, for which LCI data was not available in the main databases used. For eco-toxicity, an impact category usually subdivided in several compartments (terrestrial, freshwater, sediments, etc.) only the impact on freshwater has been included, since it is the most relevant compartment in the studied system. Finally, nutrification is also studied only for the aquatic ecosystem, and the corresponding category is called aquatic eutrophication.

In the following sections, the included categories as well as the impact models for characterisation are introduced.

3.4.1.1. Global Warming Potential (GWP)

Emissions as a result of human activities can affect the radiative forcing (heat radiation absorption) of the atmosphere. Most of these emissions enhance the radiative forcing, resulting in a rise in the earth's temperature. This, in turn, can cause adverse effects on ecosystem health, human health and material welfare.

The indicator used is the Global Warming Potential (GWP), that was created by the Intergovernmental Panel on Climate Change (IPCC). The GWP of a substance is the ratio between the contribution to the heat radiation absorption resulting from the instantaneous release of 1 kg of a greenhouse gas and an equal emission of CO_2 integrated over time (Houghton et al., 1994, 1995).

Substances contributing most to this category are CO_2, CH_4 and N_2O. It is important to note that biogenic CO_2 is not considered to be a contributor to the impact: If biogenic materials are grown on a sustainable basis (which has been assumed in the present study), then those emissions are considered simply to close the loop in the natural carbon cycle, returning to the atmosphere CO_2 that was originally removed by photosynthesis (IPCC, 1997).

3.4.1.2. Ozone Depletion Potentital (ODP)

Some substances emitted by human activities lead to the breakdown of stratospheric ozone. This in turn cause a larger fraction of the sun's UV-B radiation to reach the earth's surface than in their absence. This can have harmful effects on human health, animal health, terrestrial and aquatic ecosystems, biochemical cycles, as well as on materials.

The indicator used is the Ozone Depletion Potential (ODP) created by World Meteorological Organisation. The ODP is defined as the ratio between ozone breakdown in a state of equilibrium due to annual emissions (flux in kg/y.) of a quantity of a substance released into the atmosphere and the breakdown of ozone in a state of equilibrium due to an equal quantity of CFC-11 (WMO, 1992, 1995, 1998).

3.4.1.3. Aquatic Eutrophication Potential (AEP)

Eutrophication includes all impacts due to a too high level of macronutrients in the aquatic ecosystems. Nitrogen and phosphorus are the most eutrophicating elements. This enrichment may cause an undesirable shift in the composition of species and an increased production of biomass. In addition, high nutrient concentrations can also make surface water and groundwater unacceptable for water supply. An increased production of biomass may lead to low oxygen concentrations because the decomposition of this biomass needs oxygen. Then, contributors to this category are substances containing N, P, and also carbonaceous organic substances measured as COD.

The impact indicator is based on factors from Heijungs et al. (1992), based on the contribution of N and P to the average composition of aquatic organisms ($C_{106}H_{263}O_{110}N_{16}P$). These effect factors have been corrected for air emissions with fate factors from Huijbregts and Seppälä (2001), representative for Western Europe.

3.4.1.4. Acidification Potential (AP)

Acidifying substances cause a large number of diverse impacts on soil, groundwater, surface water, organisms, ecosystems and materials (buildings). Examples are fish dying in scandinavian lakes, forest decline and the crumbling of building materials.

The impact indicator used (Hauschild & Wenzel, 1998) is based on an assessment of the number of moles of hydrogen ions which can potentially be released to the environment from one mole of the substance in question.

3.4.1.5. Human Toxicity Potential (HTP)

This impact category contains the effects of toxic substances in the environment on humans. Toxicity categories are extremely complex. Reasons for this are the very large number of mechanisms, and the inter-media transport of substances.

The human toxicity model from Huijbregts (1999) has been used, where the fate of toxic substances, along with exposure and risk for humans with are modelled with the fate model USES-LCA. This impact model provides four different time horizons for toxicitiy assessment: 20, 100, 500 years, and infinite time. In order to be consistent with the GWP, the 100 years horizon has been chosen.

3.4.1.6. Fresh water Aquatic Toxicity Potential (FATP)

Eco-toxicological impacts are the effects of toxic substances on aquatic, terrestrial and sediment ecosystems. In the present study, as it has been already discussed, only the effects on the fresh water ecosystem have been included, since this is the most relevant compartment for the system under study. Toxicity categories are extremely complex. Reasons for this are the very large number of mechanisms, and the inter-media transport of substances.

The eco-toxicity model from Huijbregts (1999) has been used, where the fate of toxic substances, along with risk for ecosystems are modelled with the fate model USES-LCA. This impact model provides four different time horizons for toxicitiy assessment: 20, 100, 500 years, and infinite time. In order to be consistent with the GWP, the 100 years horizon has been chosen.

3.4.1.7. Photochemical Ozone Formation Potential (POFP)

Photo-oxidant formation is the formation of reactive substances (mainly ozone), which are injurious to human health and ecosystems, and which may damage crops. Precursors of photo-oxidants are mainly VOCs, CO, and NO_x. The latter, however, act as catalysts in the complex reactions.

The impact indicator used is the Photochemical Ozone creation Potential (POCP). A POCP af a VOC is is the ratio between the change in ozone concentration due to a change in the emission of that VOC and the change in the ozone concentration due to a change in the emission of ethylene (Derwent et al.,1998; Jenkin & Hayman, 1999; Hauschild & Wenzel, 1998).

3.4.1.8. Abiotic Resource Depletion (ARD)

This impact category is concerned with the extraction of different types of non-living material from the natural environment, such as iron ore, fossil fuels, etc. that occur as inflows to the system.

The indicator used (Guinée et al., 2000) is determined for each extraction of minerals and fossil fuels based on concentration reserves and rate of deaccumulation.

3.4.2. Classification and characterisation

In the classification step, the inputs and outputs are attributed to the impact categories they are expected to contribute. The contribution of the different substances is calculated by using the characterisation factors/methods used, which can be found in appendix 3. All inputs and outputs are considered to contribute to these categories to their potential full amount, which means that we did not account for the possible occurrence of parallel impacts (the contribution of the substance to one impact category diminishes the contribution to another). The results of characterisation are aggregated per impact category. Then, this yields one indicator per impact category.

3.4.3. Normalisation

In this step, the indicator result per impact category is given as a fraction of the reference contribution to this impact category of a certain region or person, over a particular interval of time. The normalisation step makes it possible to compare the contributions of the different impact categories, since they are now in the same dimensions: e.g. a fraction of the annual worldwide (or spanish) contribution to this category.

The reference region in this study should be Spain, but normalisation data for this country is not available at present. For this reason, normalisation has been based on the contribution of Western Europe in 1995, which is supposed to be more representative of the spanish situation than World normalisation data. The data used (Table 14) is from Guinée et al. (2000), although AEP figure has been adapted.

Table 14. Normalisation factors for Western Europe in 1995.

Impact category	Units	Factor (kg/year)
Global Warming Potential (GWP)	kg eq. CO_2/year	4,73E+12
Ozone Depletion Potential (ODP)	kg eq. CFC-11/year	8,30E+07
Aquatic Eutrophication (AEP)*	kg eq. PO_4^{3-}/year	2,69E+09
Acidification Potential (AP)	kg eq. SO_2/year	2,94E+10
Human Toxicity Potential (HTP)	kg eq. 1,4-d./year	7,49E+12
Fresh Water Aquatic Toxicity Potential (FATP)	kg eq. 1,4-d./year	4,72E+11
Photochemical Ozone Formation Potential (POFP)	kg eq. C_2H_4/year	8,24E+09
Abiotic Resource Depletion (ARD)	kg eq. Sb/year	1,48E+10

*** Factor adapted to include fate analysis, as the characterisation factors used.**

3.4.4. Weighting

Following normalisation, the results per impact category may be weighted. This means that the results for a certain category are multiplied by a weighting factor. Such a factor must be based on the relative importance of the particular impact category. This makes it possible to compare different categories and add them up to get one final LCA result. The weighting factors may be based on different approaches. For example, Guinée et al. (2000) recommend to base these weighting factors on some form of panel method.

ISO 14.042 does not permit weighting in cases where the results of an LCA will be used for a comparative assertion, that is, comparison of products for which the results will be used externally. This would be the case in the present study. Nevertheless, it has been decided to directly aggregate the normalisation results, which means that implicitly all impact categories are weighted with a factor of 1.

It is recognized that weighting is an extreme simplification of reality. For this reason, the weighted results will be used with care, and only in those cases where using only characterisation results yields an amount of information difficult to handle and to interpret.

3.5. Interpretation

In the interpretation phase, the results of the LCI and LCIA are summarised, analysed and discussed as a basis for conclusions, recommendations and decision making, in accordance with the goal and scope (see sections 3.1 and 3.2).

The Interpretation has been structured as folllows:

1. First, the results for the three scenarios are presented, discussed, and compared
2. Second, a sensitivity analysis is performed to check the consistency of the results
3. Finally, conclusions and recommendations are reported

3.5.1. Scenario 1

The results of the first scenario, where the AOPs are assumed to consume electricity from the grid, are presented and discussed below.

3.5.1.1. Contribution analysis

This first analysis is aimed not at comparing the different treatments among them, but at identifying the critical sub-systems for each treatment and impact category. For this purpose the characterisation results are used, disaggregating them so that the contribution of the chemical products and electricity can be analysed. Figure 20 shows, for each treatment, these relative contributions. Every impact indicator is expressed as 100% and the contribution of a sub-system is therefore a fraction of this 100%. The numerical data on which these graphics are based can be found in appendix 4.

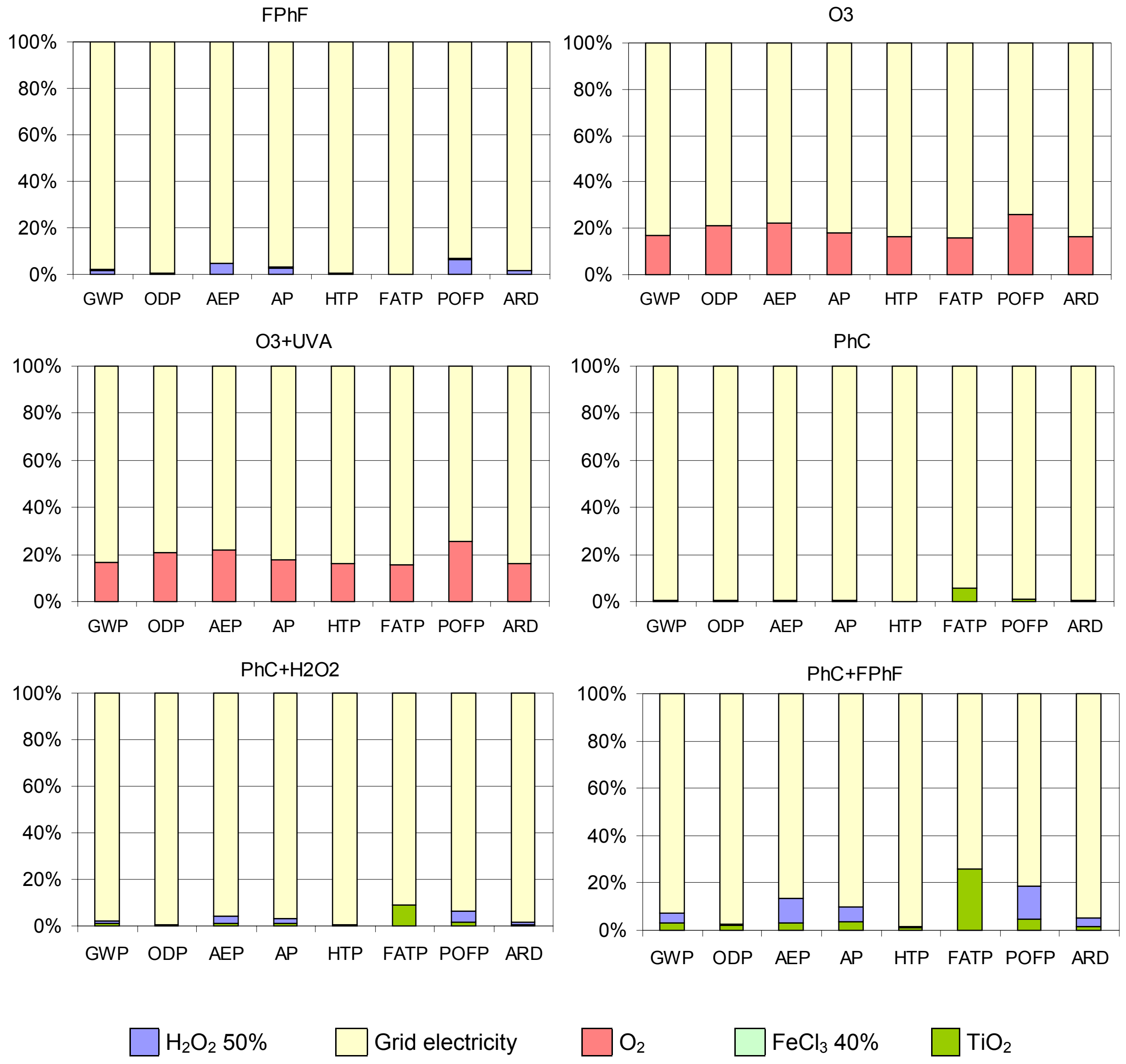

Figure 20. Contribution of sub-systems in the characterisation results of scenario 1.

From Figure 20 it can be highlighted that electricity production, either to run the UVA lamp or to produce ozone, is by far the most critical sub-system, accounting for at least 80% of the contribution to all impact categories in all treatments. In some cases electricity is responsible of almost 100% of the contribution. This noticeable impact is caused by the energy intensity of the AOPs, and the characteristics of the spanish mix for electricity production, which relies in a considerable extent on highly polluting fuels such as coal and oil.

The contribution of chemicals is low, or even negligible. Only in the treatments using ozone, oxygen production appears to be a considerable contributor to all categories, being responsible of about 20% of the overall impacts. In PhC+FPhF, TiO_2 causes a moderate contribution (25%) to FATP due to emissions of heavy metals to water in the chloride process, and H_2O_2 contributes mostly to POFP, AEP and AP, due to emissions of VOCs, NO_x and SO_x. On the other hand, $FeCl_3$ has a negligible contribution in those treatments using this salt, which can be explained by the low dose applied.

As a summary, it can be stated that the AOPs analysed are mainly energy-intensive, and this leads to an environmental impact proportional to the overall energy consumption of each technology.

3.5.1.2. Comparative analysis

In this section the different treatments are compared under scenario 1 conditions. Figure 21 shows the overall characterisation results, representing the most impacting treatment as 100% for each category. Figure 22 shows the normalisation results aggregated in a single impact indicator. The numeric data on which these graphics are based can be found in appendix 4.

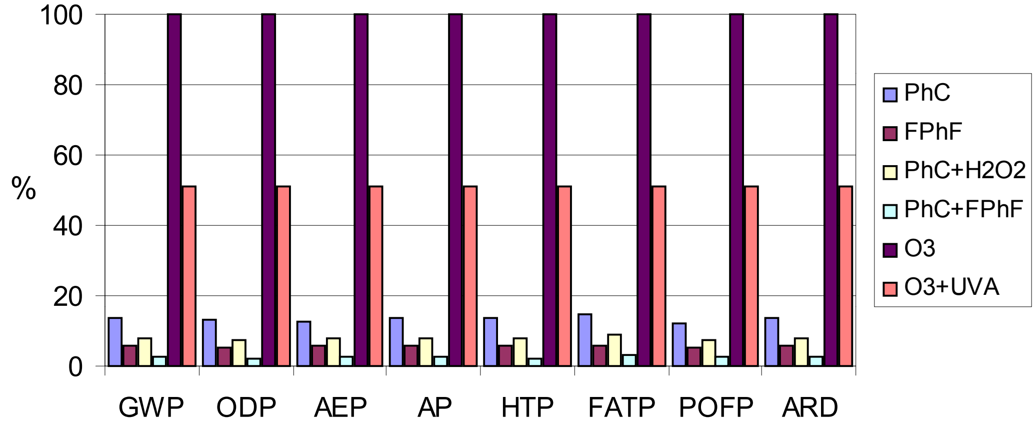

Figure 21. Characterisation results for scenario 1.

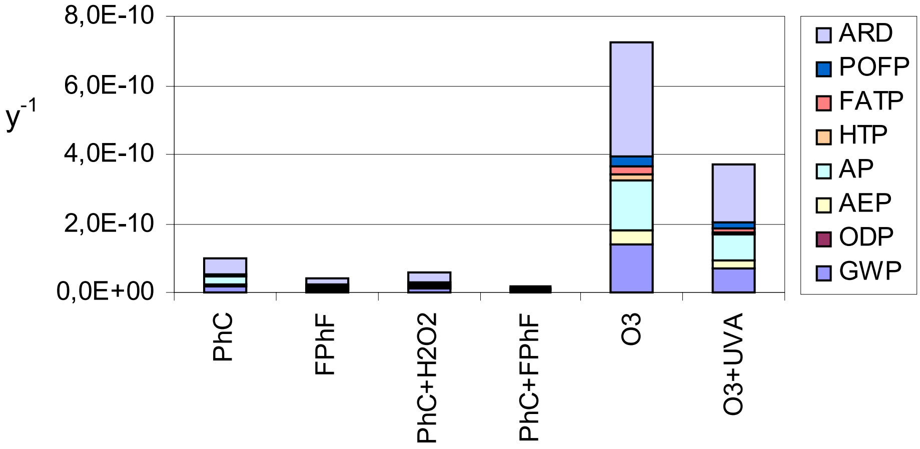

Figure 22. Total weighted results for scenario 1.

In Figure 21 it can be seen that the different treatments score different in a given impact category, but the relative score is repeated in the remaining impact categories. This is due to what was already discussed in the contribution analysis: the environmental impact is proportional to electricity consumption. In this way, the higher the electric consumption of a treatment, the higher the impact in all categories.

From this pattern, also reflected in the weighted results (Figure 22), the treatments can be ranked according to their environmental impact as follows:

- O3 and O3+UVA have the higher impact, and comparing their results it can be noticed that combining ozone with UVA light decreases the impact about 50%.

- The photo-assisted AOPs, that is, the remaining treatments, cause an environmental impact substantially lower, being the higher PhC and the lower PhC+FPhF (5 times lower). It is noticeable that photocatalysis using only TiO_2 (PhC) obtains the worst results in this group, but when this technique is combined with Fenton like reactions (PhC+FPhF), it appears as the best treatment, suggesting that a synergistic effect occurs.

The first question that arises is the big difference between using or not using ozone. As it was discussed in the hypothesis and limitations of the study (section 3.2.9.), from the inventory data it has been calculated an energy consumption of about 150 kWh/kg ozone produced, while from literature data a figure of 15 kWh/kg ozone is reported for an industrial ozonisator. It can be argued that the UVA lamps are also small scale, thus making the comparison apparently fair, but the differences between small and industrial lamps may not be so important as for ozone. For this reason, the ozonation treatments will be an object of sensitivity analysis in section 3.5.4.

From the normalisation results another information that can be drawn is the impact categories to which our system contribute most, using as reference the yearly environmental impact of Western Europe. In scenario 1, the AOPs cause the larger impacts on ARD, AP and GWP, while in AEP, HTP, FATP and POFP the contribution is moderate, and even negligible in ODP.

3.5.2. Scenario 2

The results of scenario 2, which is considered to be more representative of the kraft pulp industry, are next described and discussed, following the same structure as for scenario 1.

3.5.2.1. Contribution analysis

Figure 23 shows, for each treatment, the relative contributions of the sub-systems to the impact categories. Every impact category is expressed as 100% and the contribution of a sub-system is therefore a fraction of this 100%. The numerical data on which these graphics are based can be found in appendix 4.

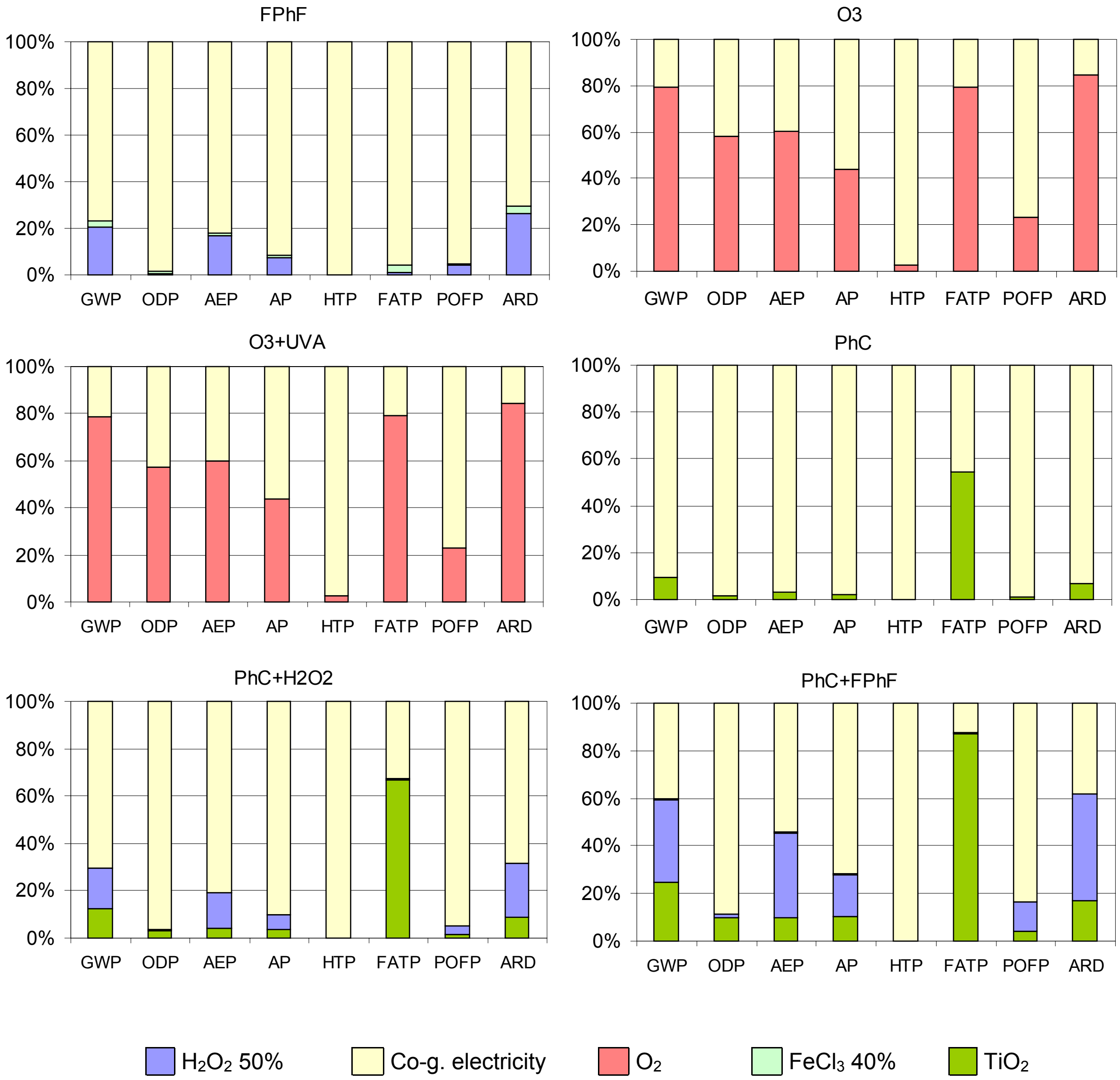

Figure 23. Contribution of sub-systems in the characterisation results of scenario 2.

In scenario 2, as can be seen in Figure 23, the sub-system contributing most to the impact categories in several treatments is, similarly to scenario 1, energy production, but the contributions of the chemical products are significantly higher, and even decisive in some cases: TiO_2 is responsible of 55% to 85% of FATP in treatments involving photocatalysis, and O_2 is responsible of between 20% and 80% of the contribution to different impact categories in those treatments using Ozone.

The lower contribution of electricity in this scenario, meaning a lower environmental impact, is a consequence of the specific energy profile of the kraft pulp industry. Two reasons explains this:

- Biomass, a renewable fuel, is mainly used.
- The energy efficiency in co-generation is about 80%, as compared to 30-40% in conventional power plants supplying electricity to the grid.

However, in two impact categories, HTP and POFP, the environmental impact of kraft mill electricity is higher as compared to grid electricity (this can not be seen from Figure 22, but will be shown when results of scenarios 1 and 2 are compared in section 3.5.2.3). For HTP this is attributed to PAH emissions, and to VOC emissions for POFP. Nevertheless, these pollutants have been calculated from rather uncertain data (see appendix 2), specially PAHs. Therefore, these categories have to be dealt with carefully in this scenario. We have decided not to perform a sensitivity analysis on this issue, because the goal of the study is not to compare different industrial energy profiles, but the AOPs that use them.

As mentioned above, the contribution of chemical products to the environmental impact is quite relevant in this scenario. The contribution of oxygen, used as feedstock for ozone production in O3 and O3+UVA treatments, is dominant in all categories, except in HTP and POFP. TiO_2 impact in FATP is remarkable for all those treatments using this catalyst, and H_2O_2 production has also relevant contributions in ARD, AEP and GWP. $FeCl_3$ impact is negligible, as it was in scenario 1.

3.5.2.2. Comparative analysis

Figure 24 shows the overall characterisation results, representing the most impacting treatment as 100% for each category. Figure 25 shows the weighted results aggregated in a single impact indicator. The numeric data on which these graphics are based can be found in appendix 4.

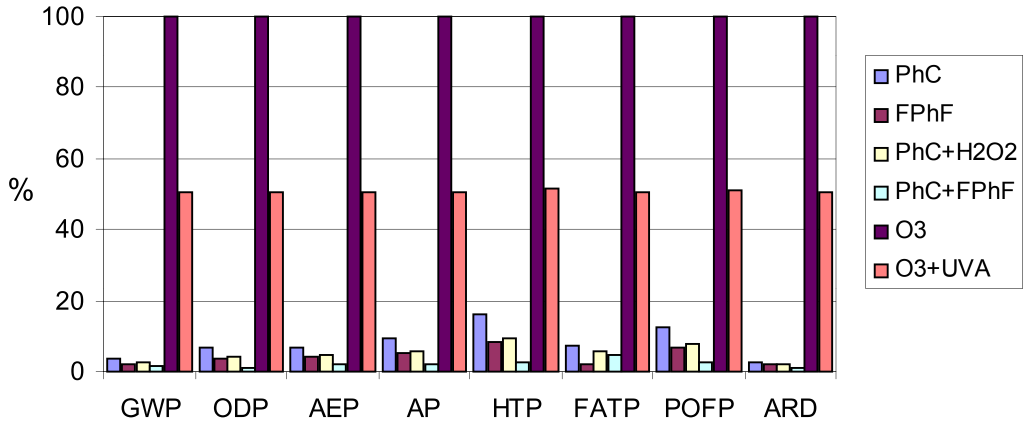

Figure 24. Characterisation results for scenario 2.

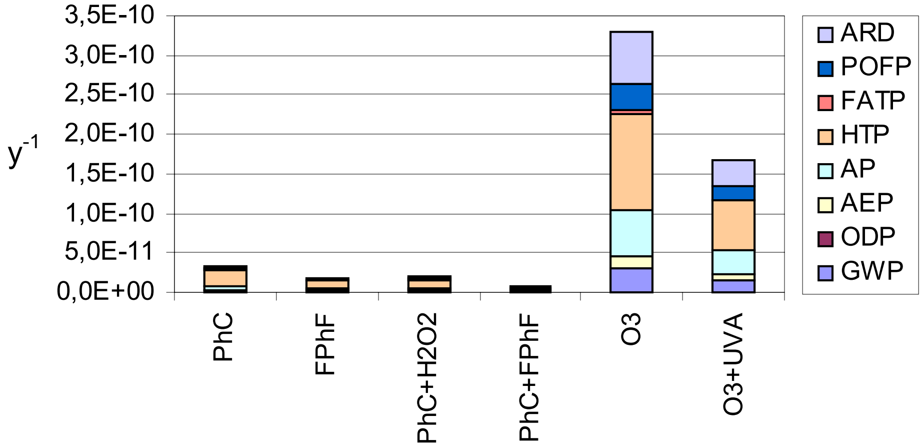

Figure 25. Total weighted results for scenario 2.

The characterisation results in Figure 24 show a similar pattern than the corresponding characterisation profile of scenario 1 (see Figure 21). Although the overall environmental impact is different in this scenario because of the different energy profile (this can not be seen in this figure, since impact indicators are expressed in relative values), comparing the different AOPs leads almost to the same point than in scenario 1:

- O3 and O3+UVA have the higher impact, and comparing their results it can be noticed that combining ozone with UVA light decreases the impact about 50%.
- The photo-assisted AOPs, cause an environmental impact substantially lower, being the higher PhC and the lower PhC+FPhF (2 to 6 times lower, depending on the category), except in FATP, where FPhF causes the lowest impact (4 times lower than PhC).

These statements are also reinforced by the weighted results (Figure 25). Aggregating normalisation results in a single score leads to the same ranking of treatments than scenario 1 (Figure 22). The differences are found in the impact categories having greater contributions in the normalised score; while in scenario 1 the main contributions are in ARD, AP, and GWP, in scenario 2 the largest contribution is found in HTP, for the reasons which have been discussed in the contribution analysis (3.5.2.1.).

3.5.2.3. Scenario 1 vs. scenario 2

In Figure 26 the weighted results for scenario 1 and 2 are represented together, showing for each treatment the differences in impacts. On the other hand, Table 15 shows the weighted environmental saving of scenario 2 with regard to scenario 1. In this case characterisation results are not shown to avoid an excessive amount of information (6 treatments x 2 scenarios x 8 impact categories).

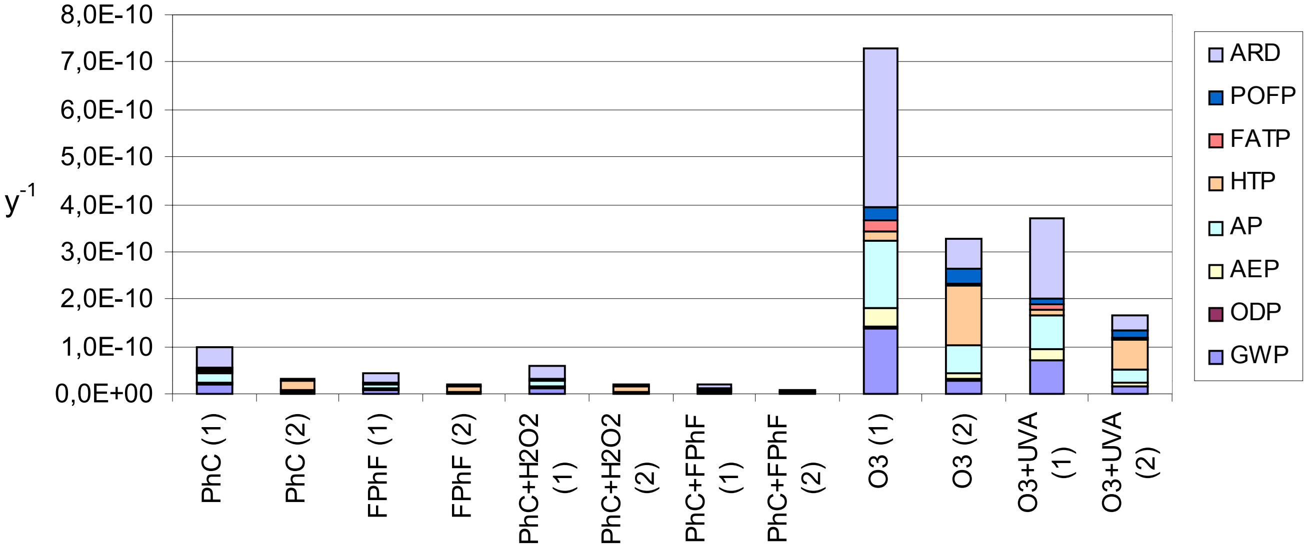

Figure 26. Total weighted results in scenarios 1 and 2.

Table 15. Total weighted impact reduction for each treatment in scenario 2.

Treatment	PhC	FPhF	PhC+H2O2	PhC+FPhF	O3	O3+UVA
% impact reduction	66	56	65	60	55	55

From both Figure 26 and Table 15 it can be stated that the application of AOPs in a kraft pulp mill would cause a lower environmental impact than the application in industrial sectors using electricity from the grid. It should be borne in mind, however, that in HTP, kraft mill energy causes an impact 7 times larger than grid electricity, due to PAH emissions, although it has been already discussed that there is a high uncertainty in the inventory data used for these emissions. In these weighted results the larger contribution to HTP is compensated by a lower contribution in the remaining categories.

3.5.3. Scenario 3

In scenario 3, the AOPs are assumed to use solar light as energy source to provide photons for use in the chemical process. Since ozone has to be produced using electricity, both O3 and O3+UVA treatments are excluded from this scenario.

3.5.3.1. Contribution analysis

Figure 27 shows, for each treatment, the relative contributions of the sub-systems to the impact categories. In this scenario the sub-systems consist only of production and delivery of chemicals. Every impact category is expressed as 100% and the contribution of a sub-system is therefore a fraction of this 100%. The numerical data on which these graphics are based can be found in appendix 4.

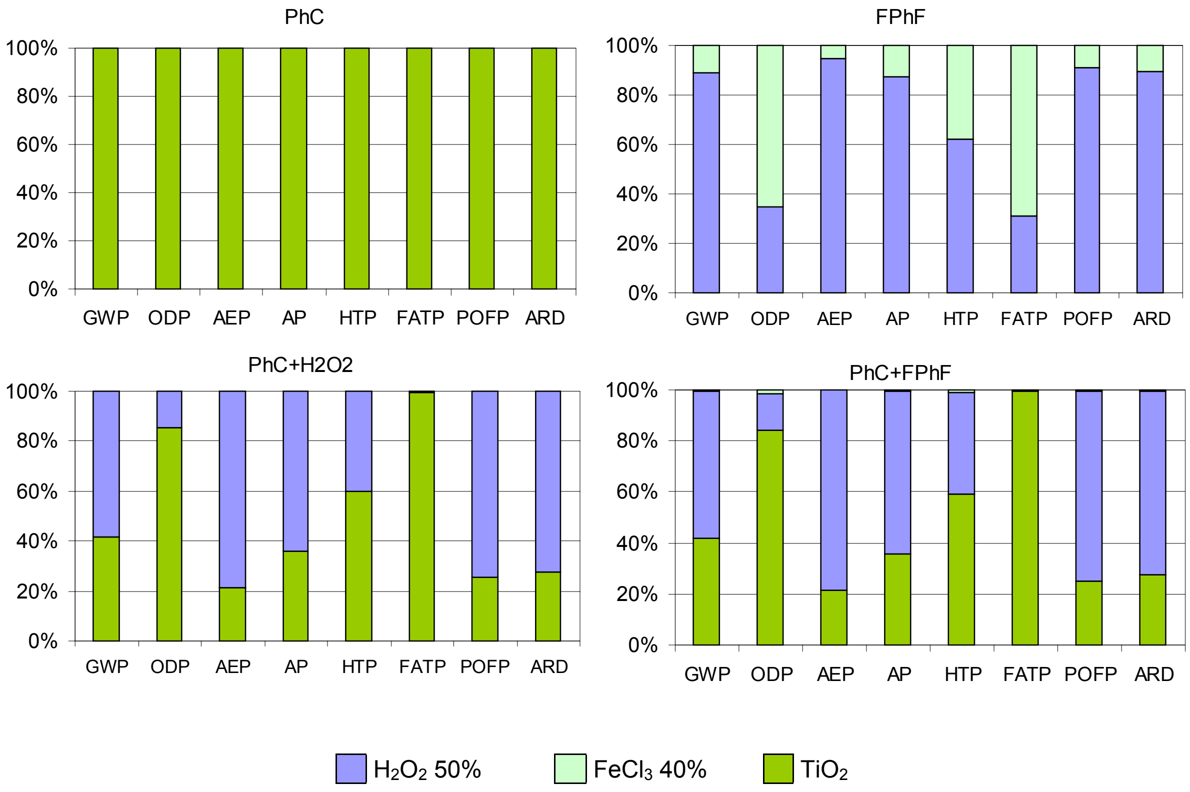

Figure 27. Contribution of sub-systems in the characterisation results of scenario 3.

The contributions to impacts in this scenario are originated by H_2O_2, TiO_2 and $FeCl_3$. There is neither electricity consumption, nor oxygen consumption, since oxygen is only used to produce ozone, a sub-system excluded from this scenario.

In the PhC treatment, 100% of the impacts are produced by TiO_2 since this product is the only input to the system. In the other three treatments, combining the use of TiO_2, H_2O_2 and $FeCl_3$, the impacts are originated mainly by TiO_2 and H_2O_2, with variable contributions, depending on the impact category. The only treatment where $FeCl_3$ has a noticeable contribution is FPhF (from 10% to 70% depending on the category); the reason is that in this treatment Fe is not recovered, thus the 20 ppm added are consumed, while in PhC+FPhF treatment 95% of Fe is recovered.

3.5.3.2. Comparative analysis

Figure 28 shows the overall characterisation results, representing the most impacting treatment as 100% for each category. Figure 29 shows the weighted results aggregated in a single impact indicator. The numeric data on which these graphics are based can be found in appendix 4.

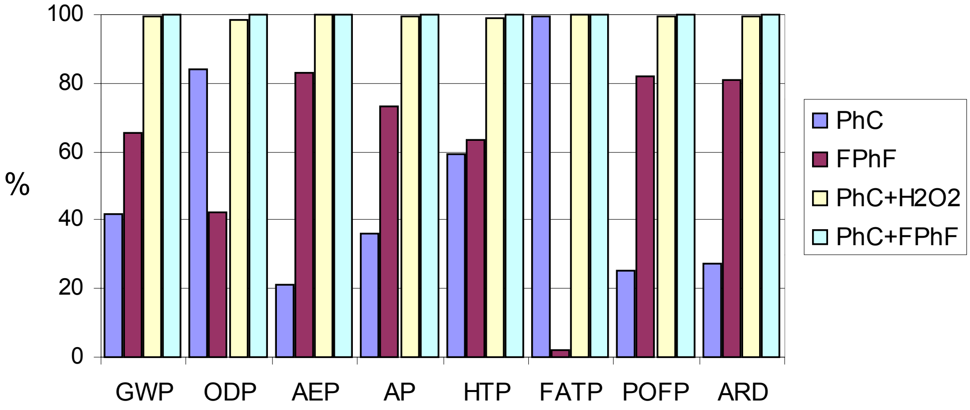

Figure 28. Characterisation results for scenario 3.

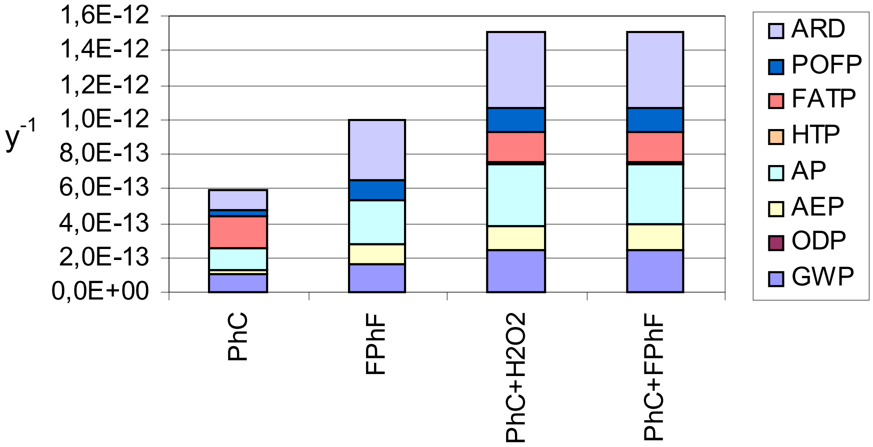

Figure 29. Total weighted results for scenario 3.

The question in this scenario is: if the AOPs are to be applied using solar energy, which of the treatments analyzed would have the least environmental impact?. In Figure 28 it can be observed that none of the treatments is preferable for all the impact categories. However, PhC and FPhF appear as the best options, since they obtain the same product (15% TOC removal) consuming less chemical products. If these treatments are compared, PhC has less environmental impact, except in ODP and FATP.

One of the important changes to observe in this scenario is that the best treatment in both scenario 1 and 2, PhC+FPhF, is far from being so in this scenario, suggesting that it is a good option when the impact of energy production is the main concern, but when it is not, as it is the case in this scenario, the extra consumption of chemicals is not justified.

When the environmental impacts are aggregated in a single score (Figure 29), the worse results for PhC+H2O2 and PhC+FPhF arise again, and PhC shows the best results, with a score 40% lower as compared to FPhF and 3 times lower than PhC+H2O2 and PhC+FPhF.

These results, however, should be handled with care, since the functional unit used is not as suitable in this scenario as it was for the other scenarios: in scenarios 1 and 2 the energy consumption was allocated to TOC removal by means of reaction time, and chemicals were allocated by means of volume of treated water. As discussed in section 3.2.11.2, the allocation method for chemicals is not satisfactory. Nevertheless, as it has been shown in the results, the critical parameter in those scenarios is by far energy, and not chemicals, reason for which the allocation for chemicals is not considered to have a serious influence. This, on the other hand, is completely different in scenario 3, because energy consumption is no longer taken into account (solar light is clean), and therefore chemicals become the critical factor. In order to assess if the results of scenario 3 could be influenced by the functional unit used, a sensitivity analysis will be performed (see section 3.5.4).

3.5.3.3. Scenario 1 vs. scenario 3

In Figure 30 the weighted results for scenario 1 and 3 are represented together, showing for each treatment the differences in impacts, aggregated in a single score. On the other hand, Table 16 shows for each treatment the weighted environmental saving of scenario 3 with regard to scenario 1. In this case characterisation results are not shown to avoid an excessive amount of information (4 treatments x 2 scenarios x 8 impact categories).

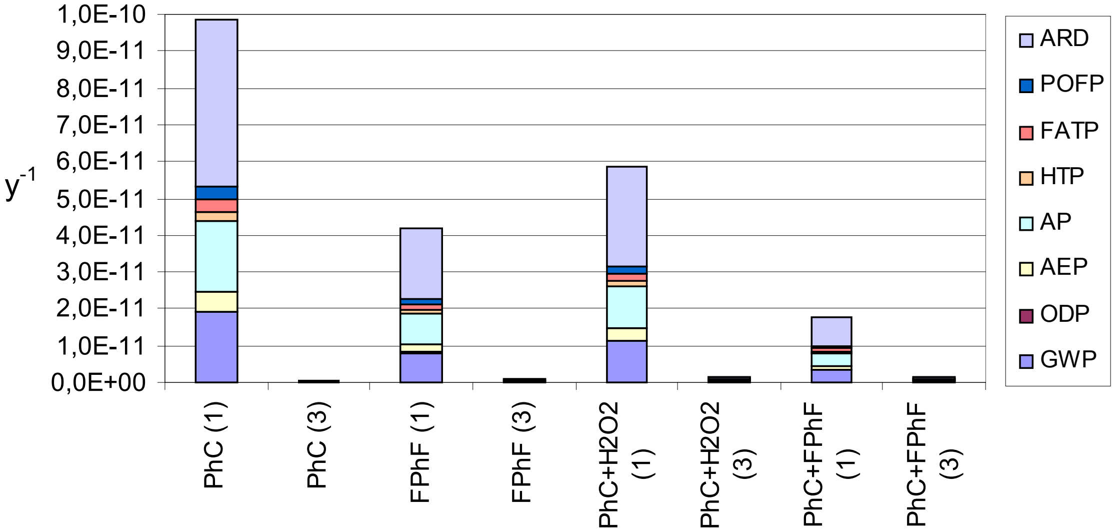

Figure 30. Total weighted results in scenarios 1 and 3.

Table 16. Total weighted impact reduction for each treatment in scenario 3.

Treatment	PhC	FPhF	PhC+H2O2	PhC+FPhF
% impact reduction	99	98	97	92

The potential improvements of using solar energy as a source of photons for the AOPs can be clearly seen in Figure 30 and Table 16. The overall environmental impact, expressed as single score, decreases more than 90% for each treatment with regard to the same treatment in scenario 1. This is of special interest in countries like Spain, where solar radiation is intense and relatively constant.

3.5.4. Sensitivity analysis

A number of different sensitivity analysis are undertaken in this section, to see the effect on the overall results. In the present study three scenarios have been analysed; this, in fact, can be considered as a sensitivity analysis, being energy the key parameter. In this section, however, the key areas on which sensitivity has been tested are:

- Energy consumption for ozone production
- Functional unit in scenario 3

3.5.4.1. Ozone production

Treatments using ozone as a precursor of OH radicals (O3 and O3+UVA) have proved to have the largest environmental impact, due to the high energy consumption of the ozonisator considered, which is a laboratory scale equipment. It has been stated before that as the UVA lamps used for the other treatments are also laboratory scale devices, the comparison among treatments is coherent. However, technical data from industrial ozonisators has been collected (http://www.ozon-sander.de/index.en.html), and energy consumptions per unit ozone produced, when using pure oxygen as feedstock, are about 15 kWh/kg O_3, whereas in the inventory analysis a figure of 150 kWh/kg O_3 was calculated for the laboratory ozonisator. Also the conversion efficiency appears to be one order of magnitude higher for industrial ozonisators, being about 0,15 kg O_3/kg O_2 fed, while from the inventory data a figure of 0,019 kg O_3/kg O_2 has been estimated.

In this sensitivity analysis we assume that in a full-scale plant, ozonation data would be in the industrial range discussed above, while for UVA lamps the laboratory data used in scenario 1 is representative, since the shift in scale would not be so important.

In order to see the effect of this hipothesis on the results, a sensitivity analysis has been performed, in which the industrial ozonisator data above discussed has been used. Transport of oxygen to the wastewater treatment plant has also been recalculated, taking into account the lower amount of oxygen needed. In Table 17 the new inventories for O3 and O3+UVA are summarised. Figure 31 shows the weighted environmental impact of O3 and O3+UVA treatments in the baseline scenario and the same treatments calculated with the industrial ozonisator data. On the other hand, in Figure 32 the new results are compared to the remaining processes in scenario 1.

Table 17. Summary of energy and chemicals consumption per functional unit for treatments using ozone in scenario 1, recalculated with industrial ozonisator data.

Inputs	O3 (ind.)	O3+UVA (ind.)
Grid electricity (kWh)	113	71
O_2 (kg)	50	25
Truck 16 t (tkm)	5,0	2,5

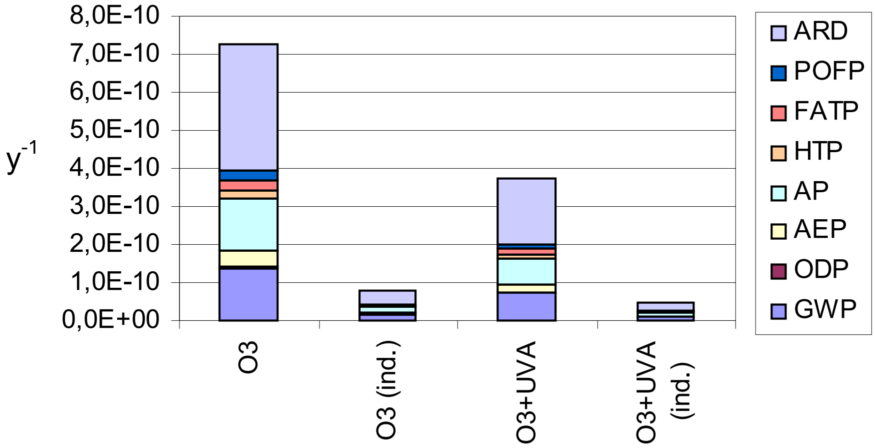

Figure 31. Total weighted results of treatments using ozone in scenario 1, and the same treatments calculated with industrial ozonisator data (ind.).

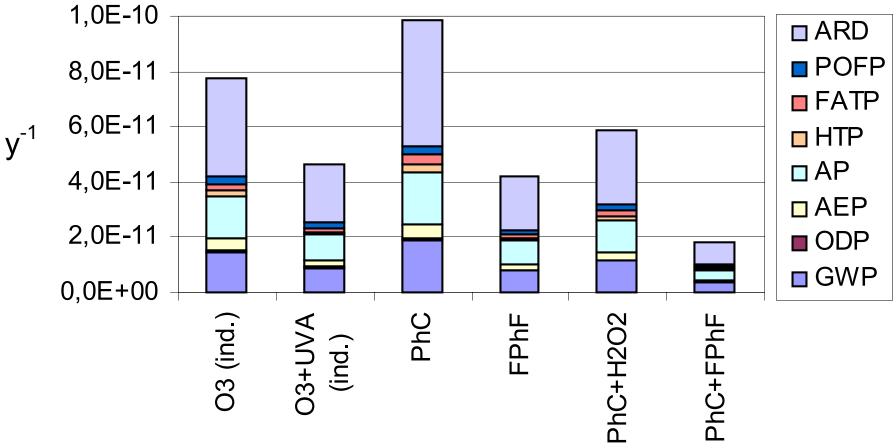

Figure 32. Total weighted results of scenario 1. Treatments using ozone are calculated with industrial ozonisator data.

As it can be seen in Figure 31, if industrial efficiency is assumed to produce ozone, both the environmental impact of ozonation in the dark (O3) and ozonation in the presence of UVA light (O3+UVA) decreases almost 90% with regard to the initial situation, in which the laboratory efficiency is used.

The difference between both treatments in this new situation can be better seen in Figure 32. As in the initial situation, O3+UVA has an environmental impact significantly lower than O3, since TOC removal is enhanced by the use of UVA light in combination with ozone. The overall impact reduction is 40%, a little lower than using the original data, where it is 50%.

If both ozonation treatments are now compared to the remaining AOPs (Figure 32), it is observed that the results differ widely from what was presented in section 3.5.1.2. If the industrial efficiency is considered to produce ozone:

- O3 and O3+UVA are no longer the most impacting treatments. In this case PhC is the worse treatment, with a weighted impact about 30% higher than O3, which is the second most impacting treatment.

- O3+UVA has a weighted environmental impact similar to FPhF, and 25% lower than PhC+H2O2.

- PhC+FPhF is still the preferable option in scenario 1.

Probably performing this sensitivity analysis to scenario 2 (where electricity is produced by means of co-generation) would have led to the same conclusions.

3.5.4.2. Functional unit in scenario 3

The second sensitivity analysis is concerned with the suitability of the functional unit (as defined in section 3.2.6) to compare the photo-assisted AOPs in scenario 3.

In scenario 3 the environmental impact of energy is set to zero, as solar energy is directly consumed. Therefore, the only inputs to the system are chemical products, which are allocated to the functional unit on the basis of volume of treated water, regardless of the amount of TOC removed. In scenarios 1 and 2 this is not a problem, since the hotspot is electricity production, and the contribution of chemicals is very low, so the allocation method for chemicals, although not satisfactory, is assumed not to be critical in these scenarios. Nevertheless, in scenario 3 this allocation method could lead to wrong results, since these only depend on the impact of chemical products.

The functional unit, as defined in section 3.2.6 does not allow another allocation method for chemicals, because it is not possible to know which fraction of the dose applied has to be allocated to the 15% TOC destroyed. For this reason, in this sensitivity analysis the functional unit is changed to be more in accordance with these limitations. The new functional unit is defined as:

Removal of 1kg TOC from a kraft pulp mill wastewater as shown in Table 5.

This is the functional unit used by Pérez et al. (2002) in the economic study on which the present LCA is based. Using this functional unit, which is also in accordance with the system function (see section 3.2.5), chemicals consumption is directly allocated to the amount of TOC removed by each treatment.

From the amount of TOC removed by each treatment after the 3 hours experiment (Table 4), the dose of chemicals applied, and taking into account the recovery of catalysts as well as the transport distances, a new inventory table for scenario 3 can be obtained (Table 18).

Apart from the limitations discussed in section 3.2.6. for this functional unit, there is another limitation when this scenario is applied: we are not taking into account that solar energy is more intense than the UVA lamp considered, in the wavelength range in which the AOPs are active. This higher intensity would enhance the processes involving Fenton and photo-Fenton reactions, but it is not likely to do so in those using only TiO_2, since the photoactivity of this catalyst attains a saturation level with the current lamp intensity (Pérez et al., 1997; 2002). Therefore, a higher TOC reduction after the 3 hours experiment would be expected in some AOPs than it was observed with the UVA lamp (see section 3.2.3). This will be taken into account when interpreting the results of this sensitivity analysis.

Table 18. Summary of energy and chemicals consumption in scenario 3, recalculated for the new functional unit.

Inputs	Treatments			
	PhC	FPhF	PhC+H2O2	PhC+FPhF
TiO_2 (kg)	1,5		1,1	0,8
Truck 40 t (tkm)	2,25		1,65	1,2
Truck 16 t (tkm)	0,15		0,11	0,08
$FeCl_3$ 40% (kg)		1,1		0,1
Truck 16 t (tkm)		0,11		0,01
H_2O_2 50% (kg)		7,6	10,8	7,6
Truck 16 t (tkm)		0,76	1,08	0,76

Figure 33 shows the overall characterisation results, representing the most impacting treatment as 100% for each category. Figure 34 shows the weighted results aggregated in a single impact indicator. The numeric data on which these graphics are based can be found in appendix 4.

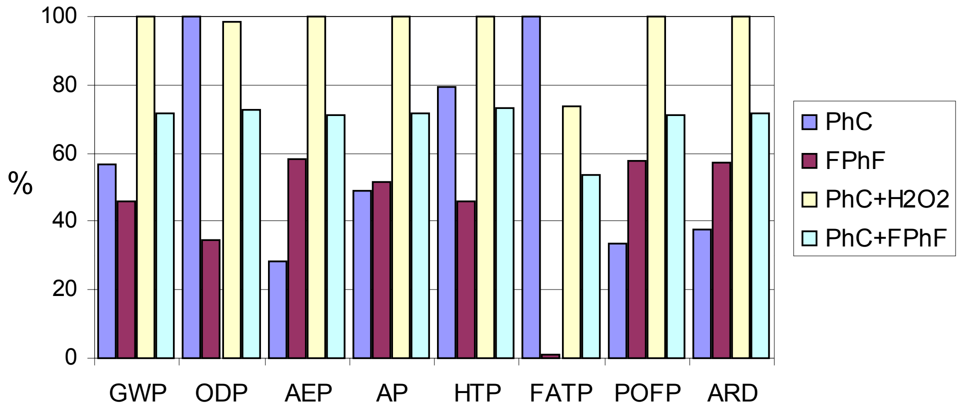

Figure 33. Characterisation results for scenario 3, recalculated for the new functional unit.

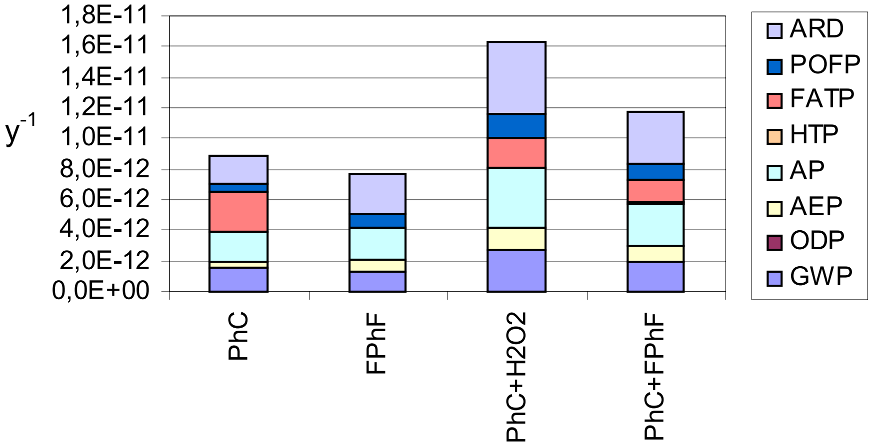

Figure 34. Total weighted results for scenario 3, recalculated with the new functional unit.

As already happened to the original functional unit, the AOP having the lowest environmental impact in scenario 3 can not be identified from the characterisation results (see Figures 32 and 29). However, some changes can be observed: the impact of FPhF decreases in most impact categories, and so does PhC+FPhF, which was one of worse options using the original functional unit.

The new weighted results also show differences with regard to the original ones:

- PhC and FPhF appear together as the low-impact AOPs, being the impact of PhC slightly higher (15%) due to the important contribution to FATP.

- As already mentioned, PhC+FPhF has a lower impact than in the original functional unit when compared to the other treatments, and PhC+H2O2 is still the worst option.

Considering the similar results obtained by PhC and FPhF (Figure 34), and if it is taken into account that solar energy would increase the rate of AOPs involving Fenton and photo-Fenton reactions respect to heterogeneous photocatalysis, it can be stated that FPhF is possibly the preferable option in this scenario, using the weighted impact approach.

3.5.5. Conclusions and recommendations

In the present LCA, six options for advanced oxidation of effluents from kraft pulp bleaching have been assessed:

- Heterogeneous photocatalysis (PhC)
- Fenton and photo-Fenton (FPhF)
- Heterogeneous photocatalysis in combination with hydrogen peroxide (PhC+H2O2)
- Heterogeneous photocatalysis in combination with Fenton and photo-Fenton (PhC+FPhF)
- Ozonation in the dark (O3)
- Ozonation in the presence of UVA light (O3+UVA)

These options have been assessed under three possible scenarios or conditions, concerning the energy sources to run the AOPs:

- Electricity from the grid
- Electricity from co-generation in a kraft pulp mill
- Solar light (in this scenario treatments involving the use of ozone are excluded)

The key findings of this study are summarised in the following sections.

3.5.5.1. Sub-systems

☑ AOPs are more energy-intensive than material-intensive processes. For this reason, the main environmental impact is generally caused by the electricity consumed, even if it is produced by means of co-generation. In scenario 1, for instance, electricity production is responsible for at least 80% of the contribution to the different impact categories. In scenario 2 it is lower, due to co-generation using biomass as fuel. Finally in scenario 3 it is zero, as solar light is a clean energy.

☑ As a consequence, in scenarios 1 and 2 chemical products contribute moderately to the different environmental impacts. In those treatments they are used:

⇒ Oxygen is responsible of about 20% of the contribution to impacts, but in scenario 2 is the main contributor in most categories.

- ⇒ Titanium dioxide has low or moderate contributions to impacts, except to aquatic toxicity in scenario 2, due to emissions of heavy metals to water during its manufacture (chloride process), leading to contributions of 50-90% to this category, depending on the AOP considered.

- ⇒ Hydrogen peroxide has also very moderate contributions in scenario 1, but higher in scenario 2 to resource depletion (45%), global warming (35%), and aquatic eutrophication (40%).

- ⇒ Ferric chloride has a negligible contribution to the different impact categories in both scenarios, due to the low dose applied (20 ppm).

3.5.5.2. Scenarios

- ☑ It can be stated that the application of AOPs in kraft pulp mills (scenario 2) would cause a lower environmental impact than the application in industrial facilities consuming electricity from the grid (scenario 1), because in kraft mills:

  - ⇒ Biomass, a renewable fuel, is mainly used.

  - ⇒ The energy efficiency in co-generation is about 80%, as compared to 30-40% in conventional power plants supplying electricity to the grid.

- ☑ Depending on the AOP, the weighted environmental impact is reduced between 55-66% with regard to scenario 1.

- ☑ However, the contribution to human toxicity appears higher in scenario 2, due to PAH emissions, although there is a high uncertainty in the inventory data used for these emissions.

- ☑ The use of solar energy as a source of photons (scenario 3), is the best option for all the photo-assisted AOPs, since this energy source is completely clean. Depending on the AOP, the weighted environmental impact is reduced between 92-99% with regard to scenario 1.

3.5.5.3. Treatments

- ☑ From the results obtained in scenario 3, with regard to the other scenarios, it can be concluded that all solar AOPs are by far better options than any AOP using a conventional energy source.

- ☑ A clear “front-runner” treatment can not be easily identified among the solar photo-assisted AOPs. The consideration of a determined AOP as the best procedure, depends on the impact category considered and the functional unit used. It can only be clearly stated that heterogeneous Photocatalysis in combination with hydrogen peroxide has obtained the worst results in this group.

☑ Ozonation is one of the treatments having a higher environmental impact, due to the energy consumption of producing oxygen and ozone. The results have shown that combining Ozonation with UVA irradiation decreases the environmental impact about 40%. Using solar energy instead of artificial UVA light would probably lead to further decrease of the environmental impact, although this has not been assessed in the present LCA.

☑ When the energy used is either electricity from the grid or from co-generation:

⇒ The AOP showing the lowest environmental impact is the coupling of heterogeneous photocatalysis with Fenton and Photo-Fenton, which has an environmental impact about 80% lower than Heterogeneous Photocatalysis alone, which is the photo-assisted AOP with the worst results.

⇒ It is difficult to compare ozone-based AOPs to photo-assisted AOPs, due to the limitations of the study, arising from the laboratory scale data used in the present LCA. However, it seems that Ozonation and Heterogeneous Photocatalysis are the most impacting treatments but it is not clear which one of them is the most.

3.5.5.4. Recommendations

The present work is a preliminary LCA of different emerging technologies for wastewater treatment. It is therefore not aimed at excluding processes from potential research and application if their results are not favourable, but at gaining insight into the environmental impact of these processes and their potential advantages or disadvanteges when compared among them. In spite of this preliminary nature, however, it has been possible to draw some clear conclusions in the last section, and also it is possible here to recommend the following priority actions:

☑ Similar studies should be performed when these technologies are developed in pilot plants and at industrial scale, to better approach the real work conditions.

☑ Solar applications should be promoted in the AOP research field, specially in geographical areas like the mediterranean basin, where this energy source has a great potential. In this way, the group of Solar Chemistry of Plataforma Solar de Almería (CIEMAT) and the group of photocatalysis of UAB are working together in research applications of solar light to photocatalytic processes.

- ☑ If AOPs are to be applied using a conventional energy source, such as electricity, the most important environmental criteria to bear in mind by researchers and engineers is to maximize energy efficiency, since the present study has shown that energy production is the main source of environmental impacts.

- ☑ Finally, it should not be forgotten that in spite of AOPs being soft technologies for wastewater treatment, they are still end-of-pipe technologies. Green Chemistry as well as Cleaner Production aim at prevention rather than treatment. In the specific case of kraft pulp industry, before thinking about applying AOPs to destroy AOX, it should be considered if these substances can be avoided by using alternative bleaching agents to chlorine.

4. LCA RESULTS AND ECONOMIC COSTS

Several AOPs have been environmentally assessed in chapter 3, obtaining information on their relative "greenness". As mentioned in section 3.2.3, the present study has been based on a previous work (Pérez et al., 2002) where these AOPs were assessed from an economic point of view. In the present chapter, both environmental and economic data are crossed in order to illustrate how this information can potentially be used to decide about the suitability of a certain AOP option.

Although economic costs were already calculated by Pérez et al. (2002), they are recalculated in the present study, to be in accordance with the functional unit used in the LCA (see section 3.2.6). The methodology for this cost analysis is described below:

- The cost is calculated per functional unit, i.e. the removal of 15% TOC from a kraft pulp mill wastewater having the composition shown in Table 3.

- Capital investments are excluded. Only chemical and energy costs are taken into account. As opposed to the methodology used by Pérez et al. (2002), the fraction of lost catalysts (TiO_2 and Fe) is taken into account, in the same way as it has been done in the LCA. The unitary prices used are shown in Table 19.

Table 19. Unitary costs considered for energy and chemicals.

Product	Price (€)	Source
Electricity (kWh)	0,07	Roca (2001)
TiO_2 (kg)	22,43	Degussa
O_2 (kg)	0,15	Hera-Segasa
$FeCl_3$ 40% (kg)	0,12	
H_2O_2 50% (kg)	0,22	

- Data from the sensitivity analysis performed in the LCA is not taken into account in the calculations. This means that the energy consumption for the ozonisator, as well as chemicals consumption in photo-assisted AOPs are those in Tables 11 and 13. Nevertheless, as the sensitivity analysis have been shown to have important effects on the results of the LCA, they are taken into account and discussed in a qualitative way.

- Scenario 2 is left out of this analysis, since calculating the cost of electricity produced by co-generation in a kraft mill is rather complex: in such a facility the fuel is constituted by part of the wood used as raw material, and a fraction of the energy produced is sold to the power supplying company. Analysing all these parameters is out of the scope of the present study. In this way, only scenario 1 (baseline) and scenario 3 (solar) are included.

In Table 20 the cost per functional unit and treatment is summarised and disaggregated showing the contribution of chemicals and energy, whereas in Figure 35 the overall cost is displayed as a percentage of the most expensive treatment.

Table 20. Economic cost per functional unit for several AOPs.

Treatment	Cost (€)					
	Total	Electricity	O2	TiO2	FeCl3	H2O2
PhC (1)	14,84	12,60		2,24		
FPhF (1)	5,49	5,25			0,02	0,22
PhC+H2O2 (1)	9,81	7,35		2,24		0,22
PhC+FPhF (1)	4,56	2,10		2,24	8E-04	0,22
O3 (1)	137,75	77,00	60,75			
O3+UVA (1)	69,93	39,55	30,38			
PhC (3)	2,24			2,24		
FPhF (3)	0,24				0,02	0,22
PhC+H2O2 (3)	2,46			2,24		0,22
PhC+FPhF (3)	2,46			2,24	8E-04	0,22

(1) scenario 1; (3) scenario 3.

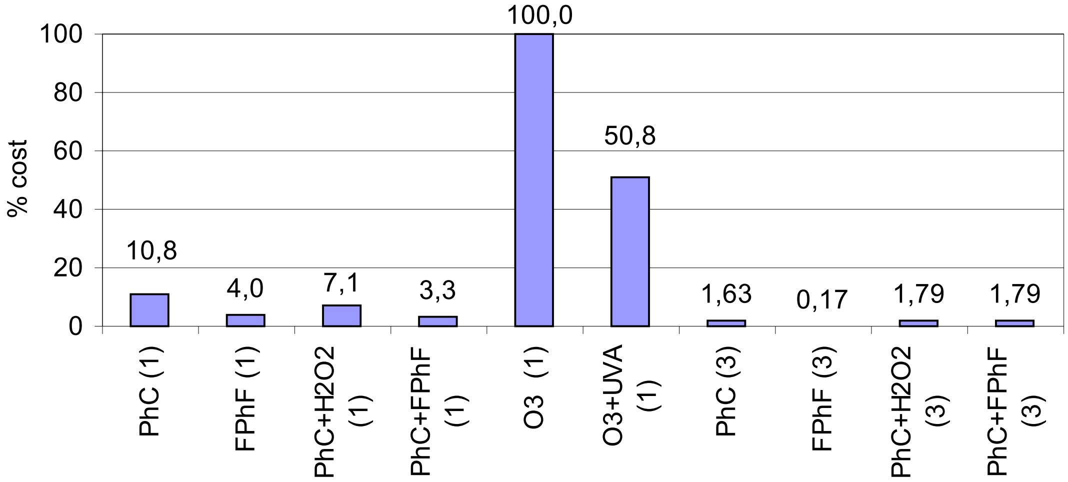

Figure 35. Relative economic cost per functional unit for several AOPs.

In Table 21 the weighted environmental impact of each treatment (obtained in the LCA), as well as its economic cost are shown. Both parameters are expressed in relative values, thus the most impacting AOP scores 100 and so does the most expensive.

Table 21. Weighted environmental impact and cost per functional unit, in relative values.

Treatment	Weighted environmental impact	Cost
PhC (1)	13,56	10,78
FPhF (1)	5,76	3,98
PhC+H2O2 (1)	8,06	7,12
PhC+FPhF (1)	2,46	3,31
O3 (1)	100,00	100,00
O3+UVA (1)	51,10	50,76
PhC (3)	0,08	1,63
FPhF (3)	0,14	0,17
PhC+H2O2 (3)	0,21	1,79
PhC+FPhF (3)	0,21	1,79

From Table 21 it can be stated that a linear relationship exists between environmental impact and economic cost, specially in scenario 1. This is mainly explained by the fact that energy consumption is the main contributor to both issues, thus the more energy is consumed, the more environmental impact (see chapter 3) and cost (see table 20 and figure 35).

The best impact – cost option in scenario 1 seems to be the coupling of photocatalysis and photo-fenton (PhC+FPhF), due its low energy demand. On the other hand, ozone-based treatments (O3 and O3+UVA) appear as the worst options in terms of impact and cost, due to the high energy demand. However, as it has been stated in the LCA after performing a sensitivity analysis, this energy demand may be overestimated, and so may be impact and cost. For this reason, the inconvenience of these treatments (O3 and O3+UVA) with regard to others included in scenario 1 can not be clearly stated.

If AOPs are designed to use a conventional energy source, as it is the case in scenario 1, the present study shows that energy consumption can be used as a simple indicator to estimate cost and impact.

The treatments in scenario 3 show the lowest impact – cost combination. If a single treatment has to be chosen among this group using both environmental and economic criteria, possibly the Fenton and photo-Fenton process (FPhF) is the most desirable option: it has a relative low impact, and is clearly the cheapest option, since the most expensive chemical, TiO_2, is avoided.

5. FINAL REMARKS AND OUTLOOK

LCA has been applied in the present study to a system (AOPs for wastewater treatment) lying into the scope of Green Chemistry. Relevant environmental information has been obtained for all the analyzed processes under different scenarios, in a quantitative and transparent way, and most important, including all the stages of the life cycle. It has also been possible to compare the different processes, and the preferable options have been identified. Furthermore, the LCA results have easily complemented an economic assessment.

It has to be said that the study has limitations coming from different aspects, such as quality and availability of experimental and LCI data. However, the LCA framework requires these aspects to be clearly stated in the scope, and taken into account in the interpretation phase. Nevertheless, limitations and uncertainty are not exclusive of LCA; as in any kind of study, e.g. social, economic or environmental, the quality of the results or outputs of the study will be in accordance to the quality of the input data.

Another possible drawback for the application are complexity and economic cost. Conducting an LCA takes time and the collaboration of different professionals (in this case chemists or chemical engineers along with environmental scientists), and this may be expensive.

Green Chemistry offers an interesting framework for chemists and chemical engineers, through its 12 principles or guidelines, but as it has been discussed before (see section 2.3), these are qualitative rules that can hardly be used to decide among options (in the case study some AOPs use catalysis, while others use less energy but not catalysis, etc.). As a consequence, Green Chemistry needs tools to quantify environmental burdens and improvements, and we suggest LCA to be an adequate tool for this purpose, as the case study has shown.

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Related Web sites

- Association of Plastics Manufacturers in Europe (APME)
  http://www.apme.org

- Conseil Européen de l'Industrie Chimique (CEFIC)
  http://www.cefic.org

- Consorzio Interuniversitario 'La Chimica per l'Ambiente' (INCA)
  http://www.helios.unive.it/inca

- Green Chemistry Network
  http://www.chemsoc.org/networks/gcn

- Green & Sustainable Chemistry Network
  http://www.gscn.net/

- Green Chemistry (journal)
  http://www.rsc.org/is/journals/current/green/greenpub.htm

- Society of Environmental Chemistry and Toxicology – Life Cycle Assessment
  www.setac.org/lca.html

- International Organization for Standardization (ISO)
  http://www.iso.ch/

- Degussa
  http://degussa-catalysts.com/

- Erwin Sander Elektroapparatebau GmbH
  http://www.ozon-sander.de/index.en.html

- European IPPC Bureau
  http://eippcb.jrc.es

- Confederation of European Paper Industries (CEPI)
  http://www.cepi.org

Abbreviations

ADt	Air dried tonne (90% dry mass)
AOPs	Advanced Oxidation Processes
AOX	Adsorvable Organic Halogens
APME	Association of Plastics Manufacturers in Europe
BOS	Basic Oxygen Furnace
BUWAL	Bundesamt Für Umwelt, Wald, Und Landschaft. Schriftenreihe Umwelt
CEFIC	Conseil Européen de l'industrie Chimique
CEPI	Confederation of European Paper Industries
CHP	Co-generation of Heat and Power
CIEMAT	Centro de Investigaciones Energéticas, Mediambientales y Tecnológicas
CML	Centre of environmental Science, Leiden University, The Netherlands
ECF	Elemental Chlorine Free
EIPPCB	European Integrated Pollution Prevention and Control Bureau
ENCE	Empresa Nacional de Celulosas
EPA	(U.S.) Environmental Protection Agency
GC	Green Chemistry
GWP	Global Warming Potential
GSCN	Green and Sustainable Chemistry Network
HHV	Higher Heating Value
IDAE	Instituto para la Diversificación y el Ahorro Energético
INCA	Consorzio Interuniversitario 'La Chimica per l'Ambiente'
IPCC	Intergovernmental Panel on Climate Change
ISO	International Standards Organisation
IUPAC	International Union of Pure and Applied Chemistry
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
NGGIC	National Greenhouse Gas Inventory Committee
NMVOC	Non-methane volatile organic carbon
OECD	Organization for Economic Cooperation and Development
PAHs	Polyaromatic hydrocarbons
POCP	Photochemical Ozone Creation Potential
PPA	Pollution Prevention Act
SEPA	Swedish Environmental Protection Agency
SETAC	Society of Environmental Toxicology and Chemistry
TCF	Total Chlorine Free
tkm	Tonne x km
UAB	Universitat Autònoma de Barcelona
USGS	United States Geological Survey
UPC	Universitat Politècnica de Catalunya
VOC	Volatile Organic Carbon

APPENDIX 1. Aggregated inventory tables for sub-systems

This appendix includes the aggregated inventory tables for the different sub-systems (chemical products and energy). This means that the tables only show elementary flows (flows from nature to the system or from the system to nature). Where possible, however, the contribution of the different processes is separated. A 1.1 includes production data of the different chemical products. A 1.2. includes data on electricity, and A1.3. includes data on transports.

A 1.1. Chemical products

Table A1. Aggregated inventory table for production of 1 kg TiO_2 (delivery excluded).

INPUTS									
Resources and energy	**Unit**	**Total**	**Ilmenite extraction and concentration (2 kg)**	**Ilmenite road transport (1 tkm)**	**Ilmenite sea transport (10 tkm)**	**Chlorine production (0,887 kg)**	**O2 production (0,2 kg)**	**Coke production (0,2 kg)**	**TiO2 production (1 kg)**
coal ETH	g	702	7,06	0,225	0,905	231	19,2	444	-
crude oil ETH	g	159	26,5	28,1	24,9	69,2	3,14	7,62	-
energy (undef.)	MJ	1,38	-	-	-	-	-	1,38	-
ilmenite	kg	5	5	-	-	-	-	-	-
iron (ore)	kg	0,000577	-	-	-	0,000577	-	-	-
lignite ETH	g	197	7,46	0,299	1,2	177	0,242	10,3	-
limestone	kg	0,0165	-	-	-	0,0165	-	-	-
natural gas (vol)	m3	0,0887	-	-	-	0,0887	-	-	-
natural gas ETH	l	48,3	2,55	1,41	1,4	-	2,74	40,2	-
pot. energy hydropower	kJ	692	2,51	1,31	5,26	639	-	44,8	-
process and cooling water	m3	0,000798	-	-	-	0,000798	-	-	-
rock salt	kg	1,07	-	-	-	1,07	-	-	-
sand, clay	kg	0,000177	-	-	-	0,000177	-	-	-
uranium (in ore)	kg	1,24E-05	-	-	-	1,24E-05	-	-	-
uranium (ore)	µg	2,48E+03	818	20,3	81,7	-	804	758	-
water	kg	34,7	29,5	0,218	0,186	-	2,16	2,61	-
wood	g	4,52	0,069	0,0022	0,00887	-	0,187	4,25	-
OUTPUTS									
Emissions to air	**Unit**	**Total**	**Ilmenite extraction and concentration (2 kg)**	**Ilmenite road transport (1 tkm)**	**Ilmenite sea transport (10 tkm)**	**Chlorine production (0,887 kg)**	**O2 production (0,2 kg)**	**Coke production (0,2 kg)**	**TiO2 production (1 kg)**
ammonia	mg	3,3	0,0769	0,00252	0,00977	1,51	0,191	1,51	-
benzene	mg	6,42	0,507	3,32	0,266	0,976	0,0708	1,28	-

benzo(a)pyrene	kg	1,2E-08	-	-	-	-	-	1,2E-08	-
carbon black	kg	0,0000648	-	-	-	-	-	0,0000648	-
Cd	µg	45,7	1,09	0,899	30,4	11,5	0,767	1,06	-
Cl2	mg	27	-	-	-	-	-	-	27
CO	mg	1740	30,8	508	28,6	710	8,86	251	200
CO2	kg	4,55	0,107	0,0925	0,0828	1,06	0,0465	0,161	3
CxHy	kg	0,000105	-	-	-	-	-	0,000105	-
CxHy aromatic	mg	11	1,31	0,554	0,658	5,68	0,478	2,31	-
CxHy chloro	µg	0,0651	0,0217	0,000531	0,00214	-	0,0209	0,0198	-
CxHy halogenated	kg	3,81E-10	-	-	-	3,81E-10	-	-	-
dust	g	3,86	0,0374	0,0381	0,0546	3,1	0,0576	0,567	-
dust (SPM)	g	13,3	12	-	-	-	-	-	1,3
F2	kg	3,8E-07	-	-	-	-	-	3,8E-07	-
fluoranthene	kg	1,2E-07	-	-	-	-	-	1,2E-07	-
H2S	kg	0,000054	-	-	-	-	-	0,000054	-
HALON-1301	µg	35,8	6,34	6,73	5,94	14,2	0,749	1,81	-
HCl	mg	383	4,59	0,189	1,93	160	9,24	7,01	200
HF	mg	11,2	0,486	0,0198	0,196	8,87	0,983	0,655	-
Hg	µg	25	1,31	0,0925	0,33	18,6	1,34	3,28	-
metals	mg	14,6	2,24	0,291	3,72	1,77	2,7	3,85	-
methane	g	5,9	0,158	0,113	0,104	2,04	0,158	3,32	-
Mn	µg	65,4	2,5	0,0758	0,304	49,7	5,05	7,8	-
N2O	mg	13,2	1,08	2,23	1,68	5,5	0,444	2,26	-
Ni	µg	2490	684	44,6	625	745	66	327	-
non methane VOC	g	4,4	0,22	0,577	0,198	3,28	0,0272	0,0937	-
NOx	g	2,27	-	-	-	-	-	0,074	2,2
NOx (as NO2)	g	8,75	0,172	1,66	0,21	6,21	0,112	0,381	-
PAH's	µg	35,6	0,81	0,698	1,05	16,9	1,59	14,6	-
Pb	µg	208	7,71	4,95	53,5	115	11	16	-
SO2	kg	0,00028	-	-	-	-	-	0,00028	-
SOx	g	13,3	-	-	-	-	-	-	13,3
SOx (as SO2)	g	12,9	0,261	0,139	1,15	10,6	0,222	0,485	-
toluene	kg	5,2E-07	-	-	-	-	-	5,2E-07	-
unspecified emission	kg	0,0000512	-	-	-	-	-	0,0000512	-
xylene	kg	5,6E-07	-	-	-	-	-	5,6E-07	-
Zn	µg	1040	705	29,6	58,3	186	14,9	43,4	-
Emissions to water	**Unit**	**Total**	**Ilmenite extraction and concentration (2 kg)**	**Ilmenite road transport (1 tkm)**	**Ilmenite sea transport (10 tkm)**	**Chlorine production (0,887 kg)**	**O2 production (0,2 kg)**	**Coke production (0,2 kg)**	**TiO2 production (1 kg)**
Al	mg	1350	11,5	0,371	1,47	302	30,8	706	300
anorg. dissolved subst.	g	4,43	0,566	0,544	0,486	0,346	0,165	2,32	-
AOX	µg	26,2	3,82	5,54	4,31	10,6	0,545	1,36	-
As	mg	2,11	0,0236	0,00185	0,0039	0,603	0,062	1,41	-
Ba	mg	102	4,22	3,56	3,24	31	2,84	57,5	-
BOD	mg	2,97	0,0875	0,127	0,0548	2,66	0,0113	0,0253	-
Cd	µg	152	1,82	1,56	1,42	19,5	1,81	35,9	90
Cl-	g	43,5	0,77	0,753	0,671	37,3	0,278	3,73	-
COD	mg	17,9	2,77	4,15	1,07	8,87	0,25	0,8	-

Cr	mg	54,6	0,124	0,0156	0,0251	3,02	0,308	7,09	44
Cu	mg	12,3	0,0586	0,00436	0,00946	1,51	0,154	3,53	7
CxHy	kg	0,000001	-	-	-	-	-	0,000001	-
CxHy aromatic	mg	6,67	1,13	1,2	1,06	2,75	0,137	0,388	-
CxHy chloro	µg	8,71	1,18	1,23	1,09	4,08	0,175	0,95	-
cyanide	µg	40,6	4,24	5,57	4,82	19,5	1,41	5,09	-
DOC	mg	1,92	0,0176	0,000667	0,00269	1,33	0,0357	0,529	-
Fats/oils	kg	0,0000834	-	-	-	0,0000834	-	-	-
Fe	g	22,8	0,0156	0,000791	0,00255	0,328	0,00964	0,229	22,2
Hg	µg	22,1	0,0288	0,0139	0,0141	0,63	0,0518	1,34	20
Kjeldahl-N	µg	1610	349	523	123	594	16,2	3,28	-
metallic ions	mg	184	9,3	8,66	7,77	79,8	4,14	74,7	-
Mg	g	1,3	-	-	-	-	-	-	1,3
N-tot	mg	11,4	2,06	3,02	1,23	4,26	0,159	0,669	-
Na	kg	0,00248	-	-	-	0,00248	-	-	-
NH4+	mg	14,8	2,24	3,09	1,27	6,74	0,308	1,17	-
Ni	mg	5,29	0,0585	0,00577	0,0108	1,51	0,151	3,55	-
nitrate	mg	11,5	0,938	0,928	0,823	7,27	0,826	0,754	-
oil	mg	122	35,2	37,6	33	-	4,24	11,5	-
PAH's	µg	100	17,3	18,4	16,2	39	2,05	6,99	-
Pb	mg	12,6	0,0715	0,00381	0,0101	1,77	0,167	3,58	7
phenols	µg	1060	172	187	179	435	23,1	64,3	-
phosphate	mg	62,6	0,685	0,0366	0,0995	17,7	1,84	42,2	-
sulphate	g	10	0,148	0,0265	0,0337	6,39	0,195	3,22	-
sulphide	µg	230	31,3	44,3	38,3	97,6	5,5	12,7	-
suspended substances	g	2,88	0,079	0,0804	0,0713	1,77	0,0136	0,0664	0,8
titanium dioxide	mg	100	-	-	-	-	-	-	100
TOC	mg	193	12,4	13	9,86	115	3,67	38,8	-
toluene	µg	900	158	167	147	373	18,9	36,6	-
V	mg	90	-	-	-	-	-	-	90
Zn	mg	32,6	0,123	0,0165	0,0255	3,02	0,31	7,12	22
Waste	**Unit**		**Ilmenite extraction and concentration (2 kg)**	**Ilmenite road transport (1 tkm)**	**Ilmenite sea transport (10 tkm)**	**Chlorine production (0,887 kg)**	**O2 production (0,2 kg)**	**Coke production (0,2 kg)**	**TiO2 production (1 kg)**
chemical waste	g	100	-	-	-	-	-	-	100
mineral waste (mining)	kg	0,0639	-	-	-	0,0639	-	-	-
produc. waste (not inert)	g	300	-	-	-	-	-	-	300
Tailings	kg	3	3	-	-	-	-	-	-
waste bioactive landfill	kg	0,0239	-	-	-	0,0239	-	-	-
waste in incineration	kg	0,000266	-	-	-	0,000266	-	-	-
Non-material emissions	**Unit**	**Total**	**Ilmenite extraction and concentration (2 kg)**	**Ilmenite road transport (1 tkm)**	**Ilmenite sea transport (10 tkm)**	**Chlorine production (0,887 kg)**	**O2 production (0,2 kg)**	**Coke production (0,2 kg)**	**TiO2 production (1 kg)**
radioact. to air	kBq	1280	71,1	1,77	7,11	1060	69,9	65,9	-

radioact. to water	Bq	11700	653	16,9	66	9760	641	605	-

Sources: Consumption of raw, auxiliary materials and emissions in TiO_2 production from Huizinga et al. (1993), except for CO_2 emissions in TiO_2 production, from Häkinnen et al. (1999). Ilmenite mining and concentration from IVAM LCA database. Transport by ship assuming 5.000 km distance. Transport by road assuming 500 km distance and a 40 tonnes truck. Chlorine production from BUWAL 250 database (Habersatter, 1996). Oxygen production from BUWAL 250 database (Habersatter, 1996), but assuming the spanish electricity mix. Coke production from Annema et al. 1992.

Table A2. Aggregated inventory table for production of 1 kg pure H_2O_2 (delivery excluded).

INPUTS		
Raw materials and energy	**Unit**	**H2O2 production**
bauxite	g	14
energy (undef.)	kJ	610
energy from coal	MJ	3,25
energy from hydro power	kJ	670
energy from lignite	kJ	430
energy from natural gas	MJ	11,3
energy from oil	MJ	2,78
energy from uranium	MJ	3,81
energy from wood	kJ	200
Fluorspar	mg	54
iron (ore)	mg	90
limestone	mg	380
NaCl	g	4,5
process water	l	6,2
sand	g	1
SO2 secondary	g	19
sulphur	g	7,7
water (cooling)	kg	150
wood	g	22
OUTPUTS		
Emissions to air	**Unit**	**H2O2 production**
CO	mg	400
CO2	kg	1,18
CO2-re	g	17
CxHy	g	2,5
CxHy aromatic	mg	150
dust (SPM)	g	2,5
H2	mg	340
HCl	mg	65
HF	mg	3
metals	mg	8
methane	g	6,9
non methane VOC	mg	410
NOx (as NO2)	g	8,7

SO2	g	6,6
Emissions to water	**Unit**	**H2O2 production**
Acid as H+	mg	25
Al	mg	29
BOD	mg	230
Cl-	g	4
COD	g	2,8
CxHy	mg	3
dissolved organics	mg	5
dissolved solids	mg	210
metallic ions	mg	69
Na	mg	840
nitrate	mg	380
phenol	mg	2
phosphate	mg	19
sulphate	mg	64
suspended solids	g	1,6
Waste	**Unit**	**H2O2 production**
chemical waste (regulated)	mg	960
final waste (inert)	g	6,3
industrial waste	g	8,4
metal scrap	mg	8
mineral waste (mining)	g	49
slags/ash	g	11
waste in incineration	mg	81

Source: CEFIC.

Table A3. Aggregated inventory table for production of 1 kg FeCl$_3$ 40%(delivery excluded).

INPUTS						
Raw materials and energy	**Unit**	**Total**	**FeCl3 40% production (1 kg)**	**Steel production (0,138 kg)**	**HCl production (0,123 kg)**	**Electricity (0,14 kWh)**
acids	kg	0,00172	-	0,00172	-	-
additives	kg	0,00366	-	0,00366	-	-
alloys	kg	0,000717	-	0,000717	-	-
auxiliary materials	kg	0,000317	-	0,000317	-	-
chromium compounds	kg	0,000119	-	0,000119	-	-
coal ETH	g	168	-	137	5,36	25,9
crude oil ETH	g	38,2	-	10,2	23,8	4,24
degreasing agent	kg	0,000179	-	0,000179	-	-
iron (ore)	kg	0,265	-	0,265	-	-
lignite ETH	g	21,9	-	19,4	2,13	0,326
limestone	kg	0,0313	-	0,0313	-	-
natural gas (vol)	l	24,1	-	17,8	6,33	-
natural gas ETH	m3	0,00521	-	-	0,00151	0,0037
pot. energy hydropower	kJ	59,2	-	48,1	11,1	-
process and cooling water	m3	0,000677	-	-	0,000677	-

process water	m3	0,00217	-	0,00217	-	-
rock salt	kg	0,00206	-	-	0,00206	-
rolling oil	kg	0,000303	-	0,000303	-	-
sand, clay	kg	8,83E-06	-	-	8,83E-06	-
scrap, external	kg	0,0463	-	0,0463	-	-
SO2 secondary	kg	0,0873	-	-	0,0873	-
uranium (in ore)	µg	991	-	921	69,2	-
uranium (ore)	kg	1,25E-06	-	-	1,63E-07	1,09E-06
water	g	3,92E+03	600	-	409	2,91E+03
wood	g	1,91	-	1,63	0,0294	0,253
OUTPUTS						

Emissions to air	**Unit**	**Total**	**FeCl3 40% production (1 kg)**	**Steel production (0,138 kg)**	**HCl production (0,123 kg)**	**Electricity (0,14 kWh)**
ammonia	µg	569	-	269	41,5	258
benzene	µg	635	-	277	262	95,6
Cd	µg	39,1	-	12	26,1	1,04
CO	g	2,22	-	2,17	0,0387	0,012
CO2	g	522	-	357	102	62,8
Cr	kg	2,07E-08	-	2,07E-08	-	-
Cu	kg	4,33E-08	-	4,33E-08	-	-
CxHy aromatic	µg	2,12E+03	-	779	691	645
CxHy chloro	kg	3,25E-11	-	-	4,26E-12	2,83E-11
CxHy halogenated	µg	0,0305	-	0,0276	0,00294	-
dust	mg	366	-	188	100	77,8
H2S	kg	1,09E-06	-	1,09E-06	-	-
HALON-1301	µg	9,13	-	2,44	5,68	1,01
HCl	mg	29,8	-	13,2	4,19	12,5
HF	mg	3,32	-	1,64	0,348	1,33
Hg	µg	5,18	-	2,5	0,865	1,82
metals	mg	11,1	-	3,79	3,69	3,64
methane	g	1,62	-	1,25	0,161	0,214
Mn	µg	298	-	290	1,2	6,82
N2O	mg	3,36	-	1,21	1,55	0,6
Ni	µg	839	-	201	548	89,1
non methane VOC	mg	935	-	123	775	36,7
NOx (as NO2)	mg	1,27E+03	-	575	541	151
PAH's	µg	7,13	-	3,72	1,25	2,15
Pb	µg	830	-	767	47,8	14,9
SOx (as SO2)	g	5,34	-	0,76	4,28	0,3
Tl	kg	4,41E-09	-	4,41E-09	-	-
V	kg	1,10E-09	-	1,10E-09	-	-
Zn	µg	109	-	34,6	54,4	20,1

Emissions to water	**Unit**	**Total**	**FeCl3 40% production (1 kg)**	**Steel production (0,138 kg)**	**HCl production (0,123 kg)**	**Electricity (0,14 kWh)**
Al	mg	270	-	221	8,08	41,6
anorg. dissolved subst.	mg	1,59E+03	-	931	438	223
AOX	µg	61,9	-	57	4,17	0,736
As	µg	542	-	441	17	83,8

Ba	mg	26,4	-	18,9	3,62	3,84
BOD	mg	23,7	-	23,4	0,195	0,0153
Cd	µg	15,8	-	11,7	1,71	2,44
Cl-	g	7,69	-	1,71	5,61	0,376
COD	mg	65,9	-	64	1,53	0,338
Cr	mg	3,26	-	2,76	0,0896	0,417
Cu	mg	1,36	-	1,11	0,0421	0,208
CxHy aromatic	mg	1,68	-	0,463	1,03	0,186
CxHy chloro	µg	15,9	-	14,5	1,14	0,236
cyanide	µg	10,2	-	3,49	4,77	1,9
dissolved substances	kg	0,000193	-	-	0,000193	-
DOC	µg	385	-	234	102	48,2
Fats/oils	mg	17,4	-	14,2	3,24	-
Fe	mg	122	-	103	5,95	13
Hg	µg	2,26	-	2,15	0,0416	0,07
Kjeldahl-N	µg	256	-	88,7	145	21,9
metallic ions	mg	39,4	-	25,7	8,13	5,59
N-tot	mg	2,17	-	0,668	1,29	0,214
Na	kg	1,32E-05	-	-	1,32E-05	-
NH4+	mg	2,79	-	0,999	1,37	0,416
Ni	mg	1,37	-	1,12	0,0429	0,204
nitrate	µg	2,90E+03	-	880	908	1,12E+03
oil	kg	3,44E-05	-	-	2,86E-05	5,73E-06
PAH's	µg	25	-	6,68	15,5	2,77
Pb	mg	1,39	-	1,12	0,0457	0,226
phenols	µg	279	-	76,1	171	31,2
phosphate	mg	20,5	-	17,5	0,49	2,48
sulphate	g	2,42	-	1,07	1,08	0,264
sulphide	µg	60,5	-	16,3	36,8	7,42
suspended substances	mg	514	-	49,4	447	18,3
TOC	mg	41,6	-	20,3	16,3	4,95
toluene	µg	231	-	63,2	142	25,6
waste water (vol)	cm3	818	-	690	129	-
Zn	mg	2,73	-	2,22	0,0902	0,419

Waste	**Unit**	**Total**	**production (1 kg)**	**Steel production (0,138 kg)**	**HCl production (0,123 kg)**	**Electricity (0,14 kWh)**
chemical waste	kg	0,00211	-	0,00211	-	-
chromium compounds	kg	0,000621	-	0,000621	-	-
dust, break-out	kg	0,00731	-	0,00731	-	-
Iron compounds	kg	0,00255	-	0,00255	-	-
mineral waste (mining)	g	163	-	160	3,09	-
rejects	kg	0,00459	-	0,00459	-	-
slag	kg	0,0439	-	0,0439	-	-
tinder from rolling drum	kg	0,00353	-	0,00353	-	-
waste bioactive landfill	kg	0,00206	-	-	0,00206	-
waste in incineration	kg	8,83E-06	-	-	8,83E-06	-
waste in inert landfill	kg	0,00767	-	0,00767	-	-

Waste	Unit	Total	FeCl3 40% production (1 kg)	production (0,138 kg)	HCl production (0,123 kg)	Electricity (0,14 kWh)
radioact. to air	kBq	195	-	80,1	20,2	94,4
radioact. to water	Bq	1,79E+03	-	738	185	866

Sources: Consumption of steel, water, HCl and electricity from KIWA Water Research (IVAM LCA Data 2.0). Steel production from BUWAL 250 database (Habersatter, 1996). HCl production from BUWAL 250 database (Habersatter, 1996). Electricity consumed using the spanish mix for electricity production.

Table A4 Aggregated inventory table for production of 1 kg O_2 (delivery excluded).

INPUTS		
Raw materials and energy	**Unit**	**O2 production (1 kg)**
coal ETH	kg	0,096
crude oil ETH	kg	0,0157
lignite ETH	kg	0,00121
natural gas ETH	m3	0,0137
uranium (ore)	kg	4,02E-06
water	kg	10,8
wood	kg	0,000937
OUTPUTS		
Emissions to air	**Unit**	**O2 production (1 kg)**
ammonia	kg	9,56E-07
benzene	kg	3,54E-07
Cd	kg	3,84E-09
CO	kg	4,43E-05
CO2	kg	0,233
CxHy aromatic	kg	2,39E-06
CxHy chloro	kg	1,05E-10
dust	kg	0,000288
HALON-1301	kg	3,75E-09
HCl	kg	4,62E-05
HF	kg	4,92E-06
Hg	kg	6,72E-09
metals	kg	1,35E-05
methane	kg	0,000792
Mn	kg	2,53E-08
N2O	kg	2,22E-06
Ni	kg	3,30E-07
non methane VOC	kg	0,000136
NOx (as NO2)	kg	0,00056
PAH's	kg	7,97E-09
Pb	kg	5,50E-08
SOx (as SO2)	kg	0,00111
Zn	kg	7,45E-08

Emissions to water	Unit	O2 production (1 kg)
Al	kg	0,000154
anorg. dissolved subst.	kg	0,000826
AOX	kg	2,72E-09
As	kg	3,10E-07
Ba	kg	1,42E-05
BOD	kg	5,66E-08
Cd	kg	9,04E-09
Cl-	kg	0,00139
COD	kg	1,25E-06
Cr	kg	1,54E-06
Cu	kg	7,69E-07
CxHy aromatic	kg	6,87E-07
CxHy chloro	kg	8,74E-10
cyanide	kg	7,04E-09
DOC	kg	1,79E-07
Fe	kg	4,82E-05
Hg	kg	2,59E-10
Kjeldahl-N	kg	8,11E-08
metallic ions	kg	2,07E-05
N-tot	kg	7,93E-07
NH4+	kg	1,54E-06
Ni	kg	7,55E-07
nitrate	kg	4,13E-06
oil	kg	2,12E-05
PAH's	kg	1,02E-08
Pb	kg	8,36E-07
phenols	kg	1,15E-07
phosphate	kg	9,18E-06
sulphate	kg	0,000977
sulphide	kg	2,75E-08
suspended substances	kg	6,79E-05
TOC	kg	1,83E-05
toluene	kg	9,47E-08
Zn	kg	1,55E-06
Emissions to water	**Unit**	**O2 production (1 kg)**
radioact. to air	Bq	3,49E+05
radioact. to water	Bq	3,21E+03

Source: BUWAL 250 database (Habersatter, 1996), assuming the spanish mix for electricity production.

A 1.2. Electricity

Table A5. Aggregated inventory table for production of 1 kWh electricity in Spain.

INPUTS								
Raw materials and energy	**Unit**	**Total (1 kWh)**	**Coal (0,304 kWh)**	**Natural gas (0,097 kWh)**	**Nuclear (0,27 kWh)**	**Oil (0,104 kWh)**	**Hydropower (0,165 kWh)**	**Others (0,06 kWh)**
coal ETH	g	192	186	5,34	0,143	0,252	-	-
crude oil ETH	g	31,4	2,57	0,0603	0,134	28,6	-	-
lignite ETH	g	2,42	1,81	0,0845	0,187	0,334	-	-
natural gas ETH	l	27,4	2,17	23,4	0,373	1,45	-	-
uranium (ore)	mg	8,04	0,123	0,00574	7,88	0,0227	-	-
wood	g	1,87	1,81	0,0651	0,00159	0,00246	-	-
OUTPUTS								
Emissions to air	**Unit**	**Total (1 kWh)**	**Coal (0,304 kWh)**	**Natural gas (0,097 kWh)**	**Nuclear (0,27 kWh)**	**Oil (0,104 kWh)**	**Hydropower (0,165 kWh)**	**Others (0,06 kWh)**
ammonia	mg	1,91	1,78	0,0188	0,0394	0,0786	-	-
benzene	µg	708	39,8	401	6,37	261	-	-
Cd	µg	7,67	1,42	0,0222	0,0332	6,2	-	-
CO	mg	88,6	38	25,9	1,53	23,2	-	-
CO2	g	465	298	74,4	1,54	91,5	-	-
CxHy aromatic	mg	4,78	3,92	0,197	0,0106	0,649	-	-
CxHy chloro	µg	0,209	0,00322	0,00015	0,205	0,000592	-	-
dust	mg	576	526	6,32	4,83	39,1	-	-
HALON-1301	µg	7,49	0,614	0,0144	0,0321	6,83	-	-
HCl	mg	92,4	91,2	0,06	0,0975	1,01	-	-
HF	mg	9,83	9,7	0,00512	0,0292	0,101	-	-
Hg	µg	13,4	11,7	1,42	0,0394	0,29	-	-
metals	mg	27	24	0,119	0,0324	2,81	-	-
methane	g	1,58	1,3	0,171	0,00373	0,114	-	-
Mn	µg	50,5	33,7	0,287	0,0524	16,4	-	-
N2O	mg	4,44	1,84	0,541	0,041	2,02	-	-
Ni	µg	660	141	47,3	1,07	470	-	-
non methane VOC	mg	272	30,4	11,9	2,69	227	-	-
NOx (as NO2)	mg	1,12E+03	766	145	5,37	204	-	-
PAH's	µg	15,9	4,16	9,67	0,125	1,98	-	-
Pb	µg	110	55,6	0,35	0,215	53,9	-	-
SOx (as SO2)	g	2,22	1,22	0,0257	0,00578	0,967	-	-
Zn	µg	149	106	0,565	2,56	39,4	-	-
Emissions to water	**Unit**	**Total (1 kWh)**	**Coal (0,304 kWh)**	**Natural gas (0,097 kWh)**	**(0,27 kWh)**	**Oil (0,104 kWh)**	**Hydropower (0,165 kWh)**	**Others (0,06 kWh)**
Al	mg	308	296	8,63	2,75	0,415	-	-
anorg. dissolved subst.	g	1,65	1,03	0,039	0,0258	0,554	-	-
AOX	µg	5,45	0,462	0,0114	0,0235	4,95	-	-

As	µg	620	599	17,3	2,18	1,98	-	-
Ba	mg	28,4	24	0,697	0,0486	3,62	-	-
BOD	µg	113	42,3	1,89	6,61	62,5	-	-
Cd	µg	18,1	15,4	0,436	0,672	1,56	-	-
Cl-	g	2,78	1,92	0,0612	0,0367	0,768	-	-
COD	mg	2,5	1,32	0,0242	0,0451	1,11	-	-
Cr	mg	3,08	2,97	0,0884	0,0094	0,0162	-	-
Cu	mg	1,54	1,49	0,0432	0,0027	0,00459	-	-
CxHy aromatic	µg	1,37E+03	110	40,6	6,37E+00	1,22E+03	-	-
CxHy chloro	µg	1,75	0,15	0,328	0,0124	1,26	-	-
cyanide	µg	14,1	1,91	6,64	0,0435	5,49	-	-
DOC	µg	357	6,63	344	5,37	0,834	-	-
Fe	mg	96,4	92,1	2,74	1,51	0,086	-	-
Hg	µg	0,518	0,423	0,0759	0,00283	0,0172	-	-
Kjeldahl-N	µg	162	21,4	0,891	1,66	138	-	-
metallic ions	mg	41,4	31	0,896	0,699	8,81	-	-
N-tot	µg	1,59E+03	165	5,49	1,15E+01	1,40E+03	-	-
NH4+	mg	3,08	0,432	0,0644	1,15	1,44	-	-
Ni	mg	1,51	1,50E+00	4,35E-05	0,00451	0,00606	-	-
nitrate	mg	8,26	7,14	0,00511	0,143	0,964	-	-
oil	mg	42,4	3,44	0,907	0,194	37,9	-	-
PAH's	µg	20,5	1,68	0,0888	0,0877	18,6	-	-
Pb	mg	1,67	1,49	0,0435	0,136	0,0043	-	-
phenols	µg	231	20,1	3,74	0,975	206	-	-
phosphate	mg	18,4	17,8	0,517	0,0171	0,0384	-	-
sulphate	g	1,95	1,32	0,0448	0,559	0,0285	-	-
sulphide	µg	55	4,26	6,29	0,637	43,8	-	-
suspended substances	mg	136	11	21,3	21,7	81,7	-	-
TOC	mg	36,7	1,5	23,2	0,842	11,1	-	-
toluene	µg	189	15,3	3,62	0,856	170	-	-
Zn	mg	3,1	2,99	0,0867	0,0154	0,0165	-	-

Non-material emissions	**Unit**	**Total (1 kWh)**	**Coal (0,304 kWh)**	**Natural gas (0,097 kWh)**	**Nuclear (0,27 kWh)**	**Oil (0,104 kWh)**	**Hydropower (0,165 kWh)**	**Others (0,06 kWh)**
radioact. substance to air	Bq	6,99E+05	1,07E+04	500	6,86E+05	1,98E+03	-	-
radioact. substance to water	Bq	6,41E+03	98,8	4,6	6,29E+03	18,8	-	-

Sources: Production profile from IDAE (2002). Production data for each technology from BUWAL 250 database (Habersatter, 1996).

Table A6. Aggregated inventory table for production of 1 kWh electricity by co-generation in a kraft pulp mill.

INPUTS					
Raw materials and energy	**Unit**	**Total (1 kWh)**	**Oil co-generation (0,05 kWh)**	**Black liquor co-generation (0,65 kWh)**	**Bark co-generation (0,3 kWh)**
coal ETH	kg	6,07E-05	6,07E-05	-	-
crude oil ETH	kg	0,00167	0,00167	-	-
energy from wood	MJ	1,19	-	0,813	0,375
lignite ETH	kg	8,07E-05	8,07E-05	-	-
natural gas ETH	m3	9,40E-05	9,40E-05	-	-
pot. energy hydropower	MJ	0,000353	0,000353	-	-
uranium (ore)	kg	5,48E-09	5,48E-09	-	-
water	kg	0,0125	0,0125	-	-
wood	kg	5,95E-07	5,95E-07	-	-
OUTPUTS					
Emissions to air	**Unit**	**Total (1 kWh)**	**Oil co-generation (0,05 kWh)**	**Black liquor co-generation (0,65 kWh)**	**Bark co-generation (0,3 kWh)**
ammonia	kg	6,56E-10	6,56E-10	-	-
benzene	kg	1,79E-08	1,79E-08	-	-
Cd	kg	2,04E-09	2,04E-09	-	-
CO	mg	348	1,92	91	255
CO2	kg	0,00556	0,00556	-	-
CO2-re	kg	0,109	-	0,0748	0,0345
CxHy aromatic	kg	4,42E-08	4,42E-08	-	-
CxHy chloro	kg	1,43E-13	1,43E-13	-	-
dust	g	3,92	0,00366	3,9	0,021
H2S	kg	6,50E-07	-	6,50E-07	-
HALON-1301	kg	3,99E-10	3,99E-10	-	-
HCl	µg	1,31E+04	129	1,30E+04	-
HF	kg	1,32E-08	1,32E-08	-	-
Hg	kg	2,22E-11	2,22E-11	-	-
mercaptans	kg	1,04E-05	-	1,04E-05	-
metals	µg	276	250	26	-
methane	kg	6,96E-06	6,96E-06	-	-
methane-re	kg	4,75E-06	-	3,25E-06	1,50E-06
Mn	kg	2,04E-11	2,04E-11	-	-
N2O	mg	4,86	0,113	3,25	1,5
Ni	kg	4,20E-08	4,20E-08	-	-
non methane VOC	mg	95,5	13,3	55,3	27
NOx (as NO2)	mg	78,9	14,1	46,8	18
PAH's	µg	390	0,0703	390	-
Pb	kg	3,59E-09	3,59E-09	-	-
SOx (as SO2)	mg	176	77	97,5	1,8
Zn	kg	3,92E-09	3,92E-09	-	-
Emissions to water	**Unit**	**Total (1 kWh)**	**Oil co-generation (0,05 kWh)**	**Black liquor co-generation (0,65 kWh)**	**Bark co-generation (0,3 kWh)**
Al	kg	9,88E-08	9,88E-08	-	-

anorg. dissolved subst.	kg	3,27E-05	3,27E-05	-	-
AOX	kg	2,90E-10	2,90E-10	-	-
As	kg	2,62E-10	2,62E-10	-	-
Ba	kg	2,17E-07	2,17E-07	-	-
BOD	kg	3,68E-09	3,68E-09	-	-
Cd	kg	9,52E-11	9,52E-11	-	-
Cl-	kg	4,51E-05	4,51E-05	-	-
COD	kg	7,17E-08	7,17E-08	-	-
Cr	kg	1,68E-09	1,68E-09	-	-
Cu	kg	6,35E-10	6,35E-10	-	-
CxHy aromatic	kg	7,12E-08	7,12E-08	-	-
CxHy chloro	kg	7,34E-11	7,34E-11	-	-
cyanide	kg	3,24E-10	3,24E-10	-	-
DOC	kg	1,80E-10	1,80E-10	-	-
Fe	kg	1,71E-07	1,71E-07	-	-
Hg	kg	9,44E-13	9,44E-13	-	-
Kjeldahl-N	kg	8,29E-09	8,29E-09	-	-
metallic ions	kg	5,22E-07	5,22E-07	-	-
N-tot	kg	8,27E-08	8,27E-08	-	-
NH4+	kg	8,54E-08	8,54E-08	-	-
Ni	kg	7,24E-10	7,24E-10	-	-
nitrate	kg	5,53E-08	5,53E-08	-	-
oil	kg	2,22E-06	2,22E-06	-	-
PAH's	kg	1,09E-09	1,09E-09	-	-
Pb	kg	6,75E-10	6,75E-10	-	-
phenols	kg	1,20E-08	1,20E-08	-	-
phosphate	kg	6,68E-09	6,68E-09	-	-
sulphate	kg	2,26E-06	2,26E-06	-	-
sulphide	kg	2,57E-09	2,57E-09	-	-
suspended substances	kg	4,79E-06	4,79E-06	-	-
TOC	kg	6,62E-07	6,62E-07	-	-
toluene	kg	9,90E-09	9,90E-09	-	-
Zn	kg	1,71E-09	1,71E-09	-	-
Non-material emissions	**Unit**	**Total (1 kWh)**	**Oil co-generation (0,05 kWh)**	**Black liquor co-generation (0,65 kWh)**	**Bark co-generation (0,3 kWh)**
radioact. substance to air	Bq	477	477	-	-
radioact. substance to water	Bq	4,43	4,43	-	-

Sources: See section 3.3.1.6. and appendix 2.

A 1.3. Transports

Table A7. Aggregated inventory table for different transport modes per tkm.

INPUTS				
Raw materials and energy	**Unit**	**Sea-ship (1 tkm)**	**Truck 16t (1 tkm)**	**(1 tkm)**
coal ETH	mg	9,05E+01	5,53E+02	225
crude oil ETH	g	2,49	69,1	28,1
lignite ETH	mg	120	736	299
natural gas ETH	l	1,40E-01	3,48E+00	1,41
pot. energy hydropower	kJ	5,26E-01	3,22E+00	1,31
uranium (ore)	µg	8,17	50	20,3
water	g	1,86E+01	5,35E+02	218
wood	mg	0,887	5,42	2,2
OUTPUTS				
Emissions to air	**Unit**	**Sea-ship (1 tkm)**	**Truck 16t (1 tkm)**	**Truck 40t (1 tkm)**
ammonia	µg	9,77E-01	6,19E+00	2,52
benzene	mg	0,0266	8,18	3,32
Cd	µg	3,04	2,21	0,899
CO	g	2,86E-03	1,25E+00	0,508
CO2	g	8,28E+00	2,28E+02	92,5
CxHy aromatic	mg	0,0658	1,36	0,554
CxHy chloro	µg	2,14E-04	1,31E-03	0,000531
dust	mg	5,46	93,9	38,1
HALON-1301	µg	5,94E-01	1,66E+01	6,73
HCl	µg	193	466	189
HF	µg	19,6	48,7	19,8
Hg	µg	3,30E-02	2,28E-01	0,0925
metals	µg	3,72E+02	7,17E+02	291
methane	mg	10,4	277	113
Mn	µg	3,04E-02	1,87E-01	0,0758
N2O	mg	0,168	5,5	2,23
Ni	µg	6,25E+01	1,10E+02	44,6
non methane VOC	g	0,0198	1,42	0,577
NOx (as NO2)	g	0,021	4,1	1,66
PAH's	µg	1,05E-01	1,72E+00	0,698
Pb	µg	5,35E+00	1,22E+01	4,95
SOx (as SO2)	mg	115	343	139
Zn	µg	5,83E+00	7,30E+01	29,6
Emissions to water	**Unit**	**Sea-ship (1 tkm)**	**Truck 16t (1 tkm)**	**Truck 40t (1 tkm)**
Al	µg	147	913	371
anorg. dissolved subst.	g	4,86E-02	1,34E+00	0,544
AOX	µg	0,431	13,6	5,54
As	µg	0,39	4,54	1,85
Ba	mg	3,24E-01	8,75E+00	3,56

BOD	µg	5,48E+00	3,12E+02	127
Cd	µg	0,142	3,85	1,56
Cl-	g	6,71E-02	1,85E+00	0,753
COD	mg	0,107	10,2	4,15
Cr	µg	2,51E+00	3,83E+01	15,6
Cu	µg	0,946	10,7	4,36
CxHy aromatic	mg	0,106	2,96	1,2
CxHy chloro	µg	1,09E-01	3,04E+00	1,23
cyanide	µg	4,82E-01	1,37E+01	5,57
DOC	µg	0,269	1,64	0,667
Fe	mg	2,55E-01	1,95E+00	0,791
Hg	µg	0,00141	0,0343	0,0139
Kjeldahl-N	mg	1,23E-02	1,29E+00	0,523
metallic ions	mg	0,777	21,3	8,66
N-tot	mg	0,123	7,42	3,02
NH4+	mg	1,27E-01	7,61E+00	3,09
Ni	µg	1,08E+00	1,42E+01	5,77
nitrate	mg	0,0823	2,28	0,928
oil	mg	3,30E+00	9,26E+01	37,6
PAH's	µg	1,62	45,3	18,4
Pb	µg	1,01E+00	9,39E+00	3,81
phenols	µg	17,9	459	187
phosphate	µg	9,95	90,1	36,6
sulphate	mg	3,37E+00	6,53E+01	26,5
sulphide	µg	3,83E+00	1,09E+02	44,3
suspended substances	mg	7,13	198	80,4
TOC	mg	9,86E-01	3,19E+01	13
toluene	µg	14,7	412	167
Zn	µg	2,55E+00	4,05E+01	16,5

Non-material emissionsr	**Unit**	**Sea-ship (1 tkm)**	**Truck 16t (1 tkm)**	**Truck 40t (1 tkm)**
radioact. substance to air	Bq	7,11E+02	4,35E+03	1770
radioact. substance to water	Bq	6,6	41,6	16,9

Source: BUWAL 250 database (Habersatter, 1996).

APPENDIX 2. Bark and black liquor emissions

In the second scenario the kraft mill uses black liquor, bark and oil to produce both electricity and heat. While oil is a very common fuel to find in LCA databases, bark and black liquor are not. This appendix includes the detailed data on emissions used to define the inventory for these two waste-derived fuels. Nevertheless, the aggregated inventory table, including also oil, is shown in appendix 1 (Table A.6.).

A.2.1. Emissions from the recovery boiler

In the inventory analysis it has been calculated that 4,43 MJ black liquor solids, or 0,29 kg black liquor solids, in turn attributable to 0,17 kg product pulp, are consumed per kWh of energy produced in the mill. The emissions related to this consumption have been extracted from several sources, which are shown in Table A8.

Table A8. Available data for recovery boiler emissions.

Substance	**Source and units**				
	NGGIC (2000) mg/MJ biomass [a]	**Habersatter (1991) g/kg pulp [b]**	**Someshwar & Jain (1995) g/kg pulp**	**EIPPCB (2000) g/kg pulp**	**Adams et al. (1997) mg/MJ bls [c]**
CO_2-re	92.120				
Dust		1,6		0,1-1,8	
CO	680	2,3			
SO_2		2,4		1-4	
NO_x	73	1,3		0,6-1,8	
C_xH_y	68				
N_2O	4,1				
HCl			0,33		
Mercaptans		0,27			
H_2S		0,02			
CH_4	4,2				
PAH					0,02-1
Metals					0,01-0,05

[a] Generic data for biomass furnace.

[b] Overall emissions from a kraft mill. Assumed to be originated mainly in the recovery boiler.

[c] Bls: black liquor solids.

The emissions originated in the recovery boiler, per kWh electricity produced in the mill can be calculated from the data in the table and the previously calculated conversión factors. As some substances are found in more than one source, some choices have to be made, according to data quality:

- Dust, NO_x, and SO_x have been collected from EIPPCB (2000), because is the most recent and specific data concerning these substances. The average value for each substance has been taken.

- CO_2-re, C_xH_y and N_2O have been collected from NGGIC (2000), as this is the most recent data for these substances. It is not, however, specific data from kraft mills, but for biomass combustion in furnaces.

- CO is collected from Habersatter (1991). It is older data than from NGGIC, but specific for kraft mills, which we have considered to be preferable.

A.2.2. Emissions from the bark boiler

For bark burning, it has been calculated in the inventory that 0,074 kg bark, or 0,52 MJ bark, are consumed per kWh of energy produced in the mill. The emissions related to this consumption have been extracted from several sources, which are shown in Table A9.

Table A9. Available data for bark boiler emissions.

Substance	**Source and units**		
	NGGIC (2000) biomass [a]	**Habersatter (1991) mg/MJ biomass [a]**	**EIPPCB (2000) g/kg bark**
CO_2-re	92.120	101.600	
Dust		195,3	0,1-1
CO	680	980	
SO_2		4,9	
NO_x	73	156	0,3-0,7
C_xH_y	68	176	
N_2O	4,1	15	
HCl			
Mercaptans			
H_2S			
CH_4	4,2		

[a] Generic data for biomass furnace.

The emissions originated in the bark boiler, per kWh energy produced in the mill can be calculated from the data in the table and the previously calculated conversion factors. As some substances are found in more than one source, some choices have to be made, according to data quality:

- Dust, and NO_x have been chosen from EIPPCB (2000), because is the most recent and specific data concerning these substances. The average value for each substance has been used.

- CO_2-re, CO, C_xH_y and N_2O have been chosen from NGGIC (2000), as this is the most recent data for these substances. It is not, however, specific data from kraft mills, but for biomass combustion in furnaces.

APPENDIX 3. Characterisation factors

The following table show the characterisation factors used in LCIA. In order to avoid an endless list, substances included in the impact models, but not inventoried in the system under study have been excluded from the table. Therefore, these impact models actually include more substances than are shown.

Table A10. Characterisation factors used in LCIA.

Class	Substance	GWP (kg CO_2 eq./kg)	ODP (kg CFC-11 eq./kg)	AEP (kg PO_4^{3-} eq./kg)	AP (kg SO_2 eq./kg)	HTP (kg 1,4-d. eq./kg)	FATP (kg 1,4-d. eq./kg)	POFP (kg C_2H4 eq./kg)	ARD (kg Sb eq./kg
Raw	bauxite								2,10E-09
Raw	coal hard								1,34E-02
Raw	coal soft, lignite								6,71E-03
Raw	iron (ore)								4,80E-08
Raw	natural gas								1,87E-02
Raw	oil crude								2,01E-02
Raw	Ilmenite								4,80E-09
Air	ammonia			0,11	1,88				
Air	Benzene					1,90E+03	8,40E-05	0,189	
Air	Benzo(a)pyrene						88		
Air	cadmium					1,45E+05	52		
Air	PAH					5,72E+05	170	0,761	
Air	chromium (III)					3,68E+01	0,081		
Air	CO							0,03	
Air	CO2	1							
Air	CO2-re								
Air	copper					4,28E+03	31		
Air	CxHy							0,398	
Air	CxHy aliphatic							0,398	
Air	CxHy aromatic							0,761	
Air	CxHy chloro							0,021	
Air	dust (PM10)					8,20E-01			
Air	Fluoranthene						18	0,377	
Air	H2S				1,88	2,20E-01			
Air	Halon 1301		16						
Air	HCl				0,88	5,00E-01			
Air	HF				1,6	9,39E+01			
Air	lead (II) ion					2,91E+01	0,12		
Air	mercury					2,64E+02	59		
Air	metals					1,62E+03	3,64		
Air	methane	21						0,007	
Air	methane-re	21						0,007	
Air	N2O	310							
Air	nickel					3,50E+04	70		
Air	NO2			0,05	0,7	1,20E+00		0,028	

Air	NMVOC							0,416	
Air	NOx			0,05	0,7	1,20E+00		0,028	
Air	NOx (as NO2)			0,05	0,7	1,20E+00		0,028	
Air	SO2				1	9,60E-02			
Air	SOx				1	9,60E-02			
Air	SOx (as SO2)				1	9,60E-02			
Air	thallium					1,60E+04	180		
Air	Toluene					3,27E-01	7,00E-05	0,563	
Air	vanadium					2,62E+02	210		
Air	xylene						6,00E-05	0,849	
Air	zinc (II) ion					9,58E+01	2		
Water	arsenic					1,32E+02	210		
Water	barium					1,46E+01			
Water	cadmium					1,13E+01	1500		
Water	PAH					2,81E+05	28000		
Water	chromium III					1,08E+00	6,9		
Water	COD			0,022					
Water	copper (II) ion					4,46E-01	1100		
Water	Kjeldahl-N			0,42					
Water	lead (II) ion					5,18E+00	9,6		
Water	mercury					1,01E+02	1700		
Water	metallic ions					1,60E-01	4,68		
Water	NH3			0,33					
Water	NH4+			0,33					
Water	nickel					4,27E+01	3200		
Water	nitrate			0,1					
Water	N-tot			0,42					
Water	phenol					4,92E-02	240		
Water	phosphate			1					
Water	P-tot			3,06					
Water	toluene					3,03E-01	0,29		
Water	vanadium					2,67E+02	8900		
Water	zinc (II) ion					2,12E-01	91		

Sources:

GWP: Houghton et al., 1994, 1995.
ODP: WMO, 1992, 1995, 1998.
AEP: Heijungs et al., 1992; Huijbregts & Seppälä, 2001.
AP: Heijungs et al., 1992.
HTP: Huijbregts, 2000.
FATP: Huijbregts, 2000.
POFP: Hauschild & Wenzel, 1998; Guinée et al., 2001.
ARD: Guinée et al., 2001.

APPENDIX 4. Life Cycle Impact Assessment results

A.4.1. Characterisation

The following tables show for each treatment and scenario, the characterisation results, disaggregated by sub-systems. At the end of this section, also the characterisation results for the two sensitivity analysis performed in the study are shown.

Table A11. Characterisation results for photocatalysis (PhC) in scenario 1.

Category	Unit	Total	TiO2	Grid electricity
GWP	kg CO_2	90	0,48	90
ODP	kg CFC11	2,17E-05	7,60E-08	2,16E-05
AEP	kg PO_4^{3-}	0,014	7,76E-05	0,014
AP	kg SO_2	0,56	0,004	0,56
HTP	kg 1,4 d	21	0,029	21
FATP	kg 1,4 d	1,51	0,08	1,43
POFP	POCP kg	0,029	2,81E-04	0,029
ARD	Sb kg	0,67	0,002	0,67

Table A12. Characterisation results for Fenton and photo-Fenton (FPhF) in scenario 1.

Category	Unit	Total	H2O2 50%	FeCl3 40%	Grid electricity
GWP	kg CO_2	38	0,68	0,08	38
ODP	kg CFC11	9,03E-06	1,32E-08	2,50E-08	8,99E-06
AEP	kg PO_4^{3-}	6,09E-03	2,88E-04	1,58E-05	5,79E-03
AP	kg SO_2	0,24	0,007	0,001	0,23
HTP	kg 1,4 d	8,6	0,019	0,012	8,6
FATP	kg 1,4 d	0,5990	4,94E-04	4,94E-04	0,60
POFP	POCP kg	0,013	8,29E-04	8,39E-05	0,012
ARD	Sb kg	0,29	0,005	5,59E-04	0,28

Table A13. Characterisation results for photocatalysis and H_2O_2 (PhC+H2O2) in scenario 1.

Category	Unit	Total	TiO2	H2O2 50%	Grid electricity
GWP	kg CO_2	54	0,48	0,68	53
ODP	kg CFC11	1,27E-05	7,60E-08	1,32E-08	1,26E-05
AEP	kg PO_4^{3-}	0,0085	7,76E-05	2,88E-04	0,0081
AP	kg SO_2	0,34	0,0037	0,0065	0,33
HTP	kg 1,4 d	12	0,029	0,019	12
FATP	kg 1,4 d	0,92	0,084	4,94E-04	0,84
POFP	POCP kg	0,018	2,81E-04	8,29E-04	0,017
ARD	Sb kg	0,40	0,0018	0,0046	0,39

Table A14. Characterisation results for photocatalysis and photo-Fenton (FPhF) in scenario 1.

Category	Unit	Total		H2O2 50%	FeCl3 40%	Grid electricity
GWP	kg CO_2	16	0,48	0,68	0,004	15
ODP	kg CFC11	3,69E-06	7,60E-08	1,32E-08	1,21E-09	3,60E-06
AEP	kg PO_4^{3-}	0,0027	7,76E-05	2,88E-04	7,61E-07	0,0023
AP	kg SO_2	0,10	0,0037	0,0065	4,60E-05	0,09
HTP	kg 1,4 d	3	0,029	0,019	0,001	3
FATP	kg 1,4 d	0,32	0,084	4,94E-04	2,38E-05	0,24
POFP	POCP kg	0,006	2,81E-04	8,29E-04	4,05E-06	0,005
ARD	Sb kg	0,12	0,0018	0,0046	2,70E-05	0,11

Table A15. Characterisation results for ozonation (O3) in scenario 1.

Category	Unit	Total	O2	Grid electricity
GWP	kg CO_2	661	111	550
ODP	kg CFC11	1,67E-04	3,50E-05	1,32E-04
AEP	kg PO_4^{3-}	0,109	0,024	0,085
AP	kg SO_2	4,2	0,8	3,4
HTP	kg 1,4 d	151	25	126
FATP	kg 1,4 d	10,4	1,7	8,8
POFP	POCP kg	0,24	0,06	0,18
ARD	Sb kg	4,91	0,81	4,10

Table A16. Characterisation results for ozonation and UVA (O3+UVA) in scenario 1.

Category	Unit	Total	O2	Grid electricity
GWP	kg CO_2	337	55	282
ODP	kg CFC11	8,53E-05	1,76E-05	6,77E-05
AEP	kg PO_4^{3-}	0,056	0,012	0,044
AP	kg SO_2	2,1	0,4	1,8
HTP	kg 1,4 d	77	13	65
FATP	kg 1,4 d	5,3	0,8	4,5
POFP	POCP kg	0,12	0,03	0,09
ARD	Sb kg	2,52	0,41	2,11

Table A17. Characterisation results for photocatalysis (PhC) in scenario 2.

Category	Unit	Total	TiO2	Co-generation
GWP	kg CO_2	5	0,48	5
ODP	kg CFC11	4,22E-06	7,60E-08	4,14E-06
AEP	kg PO_4^{3-}	0,0027	7,76E-05	0,0026
AP	kg SO_2	0,16	0,0037	0,16
HTP	kg 1,4 d	146	0,029	146
FATP	kg 1,4 d	0,16	0,084	0,07
POFP	POCP kg	0,034	2,81E-04	0,034
ARD	Sb kg	0,03	0,0018	0,02

Table A18. Characterisation results for Fenton and photo-Fenton (FPhF) in scenario 2.

Category	Unit	Total	H2O2 50%	FeCl3 40%	Co-generation electricity
GWP	kg CO_2	3	0,68	0,08	3
ODP	kg CFC11	2,22E-06	1,32E-08	2,50E-08	2,18E-06
AEP	kg PO_4^{3-}	1,68E-03	2,88E-04	1,58E-05	1,38E-03
AP	kg SO_2	0,09	0,007	0,001	0,08
HTP	kg 1,4 d	77	0,019	0,012	77
FATP	kg 1,4 d	0,039	4,94E-04	1,09E-03	0,04
POFP	POCP kg	0,019	8,29E-04	8,39E-05	0,018
ARD	Sb kg	0,02	0,005	5,59E-04	0,013

Table A19. Characterisation results for photocatalysis and H_2O_2 (PhC+H2O2) in scenario 2.

Category	Unit	Total	TiO2	H2O2 50%	Co-generation electricity
GWP	kg CO_2	4	0,48	0,68	3
ODP	kg CFC11	2,50E-06	7,60E-08	1,32E-08	2,41E-06
AEP	kg PO_4^{3-}	0,0019	7,76E-05	2,88E-04	0,0015
AP	kg SO_2	0,10	0,004	0,007	0,09
HTP	kg 1,4 d	85	0,029	0,019	85
FATP	kg 1,4 d	0,13	0,084	4,94E-04	0,04
POFP	POCP kg	0,021	2,81E-04	8,29E-04	0,020
ARD	Sb kg	0,02	0,0018	0,0046	0,01

Table A20. Characterisation results for photocatalysis and photo-Fenton (PhC+FPhF) in scenario 2.

Category	Unit	Total	TiO2	H2O2 50%	40%	Co-generation electricity
GWP	kg CO_2	2,0	0,48	0,68	0,0041	0,8
ODP	kg CFC11	7,79E-07	7,60E-08	1,32E-08	1,21E-09	6,89E-07
AEP	kg PO_4^{3-}	8,01E-04	7,76E-05	2,88E-04	7,61E-07	4,35E-04
AP	kg SO_2	0,037	0,004	0,007	4,60E-05	0,03
HTP	kg 1,4 d	24	0,029	0,019	5,73E-04	24
FATP	kg 1,4 d	0,10	0,084	4,94E-04	5,27E-05	0,01
POFP	POCP kg	0,007	2,81E-04	8,29E-04	4,05E-06	0,006
ARD	Sb kg	0,010	0,0018	0,0046	2,70E-05	0,004

Table A21. Characterisation results for ozonation (O3) in scenario 2.

Category	Unit	Total	O2	Co-generation electricity
GWP	kg CO_2	139	111	29
ODP	kg CFC11	6,03E-05	3,50E-05	2,53E-05
AEP	kg PO_4^{3-}	0,040	0,024	0,016
AP	kg SO_2	1,7	0,8	1,0
HTP	kg 1,4 d	916	25	891
FATP	kg 1,4 d	2,1	1,7	0,4
POFP	POCP kg	0,27	0,06	0,21
ARD	Sb kg	0,96	0,81	0,15

Table A22. Characterisation results for ozonation and UVA (O3+UVA) in scenario 2.

Category	Unit	Total	O2	Co-generation electricity
GWP	kg CO_2	70	55	15
ODP	kg CFC11	3,06E-05	1,76E-05	1,30E-05
AEP	kg PO_4^{3-}	0,020	0,012	0,008
AP	kg SO_2	0,9	0,4	0,5
HTP	kg 1,4 d	471	13	458
FATP	kg 1,4 d	1,1	0,8	0,2
POFP	POCP kg	0,14	0,03	0,11
ARD	Sb kg	0,48	0,41	0,07

Table A23. Characterisation results for photocatalysis (PhC) in scenario 3.

Category	Unit	Total	TiO2
GWP	kg CO_2	0,48	0,48
ODP	kg CFC11	7,60E-08	7,60E-08
AEP	kg PO_4^{3-}	7,76E-05	7,76E-05
AP	kg SO_2	0,0037	0,0037
HTP	kg 1,4 d	0,029	0,029
FATP	kg 1,4 d	0,084	0,084
POFP	POCP kg	2,81E-04	2,81E-04
ARD	Sb kg	0,0018	0,0018

Table A24. Characterisation results for Fenton and photo-Fenton (FPhF) in scenario 3.

Category	Unit	Total	H2O2 50%	FeCl3 40%
GWP	kg CO_2	0,76	0,68	0,08
ODP	kg CFC11	3,82E-08	1,32E-08	2,50E-08
AEP	kg PO_4^{3-}	3,03E-04	2,88E-04	1,58E-05
AP	kg SO_2	0,007	0,007	0,001
HTP	kg 1,4 d	0,031	0,019	0,012
FATP	kg 1,4 d	0,002	4,94E-04	1,09E-03
POFP	POCP kg	9,13E-04	8,29E-04	8,39E-05
ARD	Sb kg	0,005	0,005	5,59E-04

Table A25. Characterisation results for photocatalysis and H_2O_2 (PhC+H2O2) in scenario 3.

Category	Unit	Total	TiO2	H2O2 50%
GWP	kg CO_2	1,16	0,48	0,68
ODP	kg CFC11	8,92E-08	7,60E-08	1,32E-08
AEP	kg PO_4^{3-}	3,65E-04	7,76E-05	2,88E-04
AP	kg SO_2	0,010	0,004	0,007
HTP	kg 1,4 d	0,049	0,029	0,019
FATP	kg 1,4 d	0,085	0,084	4,94E-04
POFP	POCP kg	1,11E-03	2,81E-04	8,29E-04
ARD	Sb kg	0,006	0,0018	0,0046

Table A26. Characterisation results for photocatalysis and photo-Fenton (PhC+FPhF) in scenario 3.

Category	Unit	Total	TiO2	H2O2 50%	FeCl3 40%
GWP	kg CO_2	1,16	0,48	0,68	0,0041
ODP	kg CFC11	9,04E-08	7,60E-08	1,32E-08	1,21E-09
AEP	kg PO_4^{3-}	3,66E-04	7,76E-05	2,88E-04	7,61E-07
AP	kg SO_2	0,010	0,004	0,007	4,60E-05
HTP	kg 1,4 d	0,049	0,029	0,019	5,73E-04
FATP	kg 1,4 d	0,085	0,084	4,94E-04	5,27E-05
POFP	POCP kg	1,11E-03	2,81E-04	8,29E-04	4,05E-06
ARD	Sb kg	0,006	0,0018	0,0046	2,70E-05

Table A27. Characterisation results for ozone (O3) in scenario 1 (sensitivity analysis section 3.5.4.1).

Category	Unit	Total	O2	electricity
GWP	kg CO_2	70	14	57
ODP	kg CFC11	1,79E-05	4,32E-06	1,35E-05
AEP	kg PO_4^{3-}	0,012	0,003	0,009
AP	kg SO_2	0,45	0,09	0,35
HTP	kg 1,4 d	16	3	13
FATP	kg 1,4 d	1,1	0,2	0,9
POFP	POCP kg	0,026	0,008	0,018
ARD	Sb kg	0,52	0,10	0,42

Table A28. Characterisation results for ozone and UVA
(O3+UVA) in scenario 1 (sensitivity analysis section 3.5.4.1).

Category	Unit	Total	O2	Grid electricity
GWP	kg CO_2	42	7	36
ODP	kg CFC11	1,07E-05	2,16E-06	8,51E-06
AEP	kg PO_4^{3-}	0,007	0,001	0,005
AP	kg SO_2	0,27	0,05	0,22
HTP	kg 1,4 d	10	2	8
FATP	kg 1,4 d	0,67	0,10	0,57
POFP	POCP kg	0,015	0,004	0,012
ARD	Sb kg	0,32	0,05	0,26

Table A29. Characterisation results for photocatalysis (PhC) in scenario 3 (sensitivity analysis section 3.5.4.2).

Category	Unit	Total	TiO2
GWP	kg CO_2	7,3	7,3
ODP	kg CFC11	1,14E-06	1,14E-06
AEP	kg PO_4^{3-}	0,001	0,001
AP	kg SO_2	0,055	0,055
HTP	kg 1,4 d	0,44	0,44
FATP	kg 1,4 d	1,26	1,26
POFP	POCP kg	0,004	0,004
ARD	Sb kg	0,026	0,026

Table A30. Characterisation results for Fenton and photo-Fenton (FPhF) in scenario 3 (sensitivity analysis section 3.5.4.2).

Category	Unit	Total	H2O2 50%	FeCl3 40%
GWP	kg CO_2	5,9	5,2	0,6
ODP	kg CFC11	3,91E-07	2,01E-07	1,90E-07
AEP	kg PO_4^{3-}	0,0024	0,0023	1,20E-04
AP	kg SO_2	0,058	0,051	0,007
HTP	kg 1,4 d	0,25	0,16	0,09
FATP	kg 1,4 d	0,01	0,004	0,01
POFP	POCP kg	0,007	0,007	6,36E-04
ARD	Sb kg	0,040	0,036	0,004

Table A31. Characterisation results for photocatalysis and H_2O_2 (PhC+H2O2) in scenario 3 (sensitivity analysis section 3.5.4.2).

Category	Unit	Total	TiO2	H2O2 50%
GWP	kg CO_2	12,8	5,3	7,4
ODP	kg CFC11	1,12E-06	8,36E-07	2,86E-07
AEP	kg PO_4^{3-}	0,004	0,001	0,003
AP	kg SO_2	0,11	0,041	0,072
HTP	kg 1,4 d	0,55	0,32	0,23
FATP	kg 1,4 d	0,93	0,93	0,01
POFP	POCP kg	0,013	0,003	0,009
ARD	Sb kg	0,070	0,019	0,051

Table A32. Characterisation results for photocatalysis and photo-Fenton (PhC+FPhF) in scenario 3 (sensitivity analysis section 3.5.4.2).

Category	Unit	Total	TiO2	H2O2 50%	FeCl3 40%
GWP	kg CO_2	9,2	3,9	5,2	0,1
ODP	kg CFC11	8,27E-07	6,08E-07	2,01E-07	1,73E-08
AEP	kg PO_4^{3-}	0,0029	0,0006	0,0023	1,09E-05
AP	kg SO_2	0,08	0,029	0,051	6,58E-04
HTP	kg 1,4 d	0,41	0,23	0,16	0,01
FATP	kg 1,4 d	0,68	0,67	0,004	7,51E-04
POFP	POCP kg	0,009	0,002	0,007	5,79E-05
ARD	Sb kg	0,050	0,014	0,036	3,86E-04

A.4.2. Normalisation and weighting

The following tables include, for each treatment and scenario, the results of normalisation. The normalised impact indicators are then summed up for each treatment in the last row, leading to the weighted score. Since the normalisation results are only summed, all impact categories are equally weighted with a factor of 1. The last two tables correspond to the results of the sensitivity analysis performed.

Table A33. Normalised and weighted results for all treatments in scenario 1.

Category	Unit	PhC	FPhF	PhC+H2O2	PhC+FPhF	O3	O3+UVA
GWP	y^{-1}	1,91E-11	8,07E-12	1,13E-11	3,41E-12	1,39E-10	7,13E-11
ODP	y^{-1}	2,60E-13	1,08E-13	1,52E-13	4,44E-14	2,00E-12	1,02E-12
AEP	y^{-1}	5,20E-12	2,27E-12	3,15E-12	1,00E-12	4,06E-11	2,07E-11
AP	y^{-1}	1,91E-11	8,17E-12	1,14E-11	3,52E-12	1,42E-10	7,26E-11
HTP	y^{-1}	2,77E-12	1,16E-12	1,62E-12	4,68E-13	2,03E-11	1,04E-11
FATP	y^{-1}	3,22E-12	1,27E-12	1,95E-12	6,86E-13	2,21E-11	1,13E-11
POFP	y^{-1}	3,56E-12	1,58E-12	2,20E-12	7,27E-13	2,92E-11	1,49E-11
ARD	y^{-1}	4,55E-11	1,93E-11	2,69E-11	8,00E-12	3,32E-10	1,70E-10
Total (weighted)	y^{-1}	9,87E-11	4,19E-11	5,87E-11	1,79E-11	7,28E-10	3,72E-10

Table A34. Normalised and weighted results for all treatments in scenario 2.

Category	Unit	PhC	FPhF	PhC+H2O2	PhC+FPhF	O3	O3+UVA
GWP	y^{-1}	1,1E-12	6,87E-13	8,3E-13	4,32E-13	2,95E-11	1,48E-11
ODP	y^{-1}	5,05E-14	2,66E-14	3,02E-14	9,8E-15	7,23E-13	3,66E-13
AEP	y^{-1}	9,99E-13	6,23E-13	7,06E-13	3,07E-13	1,49E-11	7,56E-12
AP	y^{-1}	5,48E-12	3,08E-12	3,48E-12	1,28E-12	5,85E-11	2,97E-11
HTP	y^{-1}	1,95E-11	1,03E-11	1,14E-11	3,27E-12	1,23E-10	6,3E-11
FATP	y^{-1}	3,29E-13	8,28E-14	2,67E-13	2,07E-13	4,48E-12	2,25E-12
POFP	y^{-1}	4,17E-12	2,29E-12	2,55E-12	8,39E-13	3,29E-11	1,68E-11
ARD	y^{-1}	1,72E-12	1,19E-12	1,37E-12	7,42E-13	6,48E-11	3,26E-11
Total (weighted)	y^{-1}	3,34E-11	1,83E-11	2,06E-11	7,08E-12	3,29E-10	1,67E-10

Table A35. Normalised and weighted results for all treatments in scenario 3.

Category	Unit	PhC	FPhF		PhC+FPhF
GWP	y^{-1}	1,60E-13	1,02E-13	2,47E-13	2,48E-13
ODP	y^{-1}	4,59E-16	9,12E-16	1,23E-15	1,24E-15
AEP	y^{-1}	1,13E-13	2,89E-14	1,40E-13	1,40E-13
AP	y^{-1}	2,55E-13	1,25E-13	3,53E-13	3,55E-13
HTP	y^{-1}	4,19E-15	3,92E-15	6,79E-15	6,86E-15
FATP	y^{-1}	3,35E-15	1,78E-13	1,79E-13	1,80E-13
POFP	y^{-1}	1,10E-13	3,41E-14	1,39E-13	1,39E-13
ARD	y^{-1}	3,52E-13	1,18E-13	4,37E-13	4,39E-13
Total (weighted)	y^{-1}	9,98E-13	5,92E-13	1,50E-12	1,51E-12

Table A36. Normalised and weighted results for ozone-based treatments in scenario 1 (sensitivity analysis section 3.5.4.1.).

Category	Unit	O3	O3+UVA
GWP	y^{-1}	1,48E-11	8,93E-12
ODP	y^{-1}	2,14E-13	1,28E-13
AEP	y^{-1}	4,36E-12	2,59E-12
AP	y^{-1}	1,51E-11	9,09E-12
HTP	y^{-1}	2,15E-12	1,30E-12
FATP	y^{-1}	2,35E-12	1,42E-12
POFP	y^{-1}	3,16E-12	1,86E-12
ARD	y^{-1}	3,53E-11	2,13E-11
Total (weighted)	y^{-1}	7,74E-11	4,66E-11

Table A36. Normalised and weighted results for ozone-based treatments in scenario 3 (sensitivity analysis section 3.5.4.2.).

Category	Unit	PhC		PhC+H2O2	PhC+PhF
GWP	y^{-1}	1,53E-12	1,24E-12	2,69E-12	1,93E-12
ODP	y^{-1}	1,37E-14	4,69E-15	1,35E-14	9,92E-15
AEP	y^{-1}	4,33E-13	8,87E-13	1,51E-12	1,08E-12
AP	y^{-1}	1,88E-12	1,98E-12	3,84E-12	2,75E-12
HTP	y^{-1}	5,88E-14	3,39E-14	7,41E-14	5,42E-14
FATP	y^{-1}	2,67E-12	2,67E-14	1,97E-12	1,44E-12
POFP	y^{-1}	5,11E-13	8,74E-13	1,51E-12	1,08E-12
ARD	y^{-1}	1,78E-12	2,71E-12	4,75E-12	3,40E-12
Total (weighted)	y^{-1}	8,88E-12	7,75E-12	1,64E-11	1,17E-11