6th Framework programme – priority **3**

Integrated project for SMEs – contract n°: 515859

Eco-efficient activation for hyperfunctional surfaces

WORKPACKAGE: WP3

Life Cycle Assessment

LCA COMPARATIVE ANALYSIS OF TEXTILE APPLICATIONS FOR OLEOPHOBIC AND HYDROPHOBIC PROPERTIES

CONTENT

Executive Summary

This report completes the previous study and investigations provided regarding comparative analysis between PVD, SiOx plasma deposition and Chromium electroplating processes and includes the study done to obtain Oleophobic and Hydrophobic properties for textiles applications

According to the WP3 objectives, the purpose of this study is to quantify energy, resources consumption and emissions to the environment resulting from a life cycle analysis comparing plasma technologies with respect to traditional wet processes applied to two different textile substrates: PET and mixed PET and Cotton. The general scope of this study is to compare alternative technologies for surface functionalisation and to analyse how the origin and type of energy and input materials employed in each process affect the overall environmental burden evaluation. For this reason, the analysis includes a preliminary assessment of traditional processes comparable to the plasma technology for the functional output of the production system, whereas characterized by different physical/chemical properties and different process performances with respect to the other innovative solutions. Even if not explicitly mentioned, this report follows the indications provided by ISO standards 1404X series. This analysis does not address socio-economic and aesthetic issues.

The main characteristics of the study can be summarised as follow:

- most of the data used during the model implementation are primary, that means that have been collected on site by using ad hoc questionnaires, that is, customised questionnaires realised by Environment Park (EP). Secondary data, obtained by databases, previous analysis or published report, have been used with regard to the production and delivery of energy carriers (electricity, natural gas, etc.) and to the production and delivery of all raw materials entering the production plants.
- mass and energy balances have been calculated following the general principles of ISO 14040;
- the comparison between the three coating technologies with different energy mixes analysed has to be considered as a first order approximation result;
- the software Boustead Model V1 was used as calculation model and as the main source of secondary data.

The report contains:

- the main hypotheses adopted in the study;
- the main energy and environmental results;
- the significance and limits of the results;
- the suggested investigations for a possible future development of the study.

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1. Traditional and plasma technologies to obtain hydrophobic and oleophobic properties

This report completes the previous document regarding the LCA comparative analysis and includes the results obtained from the study of different technologies for textile surface functionalisation.

The following case study has been considered following LCA parameters:

- Comparative LCA Analysis between traditional and plasma processes for PET textile substrates to obtain oleophobic properties.

1.1 Traditional and Plasma technologies for oleophobic properties on PET substrates

This comparative study analyses the traditional and plasma technology for a PET substrate functionalisation.

Traditional technology includes an initial wet surface cleaning process (de-oiling) and a second chemical wet process that activates the surface mainly using fluoro-resin compounds.

Plasma technology is based on a first surface wet cleaning process followed by an atmospheric plasma process using fluorinated gases. Unfortunately data regarding a plasma process for the cleaning de-oiling steps are still not available and therefore it has been described a wet process that precedes the surface activation plasma step.

2. Scope of the Study

FUNCTIONAL UNIT

System boundaries and Functional Unit (F.U) definition is extremely important in order to have a valid comparative study.

The F.U that has been chosen is 1 kg of treated material. Due to the fact that the two different substrates (PET and PET + Cotton) have that cannot be compared in terms of surface morphology and chemico-physical characteristics, it has been decided to carry out specific analysis for each substrate, using as a reference an invariant quantity: mass. Choosing a mass unit as F.U. ensures that whatever the process is, it has been always considered the same quantity of material, eliminating the surface dependence to possible shrinking or enlargement after the treatment. It must also be considered that the mass difference before and after the surface treatment can be considered as negligible.

SYSTEM BOUNDARIES

The studied system contains the cleaning processes (de-oiling or de-sizing) and the functionalisation treatment to achieve the desired property. Environmental burdens caused by the production of the substrates, or machinery and tools used during the processes have not been taken into account. The following flow chart represents the system boundaries considered as well as the material and energy exchange with the outer environment. (see fig 2.1)

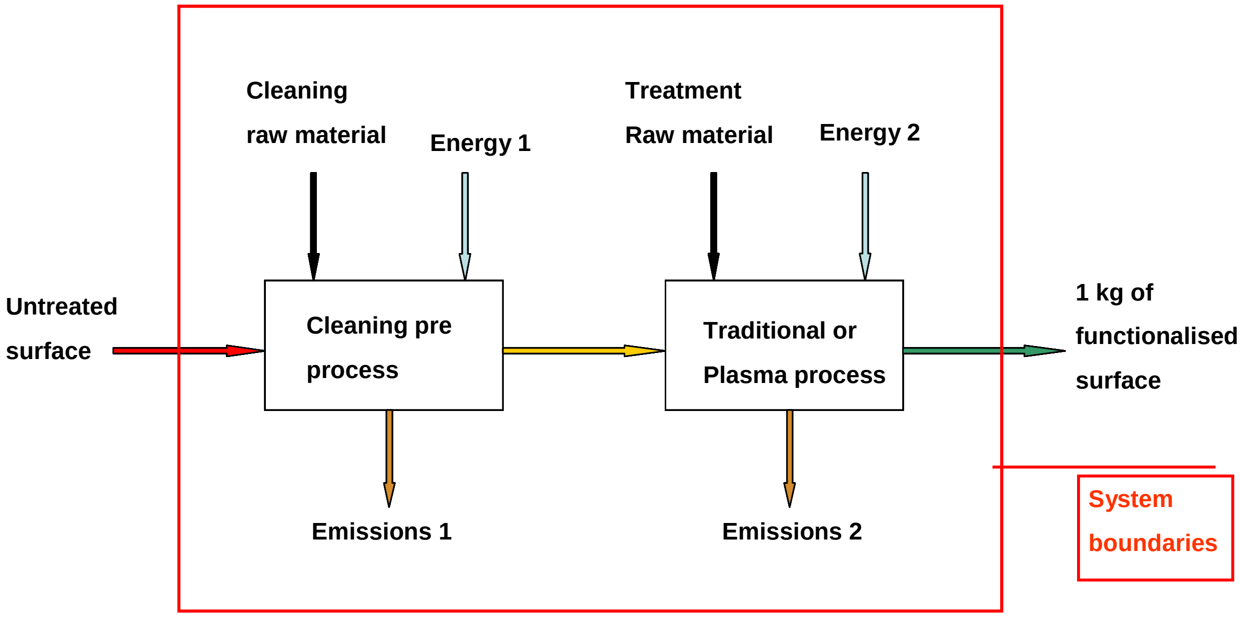

Fig 2.1. System boundaries simplified scheme

The software used for the LCA computations is Boustead V. This software calculates a single output table that includes the values for total process emissions (integrating emissions 1 and 2), a single output table containing the values that stand for the overall energy consumptions (integrating what it has been written as energy 1 and energy 2) and edit a single table that includes all the raw materials quantities used in the whole process (adding the consumptions for the cleaning pre process and the functionalisation process).

FURTHER CONSIDERATIONS

One of the main difficulties that man come across while carrying out LCA analysis is data availability accuracy and precision.. This is because this project has as additional priority the confidentiality of the data employed so that any of the processes values cannot be associated to its provider. Most of the processes described use materials and chemical composition that are restricted and its composition is protected by patents. In this case and in order to go forward with the analysis it has been decided to set specific hypotheses about general chemical compositions available for computation. These reference compounds are assumed to have equivalent performances with respect to the reference ones.

In addition, the LCA software used for the analysis library, despite its completeness, does not contain all the specified chemical compounds used in these processes. For instance, it has been particularly difficult to find data regarding CF_4 and similar PFC gases that are used as precursors in plasma processes as these gases are not included as a possible input material in Boustead library, (commonly these gases are a by-product of several industrial processes, but they are not employed as input raw materials). In order to cope with this situation, it has been decided to add these gases energy contribution to the total Gross Energy Requirement (GER) of the whole process.

All these hypothesis and critical issues are further explained in the next paragraphs regarding each process.

3. Life Cycle Inventory

The Inventory analysis provides a catalogue and quantification of the energy and material used as well as environmental releases associated with the processes included in the system boundaries. The chapter is organised in three main sections:

1. **Data collection**: it gives an overview about method, hypotheses and calculation procedures;
2. **Data quality requirements**: definition of primary and secondary input data
3. **Inventory results**: it gives a complete overview of results.

3.1 DATA COLLECTION

In this paragraph it is important to put in evidence that each energy and mass flow of the plants has been allocated according to the established Functional Unit, 1 kg of treated surface.

3.2 DATA QUALITY REQUIREMENTS

As previously specified, data and information used in LCA studies can be divided into two main categories, *primary data* and *secondary data*:

1. *Primary data* are data collected directly from the partner's contributions and, therefore, guarantee an high level of accuracy. Data regarding the process to obtain oleophobic layers on PET substrates are shown in figures 3.1-3.2. Data regarding the process to obtain oleophobic layers on PET+ cotton substrates are shown in figures 3.3-3.4. Data regarding the process to obtain hydrophobic layers on PET+ cotton substrates are shown in figures 3.5-3.6.
2. *Secondary data* are data obtained from databases, other previously carried out analysis or published reports. As far as the production of fuels, raw materials and transports in terms of energy, resources consumption and emissions to the environment are concerned, data come from the Boustead Model_V and refer to Europe energy mix.

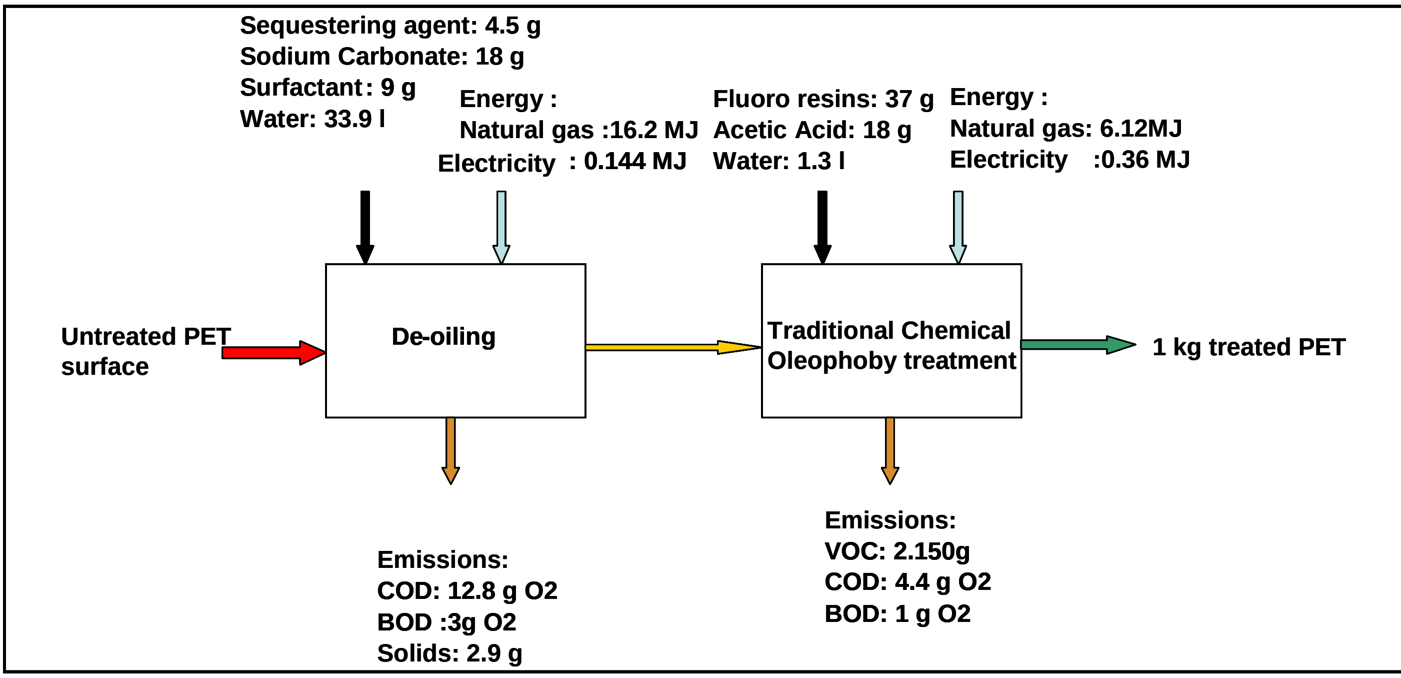

Fig 3.1. Traditional oleophobic process on PET simplified scheme

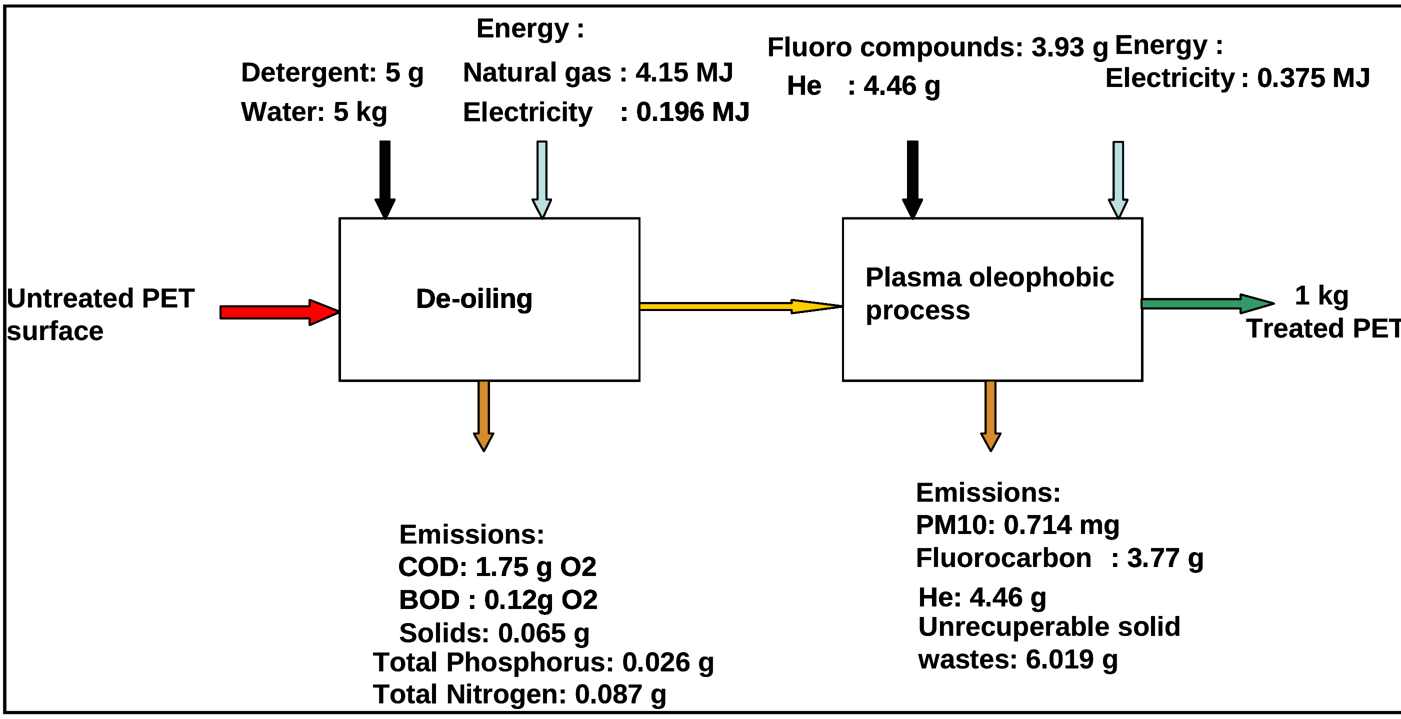

Fig 3.2. Plasma oleophobic process on PET simplified scheme

4. Inventory Results

The results of the LCA, as usual, are split into the two following categories:

1. **Energy results**: energy consumption for each functional unit (tables 4.1-2, 4.7-8,4.13-14);
2. **Environmental results**: natural resources consumption, air emissions, water emissions and solid wastes for each functional unit (tables 4.3-6, 4.9-12,4.15-18)

4.1 General Hypothesis

LCA Analysis has been carried out taking into account the following general hypothesis:

- Computation software Boustead V (last updating 2004)
- Energy consumption values regarding electricity have been considered taking into account the Europe energy mix
- Natural gas consumptions have been considered taking into account the general Italy mix
- All the results are referred to the established functional unit (1 F.U)
- This analysis contains the results coming from the data regarding the inputs and outputs of the process system and does not consider the contributions coming from the production of the substrates or the production of the machinery employed for each technology.

Specific hypothesis concerning each single case study are explained accordingly.

4.2 Case study 1 results- Oleophoby on PET substrates

In addition to the general hypothesis previously described in chapter 4.1, the following assumptions have been made for the traditional process:

- Energy contribution coming from the use of a fluoro-resin during the activation traditional process has been neglected. This value has been added to the total GER applying 19 MJ/ kg ([8]) concerning to the approximate value found in literature for the production of 1 kg of fluoro compounds. In this case, considering the total amount of substance used in this process, the energy contribution is equitable to 0.703 MJ/ kg of treated PET , value that has been added to the total GER.

Results are reported in table 4.1.

Fuel type [MJ/ f.u.]	Production energy	Process enegy	Transport energy	Feedstock energy	Total energy
Electricity	*1*	*1*	*0*	*0*	*2*
Fuel	*0*	*0*	*0*	*0*	*0*
Other	*1*	*22*	*0*	*0*	*23*
TOTAL	***2***	***23***	***0***	***0***	***25+0.703***

Table 4.1. Energy requirements (GER) for traditional oleophobic process on PET (values in MJ/f.u.)

In addition to the general hypothesis previously described, the following assumptions have been made for the innovative plasma process:

- Helium gas has been treated as Oxygen. In fact, the energy contribution of Helium gas production used in the process has been calculated considering the equivalent Oxygen production, since most of the industrial processes for Helium and Oxygen production are based on the same fraction distillation technology and energy consumption is analogous.
- This hypothesis does not apply (and therefore does not influence) the environment impact assessment as Helium is an inert gas.
- HDFDA and HDFD compounds (both used as fluoro-resin gas as raw material) have been treated as a generic PFC gas. The energy contribution value has been calculated and added to the total GER applying 19 MJ/ kg ([8]) concerning to the approximate value found in literature for the production of 1 kg of fluoro-compounds. In this case, considering the total amount of substance used in this process, equal to 0.00393 kg, the energy contribution is equitable to 0.077 MJ/ kg of treated PET , value that has been added to the total GER.
- Due to the lack of specific data concerning the composition of the exhaust gas, it has been necessary to calculate the emission quantity 3.77 g/ kg of finished PET and consider it as a generic PFC compound. This generic PFC is considered by the Boustead model as a gas that does not contribute to the GWP. Such a strong hypothesis will be largely discussed further on. The value of the emission (3.77 g/F.U.) has been calculated taking into account the thickness of the substance deposited on the surface (10 nm) and the average specific weight of a generic PFC gas (1.63 kg/l)
- PM10 emission values have been considered taking into account the worst case, so it is considering the maximum value permitted by the EEC directive 1999/30/EEC ([10]) equal to a 40 $\mu g/m^3$

Results are reported in table 4.2.

Fuel type [MJ/ f.u.]	Production energy	Process enegy	Transport energy	Feedstock energy	Total energy
Electricity	*1*	*1*	*0*	*0*	*2*
Fuel	*0*	*0*	*0*	*0*	*0*
Other	*0*	*4*	*0*	*0*	*4*
TOTAL	***2***	***5***	***0***	***0***	***7+0.077***

Table 4.2 Energy requirements (GER) for plasma oleophobic process on PET (values in MJ/f.u.)

Data regarding the raw material consumptions and the emissions are reported in the tables 4.3-4.5.

Raw material (mg/F.U)	Oleophoby traditional PET	Oleophoby Plasma PET
Bauxite	0	50
Sodium chloride (NaCl)	27900	1083
Fe	24	8
Pb	0	0
Limestone (CaCO3)	19029	15
Ni	0	0
Rutile	0	0
S (elemental)	0	749
Dolomite	0	0
Cr	0	0
O2	0	4600
N2	2	225
Air	2	12590
Olivine	0	0
Iron/steel scrap	0	0
TOTAL	**47000**	**19322**
Water (total) (l)	35	5

Table 4.3. Raw material consumption for oleophobic processes on PET (data in mg/F.U)

Substances	Oleophoby traditional PET	Oleophoby Plasma PET
dust (PM10)	1060	218
CO	1785	421
CO2	1388492	342863
SOX as SO2	758	689
NOX as NO2	2906	0
HCl	9	0
HF	0	779
hydrocarbons	1245	10
organics	0	0
metals	0	317
CH4	12081	0
perfluorocarbons (PFC) not specified else	0	3770

Table 4.4. Air emissions for Oleophobic processes on PET(data in mg/F.U)

Substances	Oleophoby traditional PET	Oleophoby Plasma PET
COD	17200	1751
BOD	4000	126
Na+	27	29
acid as H+	0	0
NH4+	0	0
Cl-	28	40
suspended solids	4694	77
hydrocarbons	0	0
phenols	0	0
dissolved solids	19	15

Table 4.5. Water emissions for Oleophobic processes on PET(data in mg/F.U)

Substances	Oleophoby traditional PET	Oleophoby Plasma PET
Unspecified refuse	100	6096
Mineral waste	1716	45
Slags & ash	1485	1711

Table 4.6. Refuses for Oleophobic processes on PET(data in mg/F.U)

5.Impact Assessment

According to ISO 14042, the general framework of the Assessment phase is composed of several mandatory elements that convert Inventory results into environmental indicators. For this analysis the following impact categories are considered (such characterization factors are also recognized by the system for Environmental Product Declarations – EPD):

- Greenhouse effect (global warming);
- Acidification;
- Photochemical ozone formation (Photo-smog);
- Eutrophication;

The values concerning each of the above factors for each process have been summarise in the table below (table 5.1):

TREATMENT	GWP ($kg\ CO_2$)	AP ($g\ eq\ SO_2$)	POPC ($g\ C_2H_4$)	EU ($g\ PO_4^{3-}$)
Plasma Oleophobic PET	***0.4***	***1.22***	***0.19***	***0.26***
Traditional Oleophobic PET	***1.67***	***2.36***	***2.81***	***0.76***

Table 5.1. Impact assessment parameters

6. Final Considerations

As a general rule, plasma innovative processes have a lower environmental impact compared to traditional ones to obtain the same surface functionality. This is proven by the obtained values of the overall set of indicators prescribed by the ISO1404X norms and summarised in the tables previously presented. It has to be noticed that in some cases resulting data may differ of one order of magnitude as for the total energy consumption represented by the GER results: plasma processes GER value is definitely lower than its corresponding value obtained for traditional treatments.

The energy consumption relative to plasma treatment is mainly due to the electricity requirements during the finishing process (direct energy), while a small fraction of the total energy consumption is due to the during the cleaning process (de-sizing or de-oiling) requirements. These pre-processes energy source is.

The energy consumption has a direct influence to the GWP value. This parameter is calculated taking into account the amount of CO_2 equivalent emitted in air during the whole process, including the production processes to obtain raw materials and energy production. The energy sources, that is to say, the origin of each type of energy for its production, transport and management determines the value of the Global Worming Potential (GWP).

As it was discussed in the previous report (WP3-D 3.2), the energy mix for electricity production has a major influence on the GWP value, as the emissions of CO_2 vary enormously from one mix to another.

In this study it has been taking into account the Europe energy mix, where more of the 61 % of the total electricity production is obtained from Fossil Fuels or gas with an important emission of CO_2 that contributes to the greenhouse effect and then to the GWP. Using renewable energy sources in the plasma process would certainly mean a visible further decreasing in the GWP parameter even if using the same quantity of direct energy. In that case, plasma process technology would be even more cleaner although already being the most environmental friendly technology nowadays available for the surface functionalisation processes taken into account.

As stated before, traditional process energy requirements is based not only in electricity consumption, but also in using a significant amount of natural gas employed to heat the water for the wet processes. This consumption determines the considerable increase of the assessed GWP value due to the CO_2 emissions.

Values regarding specific consumptions of raw materials and emissions of processes by-products have been also included for each study case.

As relevant data, it can be noticed that traditional processes have a water consumption definitely higher than plasma process (for instance, for oleophoby functionalisation on PET substrates water requirements are seven time greater than for traditional processes than for plasma process, wet processes employing 35 litres per F.U). In addition to the water consumptions, it is important to observe the values relative to the chemical and biological oxygen demand (COD and BOD), always higher for traditional processes and responsible for the Eutrophication of local water systems.

Moreover, the highest need of water employed in traditional processes cause that a lager amount of water needs to be treated before being emitted in the environment. Depuration plants capable to neutralise all the polluted water coming from the production process are compulsory, that is to say, manufacturers that still use traditional wet processes are forced to invest in these kind of installations by normative constraint that guarantee avoiding massive environmental local pollution; production plants equipped with these post-process treatments involve consumption of extra-process energy to clean all the wasted water. The energy consumption employed to run such depuration post process units, as well as the energy and materials employed to produce and install such post-process depuration systems have not been included in this study. Therefore this further source of environmental burden should be taken into account to set up a more comprehensive balance between environmental impact assessment of traditional and innovative solutions for surface functionalisation. The resulting consequences for the environment should be added to the results previously found. Such considerations put in evidence that the present analysis is quite conservative, although results show already a net unbalanced situation for the two classes of compared processes (traditional vs. innovative), favouring plasma solutions as having an overall lower environmental impact.

All the inspected issues are extremely important to be taken into account, above all if considering dry regions scenario where the availability of water is restricted, and where a suitable system to depurate the wasted water has not yet been established .

A further comment regarding water consumption should be added taking into account that all these case studies consider a wet cleaning process. Plasma technology is nowadays capable to substitute wet de-sizing or de-oiling process for innovative technologies where the water consumption is almost reduced to zero. Unfortunately, for this study data regarding plasma cleaning process were still not available but it represents a further step to be introduced as a future more refined analysis.

As far as air emissions are concerned, again the results show that values that are found for plasma process come from the production of electricity and not from the process itself, due to the fact that pollutant substances emitted during the process are negligible. Furthermore, pollutant emissions for plasma processes are in any case lower compared to traditional process, above all for CO, CO_2 and NO_x. Dramatically lower are PM10 emissions for plasma process.

REFERENCES

1. ANPA (2000), "*Banca dati italiana I-LCA*";
2. G.L. Baldo,Massimo Marino e Stefano Rossi (2005), "*Analisi del Ciclo di Vita LCA: material, prodotti, processi"*- Edizioni Ambiente 2005
3. ISO 14040 (1997), "*Environmental Management – Life Cycle Assessment – Principle and framework*";
4. I. Amato, L. Montanaro (2000), "*Scienza e tecnologia dei materiali ceramici*" Vol. III, Edizioni Libreria Cortino, Torino;
5. MSR 1999:2, "*Requirements for Environmental Product Declarations, EPD*", Swedish Environmental Management Council, 27/03/2000.
6. L. Paracchini (2003), " *Manuale di Trattamenti e Finiture*" – Tecniche Nuove
7. Christopher Ciantar, Mark Hadfield (2000) "*An Environmental Evaluation of Mechanical Systems Using Environmental Acceptable Refrigerants"*- Inernational Journal of LCA 5(4) 209-220
8. Kim, S., Overcash, M. (2003). "*Energy in chemical manufacturing processes: gate to gate information for life cycle assessment"* Journal of Chemical Technology & Biotechnology, July 2004
9. Kesley Norwood (2004) "C*hemical Energy Use in the Semiconductor Industry"* University of California at Berkeley
10. Directive 1999/30/CE Europe Council dated April 22 nd 1999 regarding the maximum values permitted and quality parameters for SO_2, NO_2 , NOx, *Official Journal n. L 163 del 29/06/1999 pag. 0041 – 0060* ***http://eur-ex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31999L0030:IT:HTML***