Life Cycle Analysis of Oxalic Acid industrial production plant

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Abstract

The Oxalic acid is an organic acid which main applications include cleaning (removing marks, stains, and rust), bleaching and setting dyes on fabrics (mordant or dye fixative). It can also be used in bees cultures as an insecticide, in chemical industry as intermediate product, or even in the semiconductor industry for electrochemical mechanical planarization of copper. The present article in collaboration with OXAQUIM S.A, the major oxalic acid productor in Europe, is the first life cycles assessment of an oxalic acid production plant with primary data at industrial scale. The calculations for a functional unit of 1 kg of oxalic acid have resulted in a Climate Change (kg CO_2eq) impact between 0.53 and 0.57 kg CO_2 eq., depending on the allocation method selected. The most important impact categories and the processes with the highest environmental impact have been also identified: electricity consumption is the process with the highest share of environmental impact in the system studied, it has a particular impact on the Climate Change indicator, freshwater ecotoxicity, use of fossil resources and water use. In addition, sugar presents the highest impact on the land use indicator. Finally, the system has been also evaluated for different scenarios of green electricity consumption.

1- Introduction

The present article works out the environmental impacts of the industrial production of oxalic acid. This process requires strong nitric acid, 98%, sugar, oxygen, strong sulfuric acid, 96%, hydrogen peroxide, ethylene-glycol, hydrochloric acid, and sodium hypochlorite to produce both oxalic acid (85wt%) and aqueous nitric acid, 60%, (15wt%). Both are intermediate products, which are sold to external companies to produce other chemical compounds. In the case of oxalic acid, it is primarily used to produce cleaning and bleaching products for rust removal or to setting dyes on fabrics (as a mordant or dye fixative). It has also some niche applications in bees cultures as a miticide against the parasitic varroa mite (Fu, 2008), and in the semiconductor industry for electrochemical mechanical planarization of copper (Lowalekar, 2006). On the other hand, nitric acid is typically used in the production of ammonium nitrate for fertilizers, making plastics, and in the manufacture of dyes (The Chemical Company, 2022).

The European Union must look to develop its own greener processes giving at the same time independence from eastern countries, where most of the oxalic acid is produced globally. The major European productor of oxalic acid, OXAQUIM S.A, is providing primary data from its production plant in Alcañiz (Spain) for the calculation of this life cycle assessment. Therefore, the functional unit selected for the study is 1 kg of oxalic acid produced in their facilities. The boundaries of the study are from cradle to gate, see figure 1 for a brief scheme of the system under study. Finally, the system has been also evaluated for different scenarios of green electricity consumption produced in Europe.

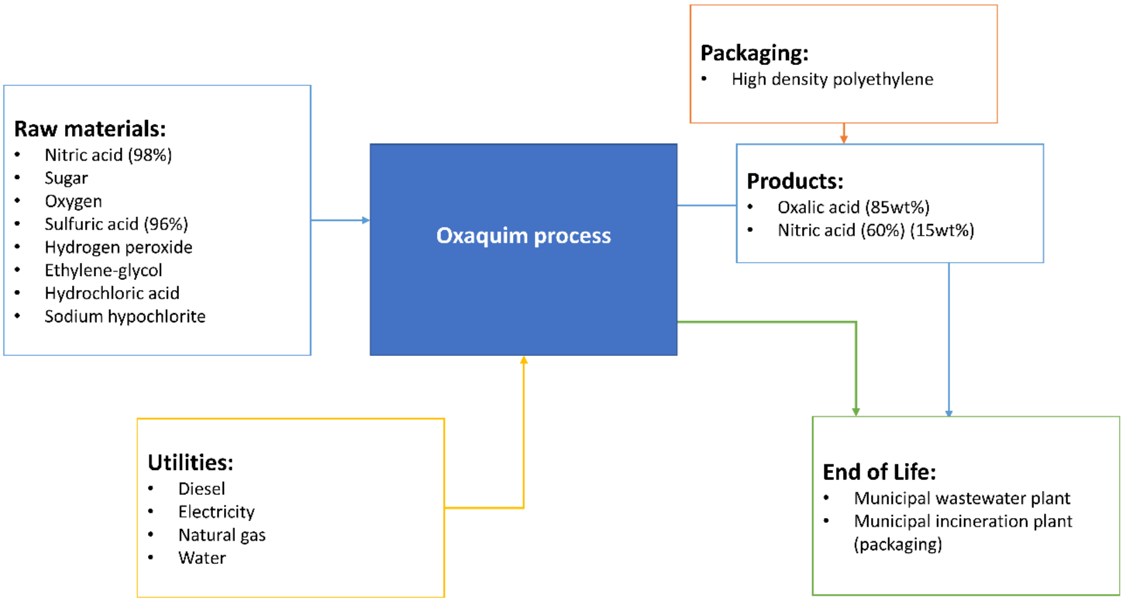

Figure 1. Scheme of the system under study

2- Methodology

2.1- Data quality and uncertainty

The data provided by the oxalic acid productor has been validated according to Pedigree matrix standards (reliability, completeness, temporal, geographic and further technical correlation) (Ciroth, 2009; Weidema and Wesnæs, 1996). The process has been modelled and simulated using the specific LCA software, GaBi (version 10.6.1.35) (Sphera, n.d.). The specific processes from GaBi which have been used for each material and transport stage are available in tables S1 and S2 from the supplementary material.

To avoid uncertainty: (i) those additives or raw materials accounting for less than 0.05wt% in the mass balance which were not found in GaBi databases have been excluded of the study; (ii) environmental impact of infrastructures and other capital goods have been also excluded of the study, they have been considered negligible when being spread over their long lifespan; (iii) packaging has been assumed to be composed 100% of polypropylene and to share 0.001 kg per each kg of the final product (this is a realistic assumption based on the information provided by the oxalic acid productors).

2.2- Life cycle assessment methods

The impact categories which will be calculated have been selected according to the European Commission recommendations for the Product Environmental Footprint (PEF) methodology (European Commission, 2013). The total environmental impact of the process is divided between the two products. This is performed with system expansion (substitution), economic allocation and mass allocation methodologies. Their results are evaluated and compared each other. The substitution methodology works out the environmental impact of one of the by-products. It isolates the desired product by subtracting the environmental impact of an alternative process to produce the undesired product. The procedure is shown in Figure 2.

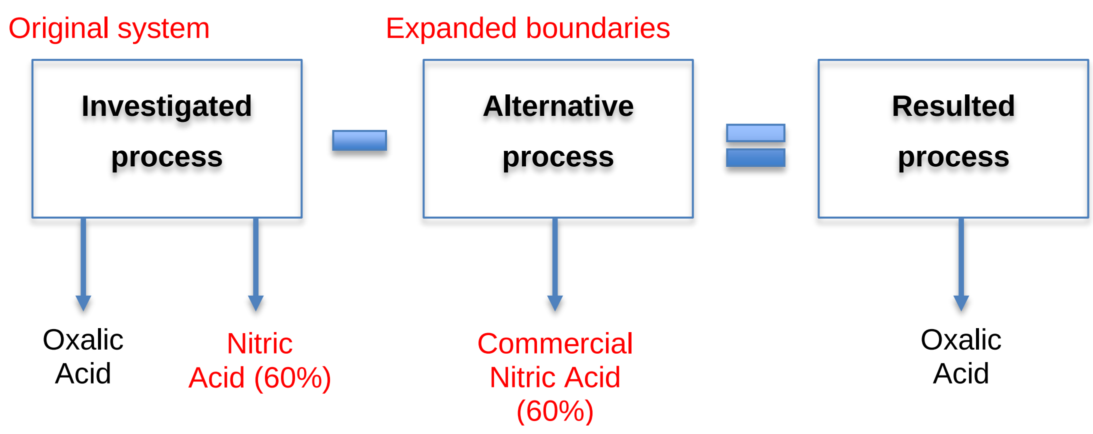

Figure 2. Allocation by substitution scheme

*The commercial nitric acid has been taken from the GaBi databases [4] from the process: DE: Nitric acid (60%)

The economic allocation is performed according to the price of coproducts. These may fluctuate affecting the reliability of the results. So on, to reduce uncertainty, it is advisable to find the economic prices in the same year, or an average of the price in previous years. The procedure is summarized in next equation (E1):

$$\%\mathrm{EI\ of\ product\ A} = \frac{\mathrm{Price\ of\ product\ A}\left(\frac{€}{\mathrm{kg}}\right)\times \mathrm{Quantity\ of\ product\ A\ (kg)}}{\sum \mathrm{Price\ of\ product\ i}\left(\frac{€}{\mathrm{kg}}\right)\times \mathrm{Quantity\ of\ product\ i\ (kg)}} \qquad \text{(E1)}$$

*EI: Environmental Impact

Price of nitric acid (60%) has been taken from GaBi databases [4]. Price from oxalic acid has been taken from online pharmaceutical databases (Pharmacompass, n.d.).

The mass allocation is the partitioning of the input and output flows of a process according to the physical magnitude of mass. In the case of two by-products, the total environmental impacts of the process will be divided in the same proportion as the kg which are produced of each.

3- Results

3.1- Life cycle inventory

Table 1 and table 2 presents the inventory data of the raw material and utilities (electricity, natural gas, diesel, and water) required to produce 1 kg of oxalic acid and 0.179 kg of nitric acid (60%) as well as the transportation distance in the case of the production plant from Alcañiz (Spain) which is being studied.

Table 1. Raw material inventory data

Raw material	Amount (kg)	Distance (km)
Nitric acid (98%)	0.160	2,650
Sugar	0.591	1,200
Oxygen	0.510	134
Sulfuric acid (96%)	0.048	135
Hydrogen peroxide	0.017	200
Ethylene-glycol	$1.37\cdot10^{-4}$	250
Hydrochloric acid	$4.79\cdot10^{-4}$	250
Sodium hypochloride	$3.42\cdot10^{-4}$	250
Packaging	0.059	250

Table 2. Utilities inventory data

Utilities	Amount
Electricity (kwh)	0.758
Natural gas (m^3)	0.024
Diesel (m^3)	$5.34\cdot10^{-7}$
Water (m^3)	0.006

3.2- Logistic system

Transport is carried out by road with diesel-powered trucks. In addition, reverse logistics is considered (the return journey of the lorries is made with cargo from the same facilities where oxalic acid is produced or from one of neighboring companies).

3.3- Waste management

The End of life of the system includes the wastewater treatment in a municipal wastewater plant, and the waste packaging treatment in a municipal incineration plant. The power and thermal energy produced in the incineration plant is accounted and compensated as electricity and steam credits.

3.4- Life cycle impact assessment (LCIA)

Table 3 presents a summary of the main environmental impacts of the process. In addition, according to the allocation rules specified in the Methodology section, the environmental impacts should be divided between oxalic acid and nitric acid (60%) based on the following percentages: (i) allocation by substitution, oxalic acid (87%) and nitric acid (13%); (ii) economic allocation, oxalic acid (91%) and nitric acid (9%); (iii) mass allocation, oxalic acid (85%) and nitric acid (15%).

Table 3. LCIA summary of results

Impact category	Total
Acidification [Mole of H+ eq.]	$1.60\cdot10^{-3}$
Climate Change [kg CO2 eq.]	0.62
Ecotoxicity of freshwater [CTUe]	4.30
Eutrophication freshwater [kg P eq.]	$1.40\cdot10^{-5}$
Eutrophication marine [kg N eq.]	$3.60\cdot10^{-4}$
Eutrophication terrestrial [Mole of N eq.]	$4.30\cdot10^{-3}$
Human toxicity cancer [CTUh]	$1.60\cdot10^{-10}$
Human toxicity non-cancer [CTUh]	$8.20\cdot10^{-9}$
Ionising radiation human health [kBq U235 eq.]	$9.90\cdot10^{-2}$
Land Use [Pt]	9.80
Ozone depletion [kg CFC-11 eq.]	$3.50\cdot10^{-12}$
Particulate matter [Disease incidences]	$1.30\cdot10^{-8}$
Photochemical ozone formation [kg NMVOC eq.]	$1.00\cdot10^{-3}$
Resource use fossils [MJ]	11.00
Resource use minerals and metals [kg Sb eq.]	$1.20\cdot10^{-7}$
Water use [m^3 world equiv.]	0.36

4- Discussion

4.1- Identification of hotspots

According to the weighing tool of GaBi, figure 2 identifies the most relevant environmental impacts (only those with >1% weight is presented in the table), the processes accounting for the major share of each environmental impact are also indicated below.

Climate Change is primarily affected by the electricity consumption (43.75%), strong nitric acid production (27.72%), and sugar beets production (11.20%); Ecotoxicity of freshwater is influenced by the electricity consumption (38.00%), sugar beets production (14.57%), and water consumption (14.43%), and strong nitric acid production (11.24%); the Land use indicator is affected by sugar beets production (80.80%) and electricity consumption (11.75%); the use of fossil resources is mainly affected by the electricity consumption (46.50%), and strong nitric acid production (18.94%); Water use is mainly influenced by electricity consumption (93.56%).

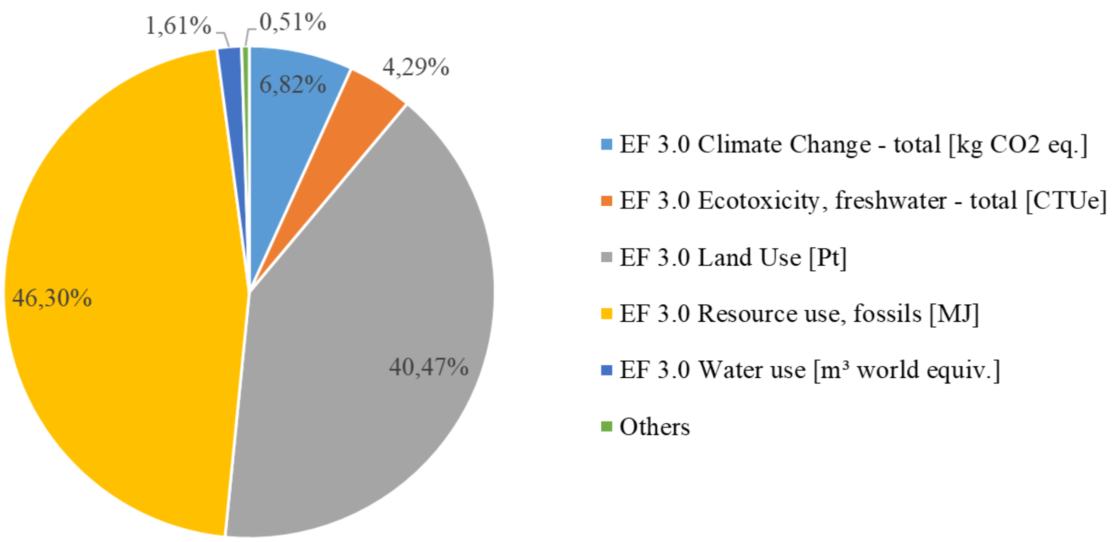

Figure 3. Most relevant environmental impacts

The two processes with more weight in the total environmental impact are the electricity consumption and the sugar beets production. The electricity might be replaced by greener alternatives such as renewable energy (i.e., solar energy, wind power, or hydropower) or nuclear (less advisable). In the Sensitivity check section this is evaluated with 3 different scenarios where European green electricity mix (according to GaBi Professional databases) (Sphera, n.d.) is included to the consumed electricity. On the other hand, sugar beets production presents an important share on the environmental impacts of land use indicator. Even though, the alternative of sugar cane production does not improve the results. According to GaBi Professional Databases, while the carbon footprint of 1 kg of sugar beet production in Poland is about 0.038 kg of CO_2e, the carbon footprint of 1 kg of sugar cane production ranges from 0.104 kg of CO_2e (when it is produced in Thailand), to 0.119 kg of CO_2e (when it is produced in Brazil) (Sphera, n.d.). In addition, this would also increase the impact associated with its transport.

4.2- Sensitivity check

In addition to the actual case presented in the Results section, we studied three alternative scenarios modifying the electricity mix: (1) The scenario 1 includes a share of 20% of green electricity; (2) The scenario 2 includes a share of 100% of green electricity; (3) The scenario 3 includes a share of 100% of green electricity plus the sale of $5 \cdot 10^6$ kwh of green electricity.

Figure 4 presents the projection of the real scenario plus the three alternative electricity scenarios.

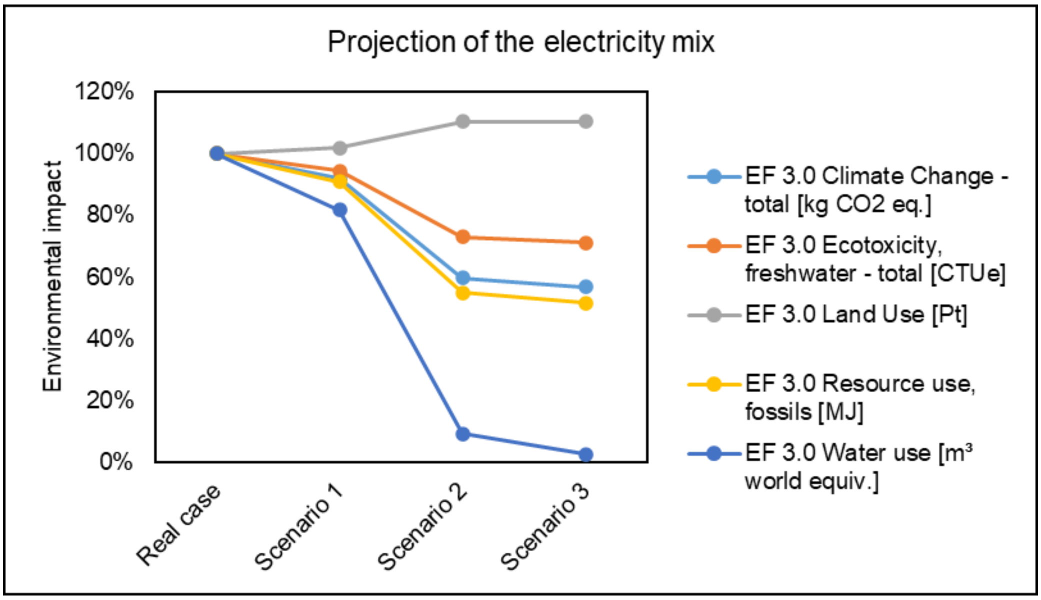

Figure 4. Projection of the electricity mix

5- Conclusions

The most important impact categories and the processes with the greatest weight in their environmental impact have been identified. Electricity and sugar are the processes with highest environmental impact share in the studied system. They impact specially on climate change (electricity), ecotoxicity of freshwater (electricity), land use (sugar), fossil resources use (electricity) and water use (electricity).

Regarding that reducing the environmental impact of sugar (which is a raw material required on the process which depends on third parties) are out of the control of the oxalic acid producer, the most recommendable practice would be to work on the electricity used: Electricity use projection implementing green electricity (self-produced or with guarantee of origin) is provided in the Sensitivity check section. Moreover, we recommend performing further work differentiating the type of green energy and the place where it is located (both for the country as for the type of soil).

6- References

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