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LCA of Starch Aerogels for Biomedical Applications

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Aerogels are a special class of nanoporous materials with increasing interest in biomedical and pharmaceutical applications due to their open pore structure and high surface area. Among them, polysaccharide aerogels are biodegradable and biocompatible and, therefore, can be used as carriers for drug delivery systems. In this work, an analysis of their production from the environmental point of view was made, following a Life Cycle Assessment (LCA) approach with the aim of reducing the total emissions. Maize starch aerogels were produced on a pilot scale using a three-step process: first, the gel is prepared using an aqueous solution, then water is replaced by ethanol forming an alcogel and finally, carbon dioxide at supercritical conditions is used as non-solvent to dry the gel and obtain the aerogel. The materials and energy consumptions were determined and the emissions to air, soil and water due the aerogel production were evaluated; all data were normalized to the functional unit (1 g of final aerogel). The environmental analysis was conducted using SimaPro 8.0.4 software and the data for the life cycle inventory were experimentally measured or recovered from the Ecoinvent database.

1. Introduction

Aerogels are promising materials that can be used as support for active substances, such as pharmaceuticals or nutraceuticals, due to their high porosities (85-99 %) and large surface areas (up to 3,000 m^2/g). Silica aerogels have been frequently used as matrices for substances such as metals (Caputo et al., 2010) or pharmaceutical products (Caputo et al., 2012). Unfortunately, they are biocompatible but not biodegradable (Smirnova et al., 2003). For this reason, bio-based materials have been used to obtain aerogels as key ingredients in the fields in which biodegradability is required (Mehling et al., 2009), as, for example, in the engineering of modified drug delivery systems (Jagur-Grodzinski, 2010). Among them, an increasing attention has been regarded to the use of natural polysaccharides, such as, for example, starch, alginate or chitosan, because they are stable, available, renewable and low toxic (García-González et al., 2011). Starch is a low-cost polysaccharide that can be used in drug delivery systems, from which it is possible to produce aerogels (García- González and Smirnova, 2013). In a previous work (De Marco et al., 2015), starch aerogel production from different sources (maize, potato and wheat) and at different operating conditions was optimized.
Although, in the last years, the attention addressed to the environment and to carbon dioxide emissions' reduction is increasing, the environmental aspects of aerogel production have been very rarely investigated. Indeed, several papers, using a life cycle assessment (LCA) approach have been published in energy (Cherubini et al., 2009), food (De Marco et al., 2016), fuels (von Blottnitz and Curran, 2007) and wastewater (García Alarcón et al., 2011) fields. Among them, LCA studies on food products are very difficult to be carried out because of the lack of databases (Iannone et al., 2014); for similar reasons, data pertaining innovative processes, like the one for aerogel production, are difficult to source. In particular, a streamlined LCA study was performed by Dowson et al., 2012 for silica aerogel produced using supercritical drying. The authors quantified the production energy and CO_2 burden and compared the impact of the production of 1 m^3 volume aerogel against the material's estimated operational cost savings over 15 years. Therefore, similar studies on polysaccharides based aerogels have not been performed. The aim of this paper is to perform a LCA analysis of starch aerogel production through a supercritical drying based process. The study has been validated using "primary data". Starch aerogels were produced on a laboratory scale using a three-step process: first, the gel is prepared using an aqueous solution, then water is replaced by ethanol forming an alcogel and finally, carbon dioxide at supercritical conditions is used as non-solvent to dry the gel and obtain the aerogel.

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2. LCA methodology

LCA is a multi-stage analysis in which a broad set of data related to the life-cycle of a product or a process are properly collected and organized in order to compare different products, different life-cycle of the same product or to individuate the most critical phase of a life-cycle from the environmental perspective. In the following sub-sections, the main steps that constitute the LCA methodology are presented.

2.1 Goal definition and scope

Goal definition is one of the most important phases of the LCA methodology, because the choices made at this stage influence the entire study. The purpose of this study is to evaluate the environmental impacts of maize starch aerogel production on bench scale. Figure 1 represents the scheme of the aerogel production chain according to the IDEF (Icam DEF for Function Modelling, where “ICAM” is an acronym for Integrated Computer Aided Manufacturing) methodology. In the top part of the figure, the complete aerogel production is represented, whereas, in the bottom part, the detailed scheme of the supercritical drying operations is shown.

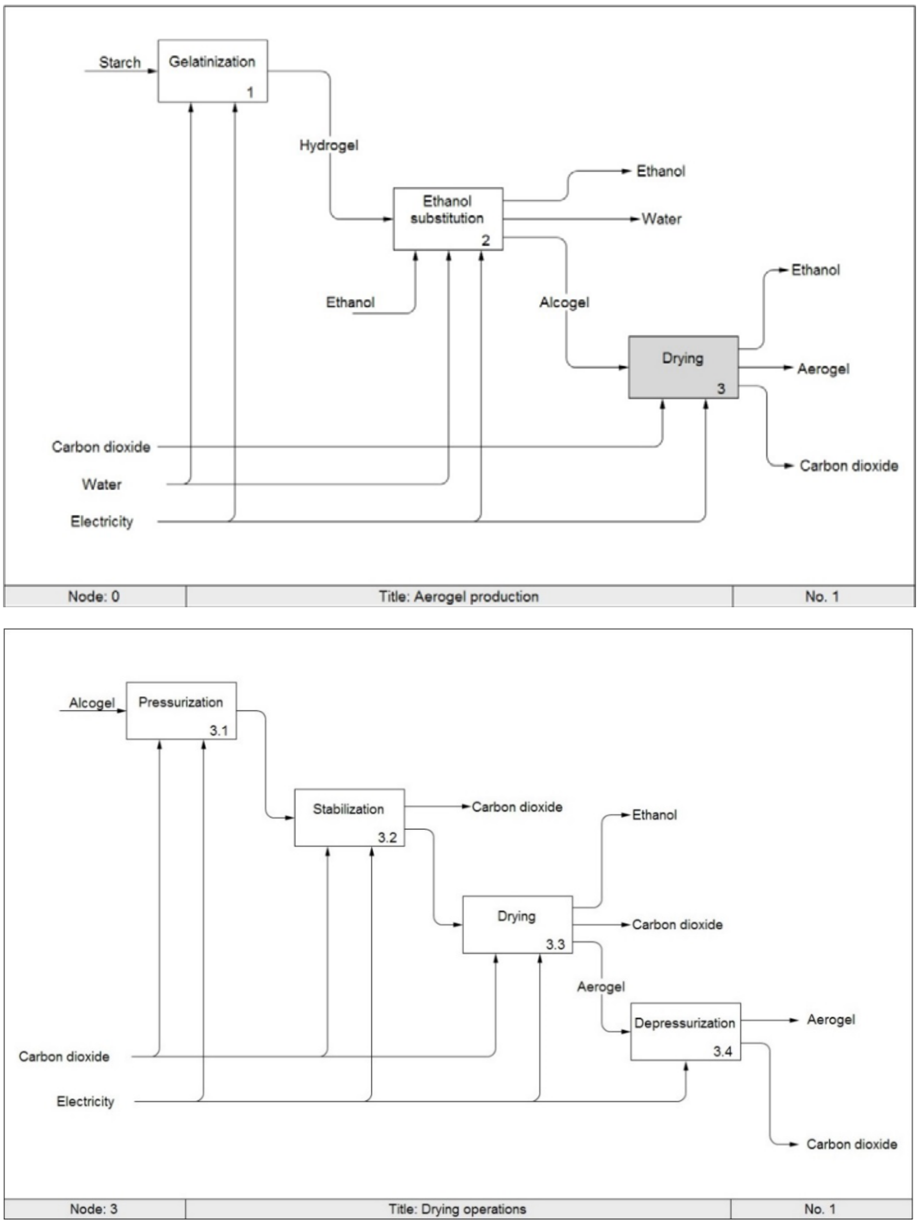

Figure 1: IDEF diagrams; top: aerogel production; bottom: details of drying operations.

2.2 Functional unit and system boundary

The definition of the functional unit (FU) is based on the quantity or mass of the product under analysis, and it is a reference to which all the inputs and outputs have to be related. The chosen functional unit is 1 g of final aerogel. The system boundaries of the analysis are schematized in the top part of Figure 1 and are set from starch powder transportation to aerogel attainment. The proposal study refers to a “from gate to gate” process, regarding the hydrogel formation, the alcogel formation and the supercritical drying (SCD) to obtain the aerogel.

2.3 Data collection

In Table 1, the main activities of the observed process are reported. The life cycle inventory (LCI) is one of the most effort-consuming step and consists on the activities related to the search, the collection, and interpretation of the data necessary for the environmental assessment of the observed system.
Aerogel processing starts with the gelation of starch, which involves melting the starch in an aqueous medium to induce changes in the structure and rearrange the structure during a cooling step. Accordingly, the process starts with the *gelatinization step*, consisting in the preparation of the maize starch solution with concentration equal to 15 % wt in distilled water; using a magnetic stirrer, the solution was stirred at 75 °C for 24 h when it became homogeneous. Then, it was poured into cylindrical moulds with an internal diameter of 2 cm and a height of 1 cm. Then, the samples were placed in the fridge for retrogradation at 4 °C for three days.
The subsequent step is the attainment of the *alcogel*, replacing the water filling the pores of the gel structure by ethanol at room temperature. The water in the hydrogel was gradually replaced by ethanol by batch equilibration with a succession of ethanol baths (Glenn and Stern, 1999). In particular, the dehydration occurs in subsequent ethanol-water baths at increasing ethanol concentration (40 %, 70 %, 90 % and 100 % (v/v)). Each ethanol bath contained two volumes of liquid for each volume of gel and the equilibration time for each bath was 24 h.
The alcogels were then dried in a homemade apparatus that mainly consists of a 316 stainless steel cylindrical high-pressure vessel (i.V. = 80 mL), equipped with a high-pressure pump (Milton Roy, mod. Milroyal B, France) used to deliver the carbon dioxide. Pressure in the vessel was measured by a manometer (OMET, mod. 0.25, Italy) and regulated by a micrometering valve (Hoke, mod. 1335G4Y, SC, USA). Temperature was regulated by temperature controllers (Watlow, mod. 305, Italy). At the exit of the vessel, a rotameter (ASA, mod. D6, Italy) was used to measure the CO_2 flow rate. To obtain the aerogels, the vessel where the samples were placed was closed and filled from the top with $scCO_2$. When the desired pressure and temperature were reached (200 bar and 45 °C), drying was performed, fixing the $scCO_2$ flow rate at 1 kg/h, corresponding to a residence time inside the vessel of about 4 min; the drying lasted 5 h. A slow depressurization (20 min) was used to bring back the system at atmospheric pressure and recover the aerogels from the vessel.
The LCA study was conducted using the LCA software SimaPro 8.0.4 in accordance with the reference standard for LCA (i.e., ISO 14040-14044). The Ecoinvent 3.1 database was employed as the principal source of background data, but the majority of the processes and materials information required for the analysis are specific of the observed system and collected using “primary data”. For each unit process within the system boundary, input data, such as energy, water, natural sources and output data in terms of emission to air, water and soil were collected. Table 2 lists the main energy and direct material input to the product systems under the study of 1 g produced aerogel.

3. Results and discussion

The aim of this study is the interpretation of the data collected through the LCI phase and to evaluate and compare the impacts related to starch aerogel production on four endpoint categories: human health, ecosystem quality, climate change and resources. The IMPACT 2002+ life cycle impact assessment methodology link those damage categories to 15 midpoint categories.

Table 1: Process details and assumptions

Process	Characteristics and details
Energy supply to facility	Italian energy mix low voltage
Gelation step	T=75 °C; t=24 h; energy and water supply
Retrogradation step	T=4 °C; t=72 h; energy supply for cooling
Alcogel formation	T=25 °C; t=96 h; ethanol and water supply; energy supply
Pressurization	t=0.08 h; carbon dioxide supply; energy supply
Operating conditions’ stabilization	T=45 °C; P=200 bar; t=0.25 h; carbon dioxide supply; energy supply
Drying	T=45 °C; P=200 bar; t=5 h; carbon dioxide supply; energy supply
Depressurization	T=25 °C; P=1 bar; t=0.33 h

Table 2: Life cycle inventory of the main inputs and outputs for starch aerogel production.

Industrial Phase	Input/Output	Unit	
Gelation step	Starch	g	6.55E-01
	Water	g	3.71E+00
	Electricity	kJ	9.90E+03
Retrogradation step	Hydrogel	g	4.36E+00
	Electricity for cooling	kJ	1.18E+03
Alcogel 40%	Hydrogel	g	4.36E+00
	Ethanol	g	6.89E+00
	Water	g	1.31E+01
	Output		
	Ethanol	g	6.14E+00
	Water	g	1.54E+01
Alcogel 70%	Alcogel 40%	g	2.84E+00
	Ethanol	g	1.21E+01
	Water	g	6.55E+00
	Output		
	Ethanol	g	1.12E+01
	Water	g	8.28E+00
Alcogel 90%	Alcogel 70%	g	1.94E+00
	Ethanol	g	1.55E+01
	Water	g	2.18E+00
	Output		
	Ethanol	g	1.46E+01
	Water	g	3.33E+00
Alcogel 100%	Alcogel 90%	g	1.73E+00
	Ethanol	g	1.72E+01
	Output		
	Ethanol	g	1.64E+01
	Water	g	1.07E+00
Drying	Alcogel 100%	g	1.52E+00
	Carbon dioxide	g	4.85E+03
	Electricity	kJ	4.78E+03
	Electricity for cooling	kJ	6.98E+03
	Output		
	Aerogel	g	1.00E+00
	Carbon dioxide	g	4.85E+03
	Ethanol	g	5.18E-01

In particular, the human health is affected by carcinogens (C), non-carcinogens (NC), respiratory inorganics (RI), ionizing radiations (IR), ozone layer depletion (OLD) and respiratory organics (RO); the ecosystem quality is affected by aquatic ecotoxicity (AET), terrestrial ecotoxicity (TET), terrestrial acidification/nitrification (TAN), land occupation (LO), aquatic acidification (AA) and aquatic eutrophication (AE); the climate change is quantified using the global warming potential (GWP); the resources are affected by non-renewable energy consumption (NRE) and mineral extraction (ME).

In Table 3, the IMPACT 2002+ midpoint results for aerogel production are reported, to quantify how much the process affects the different categories. Considering that three main steps are characteristic of the aerogel production (gelatinization with the formation of hydrogel, alcogel formation and supercritical drying to obtain the aerogel), in Figure 2, the relative contributions of these main phases on each impact category are reported. It is evident that the higher contribution, for all the categories unless respiratory organics, is due to the third step, in which alcogel is dried to form an aerogel. This evidence can be explained considering that the majority of energy consumption is due to the drying step, where supercritical carbon dioxide is used to dry the structures. On the contrary, respiratory organics are strongly affected by the second step, where an organic compound (ethanol) is used to substitute water in the hydrogel, forming the alcogel. In order to make a comparison among different impact categories, the results were normalized. The IMPACT 2002+ method employs the emission values of Western Europe as reference values (Humbert et al., 2012); indeed, the normalization factors represent the total impact of the specific category divided by the total European population. Figure 3 shows the values obtained for each category through the LCA analysis after the normalization process.

Table 3: IMPACT 2002+ midpoint results for starch aerogel production. Data are referred to the FU.

Midpoint category	Unit	
C	kg C_2H_3Cl eq	1.87E-01
NC	kg C_2H_3Cl eq	8.21E-02
RI	kg PM2.5 eq	5.55E-03
IR	Bq C-14 eq	1.15E+02
OLD	kg CFC-11 eq	6.32E-07
RO	kg C_2H_4 eq	2.08E-02
AET	kg TEG water	4.04E+02
TET	kg TEG soil	1.03E+02
TAN	kg SO_2 eq	9.30E-02
LO	m^2 org.arable	7.73E-02
AA	kg SO_2 eq	3.28E-02
AE	kg PO_4 P-lim	1.33E-03
GWP	kg CO_2 eq	6.97E+00
NRE	MJ primary	1.09E+02
ME	MJ surplus	4.22E-01

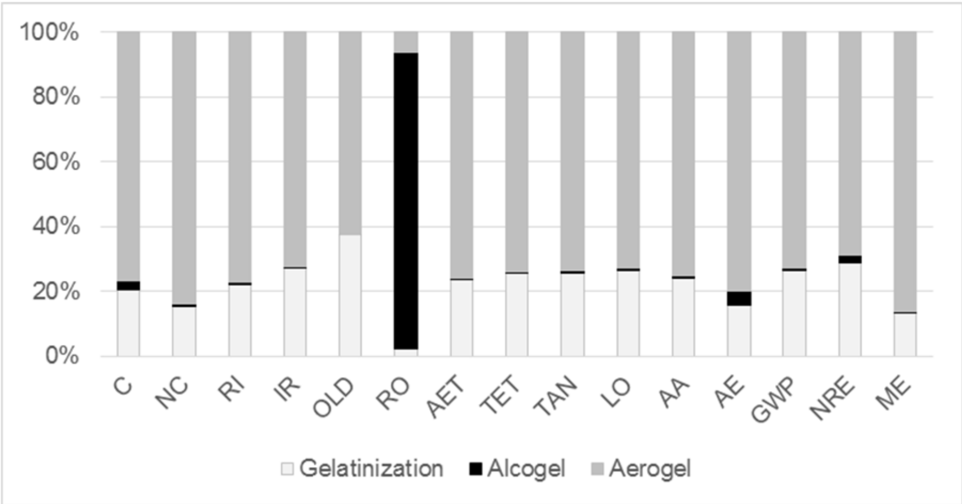

Figure 2: Relative contributions of the main stages in the starch aerogel production on the IMPACT 2002+ midpoint categories.

It is evident that the midpoint category mainly affected by aerogel production is the one of carcinogens, followed by respiratory organics and mineral extraction. Therefore, to lower environmental emissions caused by the third step (aerogel production), it is important to act on energy consumptions related to the drying steps, using, for example, lower drying times or less quantities of carbon dioxide. On the other hand, to lower emissions affecting respiratory organics caused by ethanol usage, it is favorable to use lower quantities of organic solvent, for example, using two subsequent ethanol-water baths, instead of four.

4. Conclusions

In this work, a LCA analysis on starch aerogel production was made. The study was conducted considering a three step process: 1) gelatinization with hydrogel formation; 2) ethanol replacement with alcogel formation; 3) supercritical drying with aerogel formation. It was observed that the mainly affected categories were the one of carcinogens and mineral extraction, due to the high energy consumption in the supercritical drying step and the one of respiratory organics due to the ethanol used in the alcogel formation.
In order to reduce the impact of starch aerogel production (without affecting final product quality), improved solutions with less quantities of carbon dioxide, ethanol or with shorter process times can be considered.

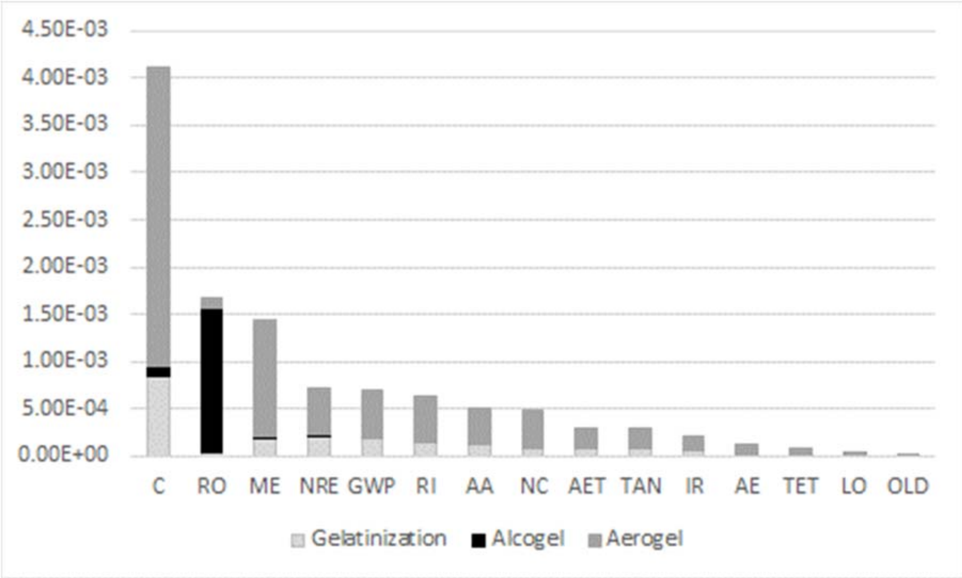

Figure 3: Normalized impact categories for aerogel production per FU.

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