ATTI

XI Convegno della Rete Italiana LCA

Resource Efficiency e Sustainable Development Goals: il ruolo del Life Cycle Thinking

Siena
22 – 23 giugno 2017

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UNIVERSITÀ DI SIENA 1240

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Immagini del volume a cura di Paola Sposato

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ISBN: 978-88-8286-352-4

Revisione editoriale: Giuliano Ghisu

Copertina: Cristina Lanari

Technological breakthrough for energy efficiency in dyes production: bio-synthetic pathway versus chemical process

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Abstract

The industry of dyestuff responds to coloring needs of a wide range of end-use industries, ranging from textile up to construction. In this context research and development activities focused on new technological solutions for low-impact dye synthesis and streamlining manufacturing operations are strategies to be adopted to improve energy efficiency in this sector. Bio-synthetic pathway for dyestuff production represents a high-tech approach that exploits the ability and efficiency of enzymes to catalyse the formation of new dyes. In this study we present the preliminary results of the cradle-to-gate life cycle analysis performed on the bio-synthetic production of dyestuff to highlight the potential energy and environmental benefits achievable through the substitution of classical chemical process with enzymatic ones.

1. Introduction

The traditional colour industry was an important activity in Europe until the end of 20th century. This sector suffers now displacement to the developing countries due to increasing production-related environmental costs as well as high labour costs in Europe. Today Asia-Pacific represents the largest regional market for dyestuff production worldwide, followed by the US, while the textile industry is the main end user for dyes application (Freedonia Group, 2015). After a brief decline in volume and values due to the economic downturn, nowadays the global market for dyes, pigments and intermediates is forecast to outreach 10 million tons by the year 2019 for a market demand of about $19.5 billions. This production trend, connected with resources and energy consumption, environmental effects and toxicity issues represents a question for the dyestuff industry.

Azoic dyes are the largest group of dyes, both in terms of tonnage production as well as the number of different structures. Unfortunately, oral acute toxicity of 4461 dyes has been measured by the lethal dose 50% and, in particular, azo and cationic dyes are the most toxics and mutagenics (Schneider et al., 2004).

Traditionally dye synthesis pathways are non worker-friendly and non environmental sustainable processes. When raw materials are imported from the far East (India, China, Indonesia), their production increases the worldwide global pollution because of unacceptable working conditions. Therefore, synthetic dyes industries have increased their interests to improve the environmental profile of their production processes and products due to (COM, 2001; EC Directive 61, 2002; EC Directive 1, 2008; EC Directive 98, 2008):

- new European regulation to establish non-toxic products (EC Regulation 1907, 2006);
- more stringent environmental regulations, especially in terms of wastewater discharges and CO_2 emissions;
- interest and growing of consumers demand for non-toxic and environmentally friendly products;
- increasing use of eco-labels and certifications in response to the demands and interests of consumers;
- evaluation of the production costs in the long-term perspective (energy, chemicals, water);
- gradual restriction of health and safety standards for workers.

At the moment, the use of available alternatives, like natural and low-impact dyes, is limited because of the employment of large amounts of water and natural resources and the requirement of very expensive processes for their applicability in the textile industry (Yusuf et al, 2017). Therefore, the growing demand for new eco-friendly processes with alternative biocatalysts prompt researchers and technicians to develop safe syntheses in the traditional chemical industry.

Use of biocatalytic processes often allows to improve the selectivity of a reaction with a reduction of downstream processes, so decreasing the material and energy waste required for product refinement steps. The main advantages are represented by the possibility to use mild reaction conditions (i.e. pH and temperature) and fewer steps than those needed in conventional chemical processes. Actually various traditional chemical processes are being substituted by cleaner biocatalytic alternatives, as in the case of fine chemicals production. Alternatives are particularly required for oxidation processes, that currently use inorganic or organic oxidants. Thus, use of alternative oxidants such as molecular oxygen and enzymes are currently under study as biotechnological advancement. In particular, in nature, laccases from different sources are able to catalyze oxidation of various phenolic and aromatic compounds to new products that may be used as dyes for textile application (Enaud et al., 2010). Accordingly, their potential application as eco-friendly biocatalysts has been proved from several studies about bioprocesses (Eggert et al., 1995; Forte et al., 2010, Pogni et al., 2010).

The goal of eco-friendly chemical processes is to improve the traditional industrial production as the key factor to meeting sustainability. In order to reach this goal, the assessment of the potential contribution of different processes to environmental impact issues is necessary in a life cycle perspective.

Life cycle assessment (LCA) is a support methodology able to highlight the environmental burdens of industrial processes commonly used (Mikolasch and Schauer, 2009; Steinberger et al., 2009; Yuan et al., 2013) and new technological solutions in order to reach and promote eco-innovation and eco-efficiency in the textile sector (Nieminen et al., 2006). In this study, LCA has been used for the evaluation of the environmental burdens associated to an innovative dyes biosynthesis compared to traditional chemical processes.

2. Materials and methods

The synthesis of a bio-dye has been investigated to verify the possibility to obtain new dyestuff by laccases for the textile industry. In this context, authors have already acquired an in-depth expertise on the laccase-mediated synthesis during the SOPHIED project (FP6-NMP2-CT-2004-505899). In particular, the primary data used in this study are based on the synthesis of a blue acid dye that has been performed dissolving chemical precursors (3-Methyl-2-benzothiazolinone hydrazine and 4-amino-5-idrossinaftalen-2,7-disulfonic acid) in sodium acetate buffer at pH 5 and at the temperature of 35°C. The precursors initial concentration has been defined at 5 g/L and their molar ratio has been defined 1:1. Then the precursor solutions has been circulated through four cartridges filled with 2 L of immobilized laccase from Coriolopsis Polyzona. The synthesis of the acid biodye has been performed through the bio-reactor set-up described in a recent paper by the authors (Parisi et al., 2015) at a semi-industrial scale with an estimated production capacity of 3 tons of biodye for 60 days of operation.

The traditional chemical production of dyestuff with similar chromophoric unit was modelled based on primary data at industrial scale supplied by a Turkish dyestuff manufacturing Company (SETAS Kimya Group). In particular the classical synthesis of an azo dye was investigated: this is a two-step reaction that takes place through the formation of a diazo compound, obtained transforming the para-nitro aniline into a diazonium salt with sodium nitrite under acidic conditions, and a coupling reaction accomplished by adding N-cyanoethyl-N-cyano ethyl ether aniline to the diazo compound in the acidic medium.

In the classical synthetic sequence, the formation of reactive intermediates (diazo compound, corrosive and unstable) requires the use of acid compounds, that makes this reaction step hihgly toxic, and the addition of huge quantity of ice to control the temperature. The coupling reaction step takes place through the formation of a reaction mixture that is corrosive, toxic and potentially explosive, thus there is a need for a very precise control of the mixture temperature to prevent any risk of explosion. Furthermore lots of additional toxic by-products are formed that persist in the reaction medium during the synthetic process and are present in the final product as residues contributing to the toxicity of the dyestuff. These by-products heavily pollut the output flows (effluents and air emissions) that require complex treatment processes.

On the other hand in the enzymatic synthesis process the ingredients mixing takes place at room temperature, no highly toxic and non volatile precursor are employed and the reaction mixture is non-corrosive and stable. The actual bio-reaction takes place at 30°C with no danger of explosion and, very importantly, without the formation of toxic by-products thanks to the catalytic action of enzymes. Thus process effluents are relatively easy to treat and in principle reusable.

The last step of both the manufacturing process concerns the concentration of the dyestuff. In the case of traditional synthesis of a powder dyestuff, concentration is realized through spry drying and blending operations in order to homogenize the final product. For the enzymatic synthesis, the concentration step has been modeled according to a protocol set-up developed to produce liquid dyestuff through a reverse osmosis operation. Thus, in order to evaluate the benefit associated to the reverse osmosis in the dyestuff manufacturing process, this technological solution has been included in a scenario for the production of liquid dyestuff via traditional chemical method.

The goal of this study was the evaluation of the environmental burdens associated to an innovative bio-synthetic process for the production of dyestuff compared to traditional chemical processes. The analysis has been performed with a cradle-to-gate approach starting from the precursors and chemicals acquisition and ending with the manufacturing of the final product for three dyestuff: the traditional dye in powder, the traditional dye in liquid formulation and the bio-dye. The functional unit used is the quantity of dyestuff necessary to dye 1 kg of wollen textile showing the same colouring characteristics. All calculations were performed with the SimaPro software version 7.3.3 (Prè Consultants, 2012) and the Ecoinvent Database version 2.1 (Ecoinvent Centre, 2011) was employed for secondary data.

In order to highlight the advantages achievable via the enzymatic process in terms of energy efficiency gain, we employed the Cumulative Energy Demand (CED) Method (Frischknecht et al., 2007). Thus results are expressed by means of an energetic indicator that quantifies the whole energy requirement during the life cycle of a product. It is expressed in equivalent of MJ of primary energy and it sums up both direct energy (like electricity, thermal energy, etc.) and indirect energy contributions (embodied energy of materials).

At this stage of the study, to further investigate the benifits obtainable by the proposed synthetic approach, some preliminary results concerning water consumption and CO_2 emissions are discussed. For the latter the Global Warming Potential (GWP) Method (IPCC, 2007) developed by the International Panel of Climate Change (IPCC) was employed.

3. Results and discussion

The energy-profiles of the chemical and bio-synthesized dyestuff are depicted in Figure 1. From the inspection of the histograms, it is evident that liquid dyestuff show a better performing energy-profile. Such a formulation, in fact, takes advantage from the fact that no filtration and drying operations are required, thus consuming almost 20 kWh of direct energy per kg of product less than the powder dyestuff manufacturing process. But the most significant difference between the powder and liquid traditional dye profiles is largely due to the embodied energy of raw materials consumed during the processes.

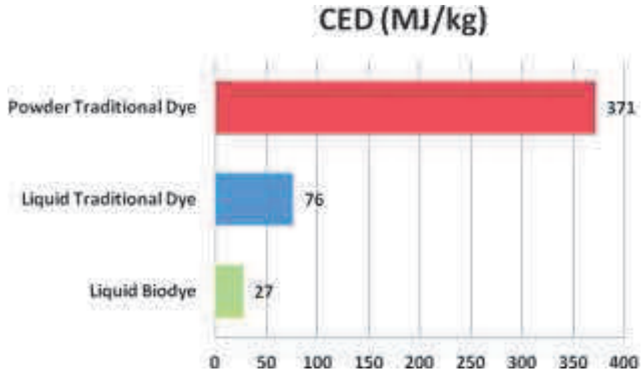

Figure 1: CED indicator values of dye quantities necessary to dye 1 kg of woollen textile.

Figure 2 shows that, given the specific CED value for a process, the raw materials contribution patterns to the indicator are very similar: para-nitro aniline and chloridric acid give the larger impact to the indicator. But in the traditional powder dyestuff case dispersing agents are required to homogenize the final product and these are particularly energy intensive materials. Moreover liquid dyestuff produced via reverse osmosis technique are characterized by a water consumption reduction of about 75% compared to traditional powder dye manufacturing. In fact, after the coupling reaction step of traditional process, filtration and following water re-dissolution stages are required for purification purposes and these are responsible for a huge consumption of fresh water in the production of powders.

The bio-transformation via immobilized laccases allows to synthesize dyestuff at mild temperatures and with reduced quantities of other chemicals and, very importantly, avoiding by-products in the output solution. As showed in Figure 2, the employment of this biotechnology leads to important positive gains in terms of primary energy required for the manufacturing of 1 kg of dyestuff. This advantage is represented by an almost 65% reduction of CED indicator value for liquid biodye with respect to liquid traditional dye. The most significant difference is given by the raw materials employed for the two processes that are characterized by much diverse embodied energy values accounting for almost 50 MJ of primary energy.

Observing the direct and indirect energy contribution analysis for the liquid biodye reported in Figure 2, it can be seen that the larger impact to the embodied energy of raw materials is given by the precursor. This is stoichiometrically consumed during the enzymatic dyestuff synthesis thanks to the continuous process set-up without environmental implications for effluents treatment process.

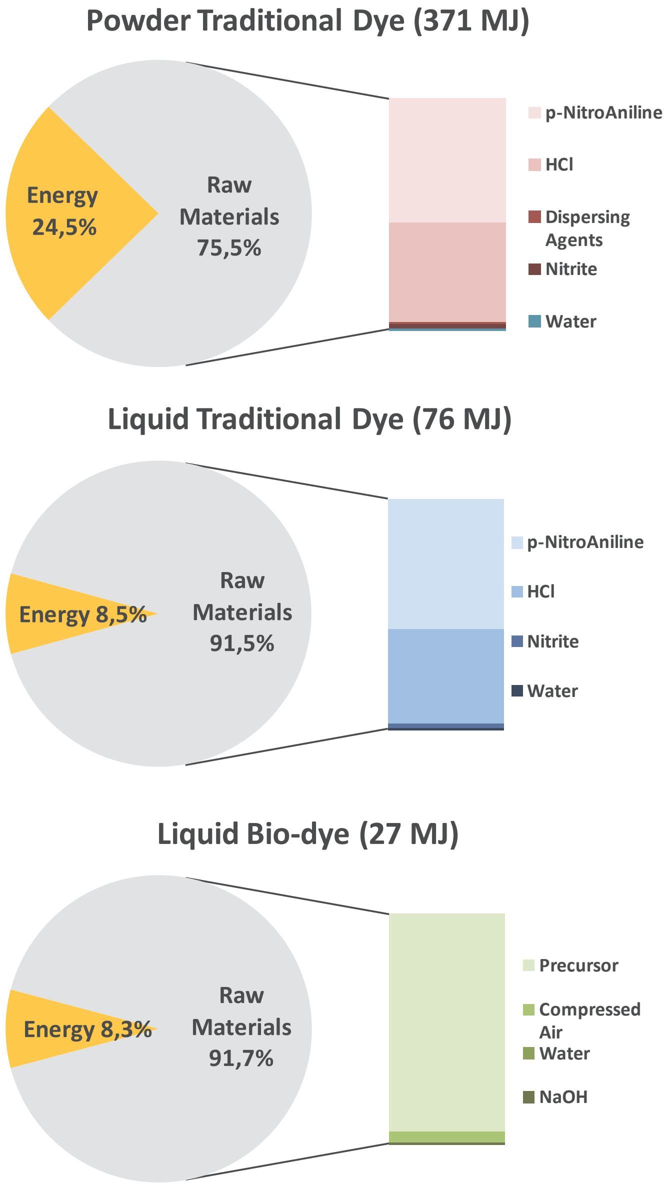

Figure 2: Direct (electricity, heat) and indirect (embodied energy of raw materials) energy contributions to the CED indicator values of dye quantities necessary to dye 1 kg of woollen textile.

In the context of a growing global dyestuff market, the control of greenhouse gas emissions related with industrial production would certainly represent an important factor to pursue environmental improvement. Figure 3 shows that the production of liquid dyestuff allows for a remarkable reduction in terms of CO_2 emissions that reach about a 95% value for the bio-synthesized dye.

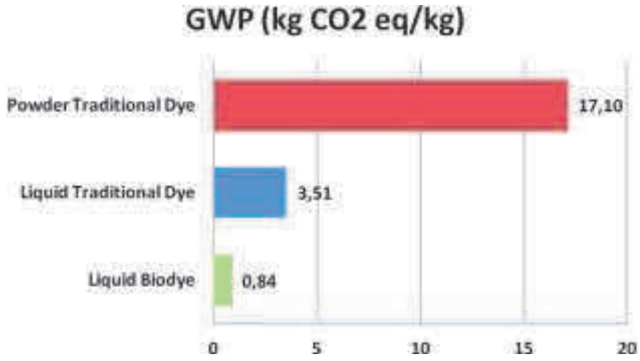

Figure 3: GWP indicator values of dye quantities necessary to dye 1 kg of woollen textile.

4. Conclusion

In this paper the outcomes of the LCA study of dyestuff bio-synthetic production have been presented in order to evaluate the potential energy benefits achievable through the substitution of classical chemical process with innovative solutions based on enzymatic catalysis. Some other preliminary results concerning the GWP and water consumption are discussed as well.

Even if the analysis has been modeled for a manufacturing capacity is at a semi-industrial scale, results highlight that, compared to traditional powder dyestuff synthesis, the bio-synthetic pathway for the production of liquid biodye allows for:

- more than 80 MJ of direct energy saving per kg of final product

- about 250 MJ of indirect energy savings through the employment of less embodied-energy intensive raw materials for the synthesis of the final product

- a 95% reduction in CO_2 emissions per kg of final product

-a significant water consumption decrease (~75%)

A further development of this study will focus on the whole eco-profile of the bio-synthetic process for dyes production in order to assess its actual effectiveness and potentially better environmental performances in comparison with classical processes.

5. Acknowledgments

This work has been supported by the Eco-Innovation European Project BISCOL (ECO/09/256112).

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