CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis

ISBN 978-88-95608- 48-8; **ISSN** 2283-9216

DOI: 10.3303/CET1757284

Supercritical Carbon Dioxide Decaffeination Process: a Life Cycle Assessment Study

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This work aimed at evaluating the environmental performances of a coffee decaffeination process driven by carbon dioxide at supercritical conditions, using a Life Cycle Assessment approach (LCA). In the last years, the global decaf coffee market has reached about 10 %, with growing diffusion mainly in developed areas. This increasing trend is mainly due to the preservation of the coffee taste related to a clear improvement in terms of quality of the decaffeination processes. The caffeine extraction stage, core unit operation of the decaffeination process, may be performed in different ways. Among the different processes, the most selective one, for removing just caffeine and no other flavour precursors from coffee, is based on supercritical carbon dioxide ($scCO_2$). The aim of this work is to carry out a LCA analysis to determine the environmental impacts of industrial stages (from gate to gate) of the caffeine extraction process with supercritical carbon dioxide, reporting all the results to the chosen functional unit (1 kg of decaffeinated coffee). The data were analysed using SimaPro 8.0.5 software in order to identify the environmental key performance indicators (KPIs). Primary data and the Ecoinvent database were used for the Life Cycle Inventory (LCI), according to the reference standard for LCA (i.e., ISO 14040-14044).

1. Introduction

Coffee is one of the most popular beverages in the world and constitutes a significant portion of the daily beverage intake in Western countries (Chen et al., 2011). Coffee grows mainly in Africa and America and between the numerous known species, only three were successfully used in commercial cultivation: *Coffea arabica*, *C. canephora* (robusta) and *C. liberica*. The commercial growth of the last one was ceased because of an epidemic, which devastated the cultivations during the 1940s. Coffee is the main source of caffeine in daily consumption, even if caffeine is contained also in tea leaves, guarana seeds and cocoa beans (Ashihara and Crozier, 2001). The caffeine content of green coffee beans varies according to the species: *C. arabica* contains about 1.0–1.2 % and *C. canephora* (robusta) about 1.6–2 %. Numerous studies, in the last years, reported the effect of caffeine on cardiovascular diseases (Riksen et al., 2009) and on central nervous system (Nehlig et al., 1992), leading to an increasing consumption of decaffeinated coffee (Mazzafera et al., 2009). Decaffeination methods employ organic solvents (mainly methylene chloride and ethyl acetate), or water or supercritical carbon dioxide ($scCO_2$) (Ramalakshmi and Raghavan, 1999). Until the mid-1970s, methylene chloride was considered the best solvent for extraction of caffeine with satisfactory results. However, subsequently, doubts have arisen about its risk to humans, due to the solvent high toxicity. Therefore, the solvent of choice has become ethyl acetate, a natural component detected in coffee aroma and found to occur naturally in many fruits. The main disadvantage related to decaffeination based on ethyl acetate is due to its high flammability and to its characteristic odour, which remains in the decaf coffee. The decaffeination using water was developed in Switzerland, and constitutes a green process with respect to the product. Unfortunately, water is not a particular selective solvent and, therefore, not only caffeine but also various flavours were removed from coffee beans using this method. As a result, a less flavourful brew with respect to other methods was obtained. The most selective process for removing just caffeine and not the other flavour precursors from coffee is based on the use of $scCO_2$. This process was successfully developed on an industrial scale in the 1970s, based on two patents developed by Zosel: in the first, the process is presented for the recovery of caffeine (Zosel, 1974), whereas, in the second one, a detailed description aimed at

Please cite this article as: De Marco I., Riemma S., Iannone R., 2017, Supercritical carbon dioxide decaffeination process: a life cycle assessment study, Chemical Engineering Transactions, 57, 1699-1704 DOI: 10.3303/CET1757284

obtaining decaffeinated coffee was proposed (Zosel, 1981). Supercritical fluids (SCFs) based techniques have been proposed as an alternative to conventional processes, thanks to their specific characteristics, mainly, solvent power and liquid-like densities coupled with gas-like transport properties that can be tuned varying pressure and temperature. SCFs have been successfully applied in several fields, such as, for example, micronization (Prosapio et al., 2014), drying (Cardea et al., 2013), and scaffolds formation (Baldino et al., 2014). Among the different $scCO_2$ based processes, one of the most studied is the supercritical fluids extraction (SFE) for the possibility of continuously modulating the solvent power/selectivity; this process has been frequently used for the extraction of essential oils (Reverchon et al., 1994). SFE has been used also for the extraction of caffeine from natural sources, such as coffee husks (Tello et al., 2011), coffee beans (Machmudah et al., 2011) and tea leaves (Kim et al., 2008).

Considering that technologies based on supercritical fluids are “eco-friendly” because of the reduced use of organic solvents, it is important to study the environmental emissions due to a specific production. One of the most common way to determine in a quantitative way the environmental impact of a process or a product is the use of life cycle assessment (LCA) analysis. Many papers based on LCA analyses were published in different research fields, such as, for example, energy (González-García et al., 2014), beverages (De Marco et al., 2016a), wines (Iannone et al., 2014), fruits (De Marco et al., 2015), pharmaceutical delivery systems (De Marco et al., 2016b) and wastewater treatments (Lassaux et al., 2007). In particular, food sector is among the most impactful ones for the environment, due to production, preservation and distribution steps (De Marco and Iannone, 2017), which consume a considerable amount of energy (Roy et al., 2009). LCA studies regarding the food sector were addressed on agricultural stages (Coltro et al., 2006), production steps (De Marco et al., 2016c) or packaging systems (De Monte et al., 2005).

Some LCA analyses on coffee were performed, considering agricultural stages (Silvarolla et al., 2004) and packaging (Büsser et al., 2009). Concerning decaffeination, logistics activities in a decaffeination plant were studied (Iannone et al., 2015), but LCA studies on decaffeination were not attempted until now.

Therefore, the aim of this work is to carry out an LCA analysis to determine the environmental impacts of the industrial stages (considering an in-depth analysis) of coffee beans decaffeination using supercritical carbon dioxide, reporting all the results to the chosen functional unit (1 kg of decaffeinated coffee).

2. Methodology

LCA analysis allows to correlate a broad set of data regarding the life-cycle of a product or a process in order to individuate the phases of the process that are critical from an environmental point of view. The main step of an LCA analysis are presented in the following sub-sections.

2.1 Goal definition, functional unit and system boundaries

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 the in-depth evaluation of the environmental impacts of coffee decaffeination using supercritical carbon dioxide ($scCO_2$). The functional unit (FU) is the reference to which all the inputs and outputs have to be related; the chosen FU is 1 kg of decaffeinated coffee. Through mass and energy balances of each operation, a gate-to-gate analysis was performed; therefore, the system boundaries (dashed line in Figure 1) are set from coffee beans transportation to decaffeinated coffee attainment.

2.2 Data collection

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. Data were recovered from an industry, which uses supercritical carbon dioxide to extract caffeine from coffee beans (the process details are listed in Table 1). Briefly, decaffeination from green coffee beans using $scCO_2$ typically involves different basic steps: steaming, supercritical CO_2 caffeine extraction and caffeine recovery. In the steaming step, the coffee beans are put in contact with superheated steam at elevated temperature until their moisture content is increased to 30 % by weight and, as a result, the beans swell considerably. Then, the coffee beans are charged in an extractor, which is pressurized by pumping carbon dioxide until the operating conditions are reached (90 °C, 250 bar); the extracting process goes on for 11.5 hours in the case of arabica and 22 hours in the case of robusta coffee, in order to extract 97 % of the caffeine from the beans. Once the extraction is completed, the extractor begins a down time, in order to be emptied and charged with fresh beans.

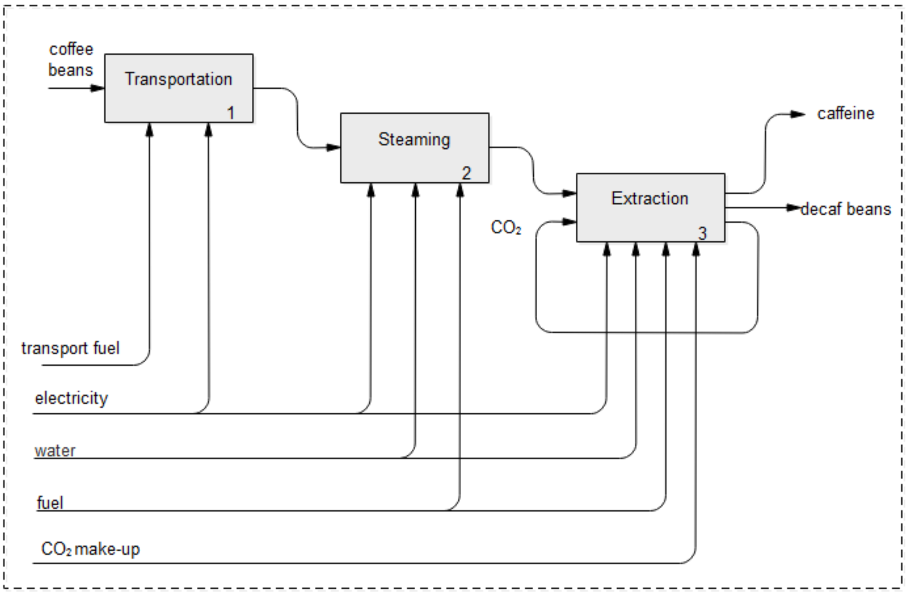

Figure 1: Scheme of the industrial production of decaffeinated coffee beans.

Table 1: Process details and assumptions

Process	Characteristics and details
Coffee beans supply to facility	*Coffea arabica* beans transport by truck, 40 t from Genoa (distance = 650 km) + by large tanker from Brazil (distance = 9100 km)
Energy supply to facility	Italian energy mix low voltage
Coffee beans steaming	T = 90 °C; t = 5h; energy, water and fuel supply
Pressurization	t=0.25 h; carbon dioxide, energy, water and fuel supply
Operation conditions' stabilization	T=90 °C; P=250 bar; t=0.25 h; carbon dioxide, energy, water and fuel supply
Caffeine extraction	T=90 °C; P=250 bar; t=11.5 h; carbon dioxide, energy, water and fuel supply
Depressurization	T=25 °C; P=1 bar; t=0.5 h

Subsequently, the stream of $scCO_2$ with the caffeine dissolved in it begins to flow through a water wash packed column, where it is counter-currently contacted with a stream of water that removes 99.5 % of the caffeine from the CO_2, considering that caffeine has a higher affinity with water with respect to $scCO_2$. The purified $scCO_2$ is pumped in the storage tank; caffeine is subsequently separated from water and furtherly purified.

2.3 Environmental analysis

The LCA study was conducted using the LCA software SimaPro 8.0.5. The majority of the processes and materials information were collected using "primary data", whereas Ecoinvent 3.1 database was employed for background data. Once estimated the emissions related to decaffeinated coffee production through a LCI analysis, the corresponding environmental impacts have to be calculated using an LCA methodology. In this paper, the IMPACT 2002+ method was used to evaluate the contributions of different processes. This method was selected because the study pertains to a European (Italian) production and IMPACT 2002+ was one of the method developed in Europe. This methodology proposed an implementation of a combined midpoint/endpoint approach, linking all types of LCI results (elementary flows and other interventions) via fifteen midpoint categories to four endpoint (or damage) categories. The fifteen midpoint categories are: human toxicity carcinogenic effects (C), human toxicity non-carcinogenic effects (NC), respiratory effects due to inorganics (RI), ionizing radiation (IR), ozone layer depletion (OLD), photochemical oxidation due to respiratory organics (RO), aquatic ecotoxicity (AET), terrestrial ecotoxicity (TET), aquatic acidification (AA), aquatic eutrophication (AE), terrestrial acidification/nitrification (TAN), land occupation (LO), global warming potential (GWP), non-renewable energy consumption (NRE) and mineral extraction (ME). According to IMPACT 2002+ method, all types of midpoint categories can be linked to damage categories (DC_i), where:

- human health (DC_1) = *f(C, NC, RI, IR, OLD,RO)*;
- ecosystem quality (DC_2) = *f(AET, TET, TAN, LO, AA, AE)*;
- climate change (DC_3) = *f(GWP)*;
- resources (DC_4) = *f(NRE, ME)*.

3. Results and discussion

The aim of this study is the interpretation of the data collected through the LCI phase and the evaluation and comparison of the impacts related to coffee beans decaffeination. The first step was the quantification of the emissions of the decaffeination process in terms of midpoint categories; in order to individuate the contribution of the single stage of the process, an in-depth analysis was performed, considering separately the impacts due to transportation of the Arabica coffee beans from Brazil, the impacts due to the steaming stage and the impacts due to the supercritical fluids extraction (SFE) of caffeine from coffee beans. The impacts of this step-by-step analysis are reported in Table 2 and their contributions on the entire process can be visualized in Figure 2. It is clear that the steaming process has a negligible contribution on all the midpoint categories. Indeed, its contribute is equal at most to 0.2 %. On the contrary, transportation and supercritical extraction differently contribute on the midpoint categories. In particular, transportation is the most impactful stage on OLD and RO (higher than 60 % of the total emissions), transportation and supercritical extraction contributes on AET and LO are comparable, whereas supercritical extraction is the main contributor to the impact on all the other categories.

Table 2: IMPACT 2002+ impacts at midpoint level for each step of the process.

Impact	Unit	Transportation	Steaming	SFE	Total
C	kg C_2H_3Cl eq	1.63E-03	2.87E-05	2.32E-02	2.48E-02
NC	kg C_2H_3Cl eq	2.66E-03	2.48E-05	8.26E-03	1.09E-02
RI	kg PM2.5 eq	2.83E-04	1.54E-06	7.08E-04	9.93E-04
IR	Bq C-14 eq	2.69E+00	2.26E-02	1.61E+01	1.88E+01
OLD	kg CFC-11 eq	1.92E-07	9.25E-11	1.17E-07	3.09E-07
RO	kg C_2H_4 eq	3.31E-04	1.78E-07	1.85E-04	5.16E-04
AET	kg TEG water	5.69E+01	7.97E-02	5.13E+01	1.08E+02
TET	kg TEG soil	6.76E+00	2.32E-02	1.36E+01	2.04E+01
TAN	kg SO_2 eq	7.65E-03	2.03E-05	1.24E-02	2.01E-02
LO	m^2org.arable	9.53E-03	2.93E-05	1.17E-02	2.13E-02
AA	kg SO_2 eq	1.50E-03	8.07E-06	4.34E-03	5.85E-03
AET	kg PO_4 P-lim	1.11E-05	3.11E-07	1.25E-04	1.36E-04
GWP	kg CO_2 eq	1.92E-01	1.20E-03	1.02E+00	1.22E+00
NRE	MJ primary	2.83E+00	1.42E-02	1.42E+01	1.70E+01
ME	MJ surplus	2.90E-03	1.50E-04	4.77E-02	5.07E-02

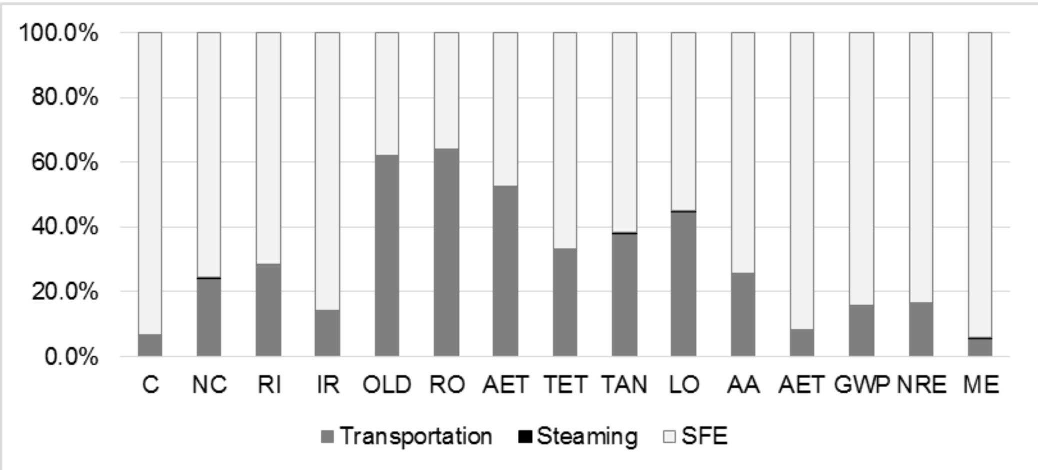

Figure 2: In depth analysis for coffee beans decaffeination.

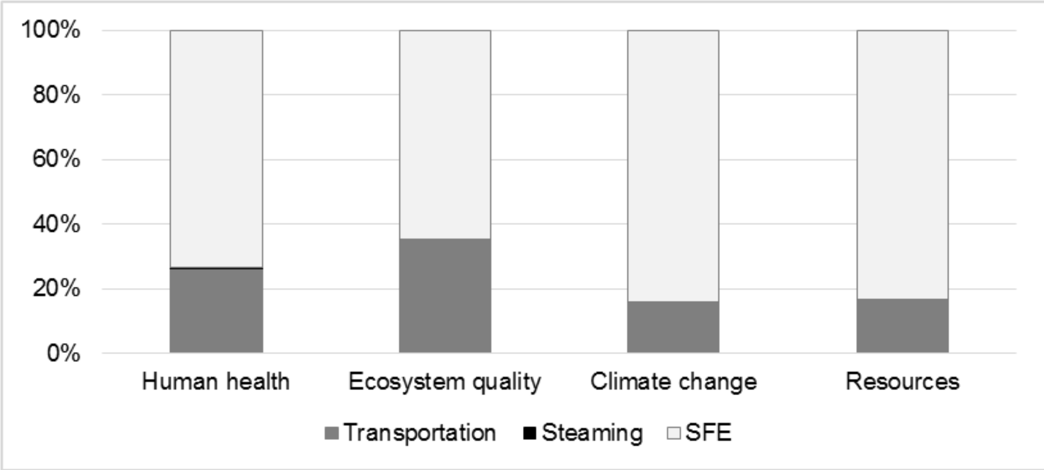

Figure 3: Global damage related to coffee beans decaffeination.

The environmental impacts were, then, grouped, according to IMPACT 2002+ method, considering the damage on the endpoint categories. Figure 3 shows the emissions due to transportation, steaming and supercritical extraction on human health, ecosystem quality, climate change and resources. The extraction process mainly affects all the categories, whereas transportation has a significant impact on ecosystem quality (35 %) and human health (26 %). Considering that the emissions due to transportation cannot be lowered without affecting the taste of the coffee, a modification of the process could be proposed aimed at lowering the emissions due to supercritical extraction stage. One of the modifications that can be proposed is, for example, the substitution of the fuel used in the heater. Moreover, considering that supercritical fluid based processes are energy intensive, a remarkable further reduction of the emissions can be obtained, adopting electricity produced in sustainable way (Fera et al., 2014).

4. Conclusions and perspectives

In this work, an in-depth quantitative LCA analysis on coffee beans decaffeination was performed, following a “from gate to gate” approach. The majority of the emissions are due to the supercritical extraction, due to electricity and fuel used during the process. Modifications of the process aimed at lowering the emissions could be proposed: for example, the fuel used in the exchangers can be substituted and the use of renewable sources of electricity can be considered too.

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