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Technical feasibility and carbon footprint of biochar co-production with tomato plant residue

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ABSTRACT

World tomato production is in the increase, generating large amounts of organic agricultural waste, which are currently incinerated or composted, releasing CO_2 into the atmosphere. Organic waste is not only produced from conventional but also urban agricultural practices due recently gained popularity. An alternative to current waste management practices and carbon sequestration opportunity is the production of biochar (thermally converted biomass) from tomato plant residues and use as a soil amendment.

To address the real contribution of biochar for greenhouse gas mitigation, it is necessary to assess the whole life cycle from the production of the tomato biomass feedstock to the actual distribution and utilisation of the biochar produced in a regional context. This study is the first step to determine the technical and environmental potential of producing biochar from tomato plant (*Solanum lycopersicum arawak* variety) waste biomass and utilisation as a soil amendment.

The study includes the characterisation of tomato plant residue as biochar feedstock (cellulose, hemicellulose, lignin and metal content); feedstock thermal stability; and the carbon footprint of biochar production under urban agriculture at pilot and small-scale plant, and conventional agriculture at large-scale plant.

Tomato plant residue is a potentially suitable biochar feedstock under current European Certification based on its lignin content (19.7%) and low metal concentration. Biomass conversion yields of over 40%, 50% carbon stabilization and low pyrolysis temperature conditions (350–400 °C) would be required for biochar production to sequester carbon under urban pilot scale conditions; while large-scale biochar production from conventional agricultural practices have not the potential to sequestrate carbon because its logistics, which could be improved. Therefore, the diversion of tomato biomass waste residue from incineration or composting to biochar production for use as a soil amendment would environmentally be beneficial, but only if high biochar yields could be produced.

1. Introduction

1.1. Biomass waste generation from tomato crops

World tomato production increased 42.9% between 2000 and 2013 (FAOSTAT, 2015). Consequently, tomato crop wastes have increased too. In 2013, 163.43 Mt of tomatoes were produced worldwide (FAOSTAT, 2015). Assuming a dry waste production (leaves and stems) of 9 t/ha·year for tomato crops (López et al.,

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Abbreviations: BQM, Biochar Quality Mandate; BTP, Biochar testing protocol; C, Carbon; CC, Climate change; CO2, Carbon dioxide; DSC, Differential scanning calorimetry; DTA, Differential thermal analysis; EBC, European Biochar Certification; IBI, International Biochar Initiative; ICPS-MS, Inductively coupled plasma mass spectrometry; i-RTG, Integrated rooftop greenhouse; LCA, Life cycle assessment; $m_{dry\ biomass}$, Mass of dry biomass; RTG, Rooftop greenhouse; TGA, Thermogravimetric analysis; UA, Urban agriculture; $\%_{Stable\text{-}C}$, Percentage of stable C remaining in the biochar.

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Table 1
Total world, European and Spanish tomato production, crop area, waste generation (FAOSTAT, 2015) and C fixed within waste biomass during 2013. Waste production was calculated assuming 9 tonnes of biomass waste per ha of crop (López et al., 2004) and fixed C by supposing that 18% of the total dry biomass weight corresponds to the C content (Mota et al., 2008).

	Annual total values for 2013					
	Tomato production (Mt)	Area harvested (ha)	Approx. wet waste* (Mt)	Approx. dry waste* (Mt)	C fixed in dry waste* (Mt)	CO_2 eq. fixed in dry waste* (Mt)
World	163.43	4,688,335	332.87	42.19	7.6	27.9
Europe	20.96	500,872	35.56	4.51	0.81	2.97
Spain	3.68	45,300	3.22	0.41	0.07	0.26

* Only stems and leaves are considered.

2004), in 2013, approximately 42.19 Mt of dry waste may have been produced worldwide (Table 1).

As the amount of tomato waste residues increase with increased crop production, waste management solutions should be used to minimize their environmental impacts and help mitigate climate change (IPCC, 2013). Sustainability is included in most conventional tomato plant waste management scenarios as waste is re-used or recycled to feed farm animals, produce compost or for energy valorisation (i.e.; incineration). Some institutions have already developed waste management solutions that could help to fix the C captured by tomato plants and reduce resources depletion. Wageningen University has developed a technology to produce cardboard for packaging with tomato plants stems and leaves (Wageningen UR, 2014). Ford Motor Company, in collaboration with Heinz ketchup, is developing new bio-composites based on tomato processing wastes (Ford Motor Company, 2014). Moreover, the Biocopac Project has developed bio-resins based on tomato processing wastes to cover the inside part of food cans (Biocopac Project, 2013).

Although GHGs emissions may be reduced or delayed under such waste management scenarios, carbon sequestration into stable carbon forms is not considered. The carbon content of tomato plant (corvey variety) stem and leaves is 18% of total dry tomato plant weight (Mota et al., 2008). Consequently, the annual world tomato waste (stems and leaves) would contain approximately 7.6 million tonnes of C, equal to an approximate 27.9 million tonnes of CO_2 (Table 1), which is returned to the atmosphere.

1.2. Agricultural wastes & biochar production

A potential waste management solution that captures and stores carbon from agricultural waste into stable forms by reductive thermal processes is the production of biochar. (Lehmann et al., 2006). Biochar is defined as ‘a solid material obtained from the thermochemical conversion of biomass in oxygen-restricted conditions which is used for any purpose that does not involve its rapid mineralisation to CO_2’ (Shackley et al., 2016 BOOK chapter 1 pg 6). Due to its long-term storage of stable carbon, biochar is commonly used for soil improvement (Lehmann et al., 2008; Woolf et al., 2010). Other 50 biochar applications have been already listed (Hans-Peter and Kelpie, 2014), such as (1) a feed complement in farms (Gerlach and Schmidt, 2014); (2) to increase the biogas production efficiency (Inthapanya, 2012); (3) to produce thermal insulation materials (Lin and Chang, 2008) and (4) to fill mattresses and pillows (Hans-Peter and Kelpie, 2014).

The use of biochar depends significantly on its quality (i.e., porosity, nutrient content or heavy metal content). In the case of biochar for soil amendment, in Europe, two different voluntary certifications, without legal implications, have been developed: the Biochar Quality Mandate (BQM) elaborated by the British Biochar Foundation (Hackley et al., 2014) and the European Biochar Certification (EBC) criteria (EBC, 2012). In USA and Canada, can be applied the International Biochar Initiative (IBI) mandate (IBI, 2015). These voluntary certifications provide minimum quality parameters of biochar for its application in soils. The information supplied by these schemes has been compiled into the Biochar testing protocol (BTP) to provide information on biochar materials and biochar products. This information allows the user to describe and define the properties of the biochar product (Shackley et al., 2016).

Agricultural wastes have previously been considered as feedstocks and used to produce biochar as a solution for carbon sequestration (Lehmann et al., 2006; McHenry, 2009). Some examples of the agricultural feedstocks include rice hull, groundnut shells, olive husk and tea (Lehmann et al., 2006; McHenry, 2009). One study analysed the use of biochar produced with tomato plant feedstocks as a substrate for tomato hydroponic crops (Dunlop et al., 2015). This research focuses on the specific properties for the application under study (i.e., N, P, and K contents; thermal conductivity; and pH) but does not communicate other important parameters such as the metal content of tomato plant feedstock or its environmental performance with life cycle assessment (LCA) methodology. LCA is a recognised methodology to quantify the environmental impacts of systems, products or services for proper decision making (European Commission, 2001; UNEP, 2002). Present study uses LCA methods to determine the carbon footprint of biochar co-production with tomato plant feedstocks.

1.3. Urban agriculture (UA): new organic feedstocks and by-products in cities

The United Nations predicts that the world population will reach 9.550 million habitants by 2050, of which more than the 70% will live in urban areas (UN, 2012); consequently, the food demand in cities will increase. Some strategies, such as UA, are gaining presence in urban areas to increase cities' food self-sufficiency (Orsini et al., 2013; Specht et al., 2013).

UA has a great potential to provide social and environmental benefits to cities' feeding systems (Sanyé-Mengual et al., 2015, 2013; Tomlinson, 2011) due to social integration, job creation, simpler logistics and packaging reduction. However, UA produces organic wastes that increase the organic fraction generation of urban areas (Baumgartner and Belevi, 2001). The circular economy concept (Andersen, 2007) promotes the conversion of wastes back to resources. Biochar opens a wide range of possibilities for the creation of new local products with local UA wastes, helping to reduce the organic fraction volume of urban areas while reducing resources depletion.

One of the multiple UA typologies consists of installing greenhouses on the top of buildings, named Rooftop Greenhouses (RTGs). Inspired by the Industrial Ecology concept (Jacobsen, 2008), RTGs can be integrated with buildings to exchange energy, water and CO_2 (from human respiration) flows and increase system efficiency. Integrated RTGs (i-RTGs) allow an intensive food production, which will generate organic wastes that could be used to produce new products. Therefore, urban production systems, conceptually, could also be considered raw material farms.

UA wastes have not yet been studied for economical valorisation. UA wastes are of great interest if are considered as local low-cost sources that may not require transportation. Moreover, the lack of waste management solutions that could fix the C captured by UA crops and the actual environmental concern about climate change (IPCC, 2013) make biochar production with UA feedstocks interesting from an environmental perspective.

The present research mainly intends to elaborate a first approximation of the carbon footprint of a local pilot-scale biochar production system with UA feedstocks using LCA methodology to discuss how this strategy could help to reduce cities, urban agriculture and new products carbon footprint. Moreover, data collected for the study is used to simulate a larger scale scenario which is then compared with the urban pilot-scale scenario.

In addition the article does a basic assessment to determine the quality of tomato plant feedstocks from UA crops for biochar co-production. For that, the cellulose, hemicellulose and lignin contents of UA tomato plant feedstock were quantified. Furthermore, a thermogravimetric analysis (TGA) was developed to study the potential biochar yields and a metal content analysis was performed to determine if cities' air pollution influences the urban crop pollutant content and, consequently, biochar quality.

From an LCA perspective, it is expected that the low transportation requirements of UA feedstocks and biochar may contribute significantly to ensure that biochar production with UA feedstocks may result in a carbon sink strategy. It is also foreseen that UA tomato feedstocks may have a sufficient quality for biochar production; however, the metal content in the feedstock due to cities' air pollution may worsen its properties.

2. Materials & methods

2.1. Samples obtaining and preparation

The present research was developed in the framework of the Fertilecity Project[1]. This project aims to study the potential environmental, economic and social benefits of urban food production through i-RTGs. During the project, there were a lack of solutions that could sink the C captured by urban crops, which could help to reduce the carbon footprint from urban feeding systems. Waste tomato plant leaves and stems from experimental crops were used in the present research. Tomato plants were cultivated using the same soilless systems (with perlite substrate) conventionally used in Mediterranean areas. The i-RTG used for tomato cultivation is located on the top of the ICTA-ICP building of the Autonomous University of Barcelona campus (Bellaterra, Spain).

Tomato plants (*solanum lycopersicum Arawak* variety) used for the experiment were cropped between February and July 2015. At the end of the crop, the plants were air dried at room temperature (as described for the LCA study – Fig. 1) in the same i-RTG for 4 weeks. Later, the leaves and stems were manually separated and homogenised with an electric grinder (to a particle size of less than 0.2 mm) to prepare them for the TGA.

2.2. Cellulose, hemicellulose and lignin contents

The cellulose, hemicellulose and lignin contents were determined through a gravimetric method. To obtain the cellulose content, the sample was processed with basic and acidic digesters. For cellulose, the sample was submitted to a neutral digestion, and for lignin, the sample was administered sulfuric acid and dried (Kaloustian et al., 2001).

2.3. Thermogravimetric analysis of biochar feedstock

A pyrolysis test was conducted in a thermobalance carrying out a simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry/differential thermal analysis (heat flow DSC/DTA) system NETZSCH -STA 449 F1 Jupiter (Puy et al., 2011). The sensitivity of the balance was 0.07 micrograms. The furnace operated from room temperature to 1400 °C. The solid weight loss and heat flow, together with other process variables, such as temperature, were recorded. A heating rate of 10 °C/min was applied from room temperature up to 800 °C, placing 166 mg of biomass in the alumina crucible. The atmosphere of the analysis was N_2 (80%) and O_2 (20%) with a purge flow of 20 ml/min. The sample consisted of a mixture of tomato leaves (50%) and stem (50%) which were crushed together with an electric grinder until obtaining a particle size of less than 0.2 mm.

2.4. Characterisation of biochar feedstock quality

Currently, there are three main schemes available to assess biochar products. The IBI, the EBC and the BQM. The requirements are very strict to ensure that no contaminants are added to the soil, which could finally pollute and damage groundwater, plants, crops or animals. In this sense, limitations consist of establishing thresholds for the heavy metal content in biochar.

For the present study, tomato plant ashes (mixture of 50% leaves and 50% stem) from the TGA were analysed to determine their heavy metal contents (As, Cd, Cr, Cu, Pb, Hg, Mn, Mo, Ni, Se and Zn) for a subsequence comparison with the BQM, IBI and EBC thresholds. Moreover, results were contrasted to the metal content of other biochar materials found in the literature.

The metal content of the ashes was determined by Inductively coupled plasma mass spectrometry (ICP-MS). The equipment used was an Agilent ICP-MS 7500ce. The samples were microwave digested with HNO_3 and HCl, and a semi quantitative estimation was carried out from the response curve vs molar atomic weight.

2.5. Biochar carbon footprint assessment

LCA methodology, according to ISO 14044 (ISO, 2006), was used to calculate the potential carbon footprint of producing biochar with UA tomato plant feedstock. LCA is an accepted methodology that is used to approximately quantify the greenhouse gas emissions in equivalent CO_2 emissions from products, systems or processes from a life cycle approach (Berners-Lee et al., 2011; Pandey et al., 2011).

The scope of the analysis was to quantify the carbon footprint of biochar production from UA tomato plant feedstocks at pilot and smale-scale and to determine whether CO_2 emissions from this biochar production were higher or lower than the CO_2 emissions that remained fixed as stable C within the biochar. The selected *functional unit for study is the production of 1 tonne of biochar with tomato plants feedstocks*. For the analysis, the Ecoinvent 3.2 database and IPCC, 2013 (100a) calculation method were used. SimaPro 8.2.3 was used as a support program. The impact category used to obtain the carbon footprint from biochar production was Climate Change (kg CO_2 eq.).

2.5.1. System boundaries and allocations

Describing the carbon flows (Fig. 1) from biochar production from UA tomato plant feedstock was considered crucial for determining whether the final CO_2 fixed in the biochar was higher than the CO_2 emissions into air generated during the production of biochar. In our research, biochar samples were not elaborated because of the high level of ashes production (see Table 5) when tomato plant feedstocks undergo to thermal processes, which may damage

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[1] http://www.fertilecity.com.

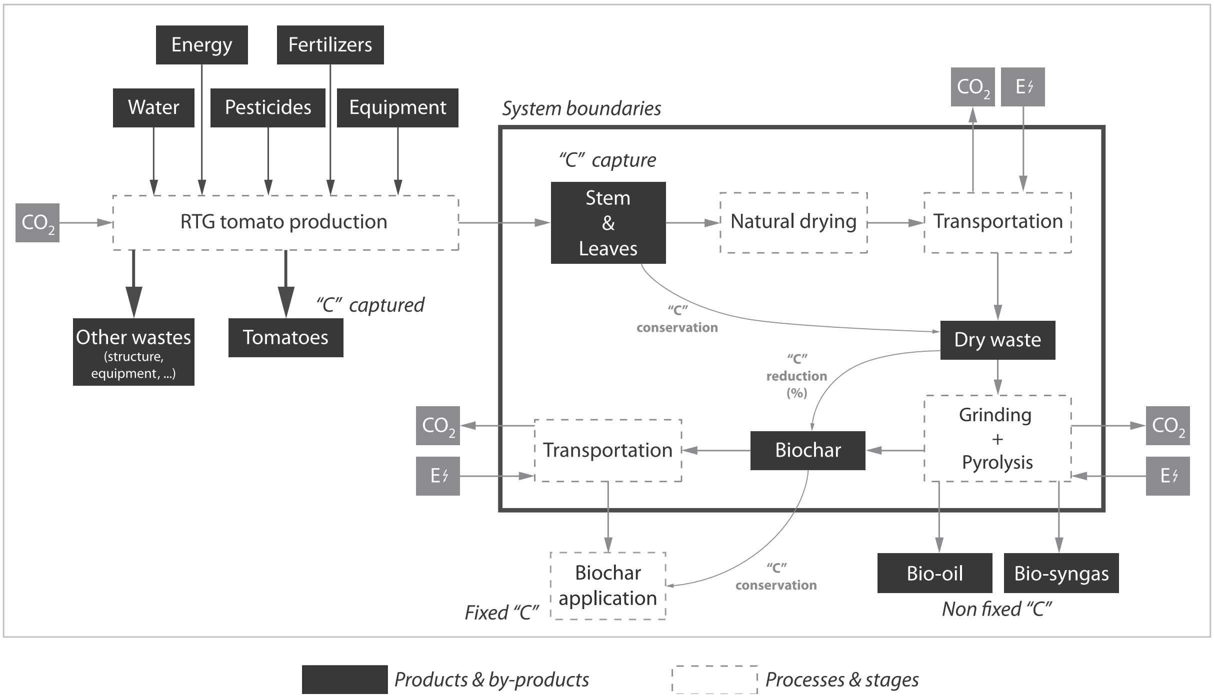

Fig. 1. Carbon flows from biochar production with tomato plant feedstocks and system boundaries under study.

Table 2
Description of the hypothetic scenarios under study. Scenarios A, B and C refer to the %stable-C, while scenarios 1, 2 and 3 refer to the biochar yield.

	Combination of scenario A, B and C with 1, 2 and 3								
	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3
$\%_{\text{Stable-C}}$ assumed	20%	20%	20%	50%	50%	50%	80%	80%	80%
Biochar yield assumed	35%	40%	45%	35%	40%	45%	35%	40%	45%

Table 3
Energy consumption and transportation distances for the production of 1 tonne of biochar according to an input biomass flow rate of 90 kg/h and a different percentage of biochar yields.

	Biochar mass yield (%)	Process	Operation time (h)	Energy consumption (kWh)	Dry feedstock transportation		Biochar transportation	
Scenarios					Mass (t)	Distance (km)	Mass (t)	Distance (km)
A-1/B-2/C-3	35	Pyrolysis	31.7	304.8	2.9	25.0	1	10
		Grinding	51.9	124.7				
A-2/B-2/C-2	40	Pyrolysis	27.8	266.7	2.5			
		Grinding	45.5	109.1				
A-3/B-3/C-3	45	Pyrolysis	24.7	237.0	2.2			
		Grinding	40.4	97.0				

Table 4
Cellulose, hemicellulose and lignin contents of different agricultural and forestry feedstocks.

	Tomato plant		Forestry biomass		Agricultural biomass			Fruit production biomass	
	Tomato stem	Tomato leaf	Softwood	Hardwood	Wheat straw	Switchgrass	Cotton stem	Olive (pruning)	Almond (pruning)
Reference	*	*	McKendry (2002)	McKendry (2002)	McKendry (2002)	McKendry (2002)	Ververis et al. (2004)	Ververis et al. (2004)	Ververis et al. (2004)
Cellulose (%)	28.8	13.7	35–40	45–50	33–40	30–50	40–44	38–42	36–41
Hemicellulose (%)	8.2	3.2	25–30	20–25	20–25	10–40	n/a	n/a	n/a
Lignin (%)	19.7	6.1	27–30	20–25	15–20	5–20	14–16	16–20	24–28

[*] Specifically analysed for the study from a solanum lycopersicum arawak (tomato) crop.

Table 5
Percentage of ashes for different biomasses.

	Agricultural biomass				Forestry biomass		
	Tomato stem*	Tomato leaf*	Rice husk (Yoon et al., 2012)	Olive kernel (Vamvuka, 2009)	Pine woodchips (Puy et al., 2011)	Larch dust (Yoon et al., 2012)	Willow woodchips (Ryu et al., 2006)
% ashes	8–15%	18–23%	16.3%	4.4%	0.39%	0.8%	1.0%

[*] Solanum lycopersicum arawak (tomato) variety.

the pyrolysis plant. This information is explained in more detail in Section 3.1. from the discussion. Since the biochar was not produced, the final C within the biochar was neither quantified. For this reason, different scenarios considering different C contents assumed from the literature were analysed to determine the influence of this parameter on the LCA results.

As Fig. 1 shows, the present study specifically analysed the production of biochar with tomato feedstocks. System boundaries (Fig. 1) do not include tomato production or the related required inputs (i.e., water, fertilizers, and equipment). No environmental impact from tomato production is allocated to the waste stems and leaves and consequently to biochar. The environmental impact of the generation of stems and leaves, which do not have any economic value, was associated with tomato production, the main objective of the crop. Therefore, the impact of this process is associated with tomato production and not with biochar. The system boundaries include the natural drying process of tomato plant waste (leaves and stems), the pyrolysis for biochar production and dry wastes and biochar transportation (see Fig. 1).

As Fig. 1 shows, three different coproducts are produced during pyrolysis. The main high-value coproducts that can be obtained from the pyrolysis process are solid (biochar), liquid (bio-oil) and gas (non-condensable gas) (Xiao et al., 2010). Depending on the temperature and length of the pyrolysis process, different percentages of solid, liquid or gas coproducts can be obtained (Bridgwater, 2003). The environmental impacts for each coproduct were allocated according to the percentage of product mass obtained from original green waste, parameter that is further discussed and described in the following section.

2.5.2. Inventory analysis & description of biochar production with UA feedstocks at urban pilot-scale

From waste stems and leaf generation, no CO_2 emissions were considered, as described in the previous Section 2.5.1. The drying process, which consists of natural drying in or next to the same i-RTG where plants are cropped, see Fig. 1, does not require any energy or specific equipment. Consequently, no CO_2 emissions were associated with this process. For the case of pyrolysis energy consumption, CO_2 emissions were associated with a Spanish medium-voltage energy mix from 2015.

Two transportations may be required during this process: (1) dry feedstock transportation to the pyrolysis plant and (2) biochar transportation to its final destination for soil amendment (see Fig. 1). For the first transportation, it was assumed a distance of 25 km (Table 3), which is the average distance between Bellaterra (where the plants used for the study were cropped) and the industrial areas of northern and southern of Barcelona. For the second transportation, a 10 km distance was selected (Table 3). That is the extension between industrial areas of Barcelona and the periurban crops of the city. For such transportations, the use of lorries with EURO-6 engines with a maximum load between 3.5 and 7.5 metric tonnes was considered.

At the end of the tomato crop used for the study, the plant C content, which was 30.3% for leaves and 35.7% for stems of total dry weight, was analysed through an elemental analysis with a LECO elemental analyser. An average of both values was used for the study. However, not all of the C that is transformed into biochar remains as stable carbon ($\%_{\text{Stable-C}}$) (Mohan et al., 2006). Part of the C in the biochar is realised as biogenic CO_2 into the atmosphere within the first years after the production of biochar (Mašek et al., 2013). The final $\%_{\text{Stable-C}}$ content in biochar produced with forest and agricultural biomasses is between 20% and 80%, of the C into the biochar, depending on the pyrolysis conditions (Mašek et al., 2013; McBeath et al., 2015). To study how the $\%_{\text{Stable-C}}$ influences LCA results and with the aim of covering the ranges of $\%_{\text{Stable-C}}$ found in the literature (from 20% to 80%) *3 scenarios assuming different percentages of* $\%_{\text{Stable-C}}$ *were studied: (SCENARIO A) 20%; (SCENARIO B) 50% and (SCENARIO C) 80%.*

A semi-industrial reactor pyrolysis plant developed by "Energies Tèrmiques Bàsiques SL" was the technology selected to produce biochar with a capacity of 100 kg/h and scalable up to 1 tonne/h. This consists of an intermediate pyrolysis process. The plant comprises eight main parts: a grinding module (obtaining a maximum particle size of 4 mm), the feeding system, a drying reactor, the pyrolysis reactor, a cooling screw, the vessel for solids collection, the cyclone and the condensing system. The process is carried out continuously, and temperature profiles along the reactor are measured using several thermocouples during the process.

This pyrolysis plant selected as a reference has a total energy consumption of 12 kW per operation hour. 9.6 of this 12 kW are consumed during the pyrolysis process when it is carried out at 400 °C

The optimum temperature to increase biochar yield during pyrolysis is from 350 to 400 °C (Tripathi et al., 2016). For the present study, it will be considered that the pyrolysis process for all scenarios occurs at 400 °C due to a lack of data about the energy consumption of the plant for other working temperatures. However, this limitation is not considered relevant because a working temperature of 400 °C is a suitable temperature to obtain high biochar yields from agricultural feedstocks (Colantoni et al., 2016). T*he remaining 2.4 kW, from the 12 kW that the plant consumes, are required during the grinding process to homogenise biomass particles size.*

As mentioned before, many coproducts are obtained from pyrolysis. The percentage of solids liquids or gases varies depending on some parameters of pyrolysis, such as type of pyrolysis, type of reactor, volumetric flow rates, rotation speed of the screws in the reactor and the heat carrier inlet temperature (Brown and Brown, 2012). According to these parameters, the final ratio of total initial solid biomass that results in biochar (from now on referred to as biochar yield) after pyrolysis could be between 11% and 52% (Brown and Brown, 2012; McBeath et al., 2015; Sánchez et al., 2009).

Intermediate pyrolysis plants, which undergo pyrolysis with intermediate conditions between slow and fast pyrolysis (Tripathi et al., 2016), such as the semi-industrial reactor used as a reference for the study, transform between the 35% and the 45% of the initial mass of the feedstock into biochar if the working temperatures are approximately between 350 or 450 °C (Mašek et al., 2013). This value depends on the C-H-O feedstock content

(Shackley et al., 2016), data that was not analysed in the present research. For these reason it was decided to study three *scenarios with different ratios of biochar production yields, between 35% and 45% from initial mass,* to determine how yields influence LCA results*. Concretely biochar yields of (SCENARIO 1) 35%, (SCENARIO 2) 40% and (SCENARIO 3) 45%* were analysed. Then, if these scenarios are combined with the scenarios previously mentioned (A, B and C), 9 scenarios are studied as described in Table 2. The remaining mass that is not transformed into biochar is considered to be transformed into bio-oil or gas; however, the specific mass yields of these two by-products were not determined as they are out of the scope of the study.

Table 3 shows the different energy consumptions calculated for scenarios 1, 2 and 3 to produce 1 t of biochar. Depending on the yield of biochar obtained per unit of input dry feedstock, more or less feedstock will be required to produce 1 t of biochar. The lower percentage of biochar yield is, the more operation time and energy consumption are required per unit of biochar produced for both the grinding and pyrolysis process. The selected pyrolysis, a semi-industrial plant, has a biomass flowrate of up to 100 kg/h. For our study a biomass flowrate of 90 kg/h was assumed, which is an efficient flow rate but not the maximum to ensure more fair scenarios. The grinding engine of the plant had a flow rate of 55 kg/h.

2.5.3. Inventory analysis & description of biochar production with agricultural feedstocks at large-scale in southern Spain

Southern Spain concentrates the largest areas of tomato production in the country. Almeria, is one of the provinces from the region, which concentrates more than 7000 ha of greenhouses intended for the production of tomatoes (MAGRAMA, 2015). For this reason, Almeria province was selected to simulate the production of biochar with agricultural feedstocks at large-scale.

The following data from the pilot-scale scenario in cities was used to create the large-scale scenario:

- C content of tomato plants (30.3%).
- Lorries with EURO-6 engines with a maximum load between 3.5 and 7.5 metric tonnes for transportation.

Due to a lack of data in the literature of slow pyrolysis plants technologies, the pyrolysis plant applied for the present scenario is the same conceptual plant assumed in previous LCA studies of biochar production at larger scale (Roberts et al., 2010). The plant has a dry feedstock flow rate capacity of 10 t h^{-1} and consists of an exothermic process, which needs 58 MJ t^{-1} for the initial start-up of the process. The plant uses 11.1% of the gas coproducts (equivalent to 886 MJ t^{-1}) to produce energy for the drying and pyrolysis processes.

As for the pilot-scale biochar production in cities, two transportations are considered. The first one consists on the transportation of feedstock from the greenhouse to the pyrolysis plant. However, for the larger scale scenario it is considered that the feedstock is still wet. That means that the weight to be transported includes the 80% of water content in the tomato plants stems and leaves used for the study. The second transportation considers the shipping of biochar to the region where will be applied for soil amendment. The distance considered for both transportations was 20 km, which is approximately the average distance between the center of Almeria province and its borders.

For the large-scale biochar production study only an intermediate scenario, such scenario B-2, assuming a biochar yield of 40% and a percentage of final carbon stable of 50% is studied. This is then compared with the production of biochar at pilot-scale in cities.

3. Results and discussion

3.1. Thermogravimetric analysis

As Table 4 shows, on the one hand, the tomato stem lignin content (19.7%) is similar to that of other crop feedstocks (i.e., cotton or olive) but lower than that of softwood (27–30%). This content lignin makes tomato plants interesting for biochar production because biomasses rich in lignin produce higher yields of biochar with higher $\%_{\text{Stable-C}}$ when are pyrolyzed at low temperatures (300–400 °C) (Demirbas, 2006; Fushimi et al., 2003). On the other hand stem's, hemicellulose and cellulose contents (8.2% and 28.8%) are significantly lower compared to the other biomasses in Table 4. In tomato leaf, the cellulose, hemicellulose and lignin contents are lower than the rest of the biomasses from Table 4, making the leaf less interesting for biochar production.

According to the TGA results (Fig. 2), the tomato stems and leaves start to devolatilize from 200 °C to 500 °C. First, hemicellulose decomposition occurs, followed by cellulose decomposition; finally, lignin decomposition starts and lasts until 410 °C. As the TGA shows, a mass loss up to 47% is achieved at 300 °C. It can be observed that at 500 °C, the 83% of biomass conversion is ensured. Hence, the ideal maximum temperatures for tomato plant biochar production may be between 350 °C and 400 °C, resulting in a solid yield between 45% and 38%, respectively. These results agree with previous references that suggest low pyrolysis temperatures to increase biochar production (Tripathi et al., 2016) and are in harmony with the yields defined for the carbon footprint study of 35%, 40% and 45% for scenarios 1, 2 and 3, respectively.

It was also observed that tomato plants stem and leaves produce significant percentages of ashes, probably because of their high content of mineral salts. Respectively, from 8 to 15% and 18 to 23% of the initial mass results in ashes (Table 5). Other biomasses, such as wood or waste wheat biomass, produce less ash, 0.5% and 7% respectively (Table 5). The high ash production of tomato plant feedstock during the thermal processes could represent an important limitation for its use in conventional combustion due to corrosion processes. Additionally, the presence of inorganic compounds, such as metals, could affect the pyrolysis performance and equipment (see Table 5). Therefore, tomato plants feedstocks may be mixed with other biomasses to produce fewer ashes during thermal processes, such as forestry biomasses, which produce low amount of ashes (Table 5). For this reason, other strategies, such as using biochar as a soil amendment, must be addressed to add value to tomato plant feedstocks, which is further developed in the following section.

3.2. Biochar quality and applications

Table 6 contrasts the heavy metal content of our tomato plant feedstock with that of some biochar samples from the literature and the IBI, BQM and EBC heavy metals thresholds. The results show that all of the biochars from the table and our tomato plant feedstock could obtain the IB and BQM certificates. In the case of the EBC certification, all of them could obtain the highest qualification. In general, all of the metals analysed from our tomato plant feedstock were similar to the biochars from the literature. However, the manganese content (Mn), despite being under the thresholds from the certificates, is between 2 and 5 times higher than in the other biochars. This fact could be explained by the retention and accumulation of Mn provided through a micronutrient fertilizer with a 2.5% Mn content. However, it seems that air pollutants caused by traffic do not have a negative effect on these results.

According to the results in Table 6, tomato plant feedstock has a great potential for the production of biochar for soil amendment.

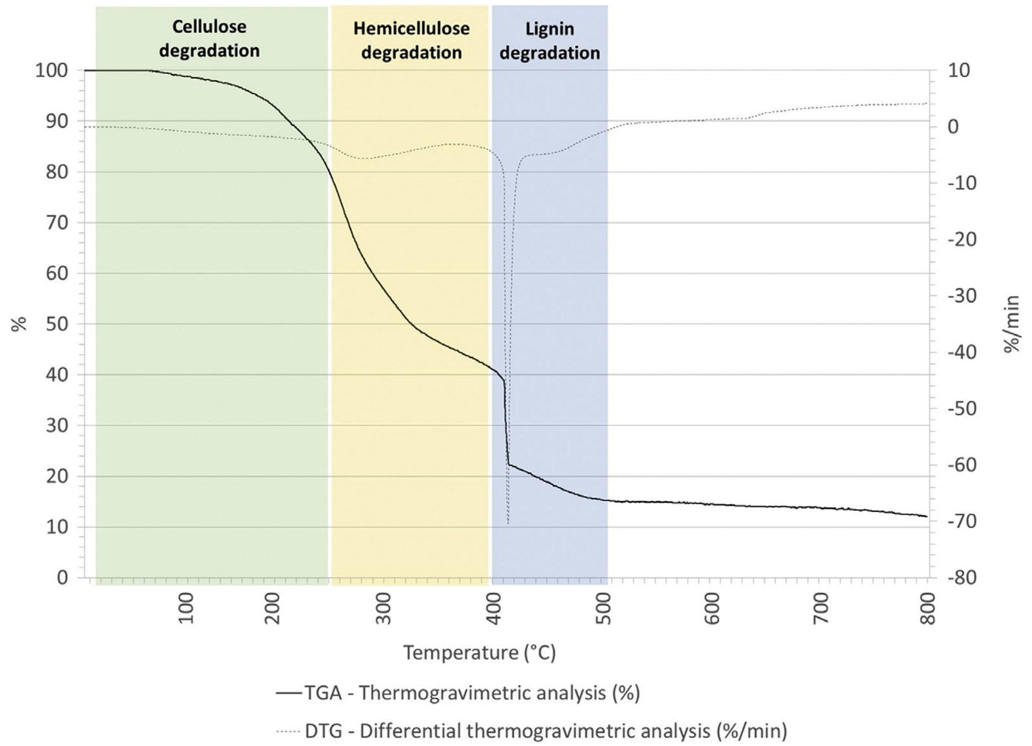

Fig. 2. TGA of *Solanum lycopersicum arawak* (tomato) stem mixed with leaves. The figure also shows the main compounds (cellulose, hemicellulose or lignin) that are degraded at certain temperatures.

Table 6
Metal content of tomato plant feedstock and different agricultural and forestry biochars compared to the IBI, BQM and EBC biochar certification thresholds.

			Agricultural biomass			Forestry biomass				European biochar certificate (EBC, 2012)		
		Units	Dry tomato feedstock (ashes from TGA realized)	Corn (300 °C-12 h and 600 °C–2.5 h) (Freddo et al., 2012)	Vine shoots (400 °C-3 h) (Venegas et al., 2015)	Tree barks (400 °C-3 h) (Venegas et al., 2015)	Bamboo (600 °C-2.5 h) (Freddo et al., 2012)	IBI guidelines thresholds (IBI, 2015)	BQM thresholds (Hackley et al., 2014)	Premium biochar thresholds	Basic biochar thresholds	High grade biochar thresholds
Arsenic	As	mg/kg	<0.81**	0.25	n/a	n/a	0.29	12–100	100	n/a	n/a	10
Cadmium	Cd	mg/kg	<0.81**	0.03	0.6	1.2	0.03	1.4–39	39	1	1.5	3
Chromium	Cr	mg/kg	5.07	5.09	n/a	n/a	4.39	64–100	100	80	90	15
Copper	Cu	mg/kg	20.27	10.6	17	33	6.31	63–1500	1500	100	100	40
Lead	Pb	mg/kg	1.27	0.06	1.7	4.2	3.87	70–500	500	120	150	60
Mercury	Hg	mg/kg	<0.81**	n/a	n/a	n/a	n/a	1–17	17	1	1	1
Manganese	Mn	mg/kg	147.43	n/a	56	27	n/a	n/a	n/a	n/a	n/a	3500
Molybdenum	Mo	mg/kg	0.95	n/a	n/a	n/a	n/a	5–75	75	n/a	n/a	10
Nickel	Ni	mg/kg	1.55	0.37	1.6	13	1.25	25	600	30	50	10
Selenium	Se	mg/kg	<0.81**	n/a	n/a	n/a	n/a	1–100	100	n/a	n/a	5
Zinc	Zn	mg/kg	49.2	92	105	73	0.29	200–2800	2800	400	400	150

*Mix of stem (50%) and leaves (50%).
** Below detection levels.

Moreover, other applications for biochar produced with tomato feedstock could be studied. Depending on the porosity, thermal conductivity, heating power, final nutrient content or mechanical properties of biochar obtained, it could be used to substitute raw materials from products (i.e., insulation materials, mattresses, active carbon filters, paints, or cosmetics) and consequently reduce resource depletion while storing stable C.

3.3. Biochar carbon footprint

The final amount of C that finally remains stable into the biochar depends on: (1) the percentage of feedstock mass y_s that is transformed into biochar and (2) the percentage of the total C available in the transformed biomass that stays as stable C and not as volatile. To calculate the final kg of CO_2 equivalent fixed by plants (Fig. 3) that remains as stable C ($\%_{Stable\text{-}C}$) within the biochar, formula 1 was used:

$$CO_2eq. = (m_{drybiomass} \cdot y_s \cdot \%_{C-content} \cdot \%_{Stable-C}) + m_{oxygen} \qquad (1)$$

where $m_{dry\ biomass}$ is the mass of dry biomass required to produce 1 tonne of biochar (according to functional unit); is the biochar yield produced; $\%_{C\text{-content}}$ is the C content of tomato plant (*Solanum lycopersicum arawak* variety) biomass used for this study which was

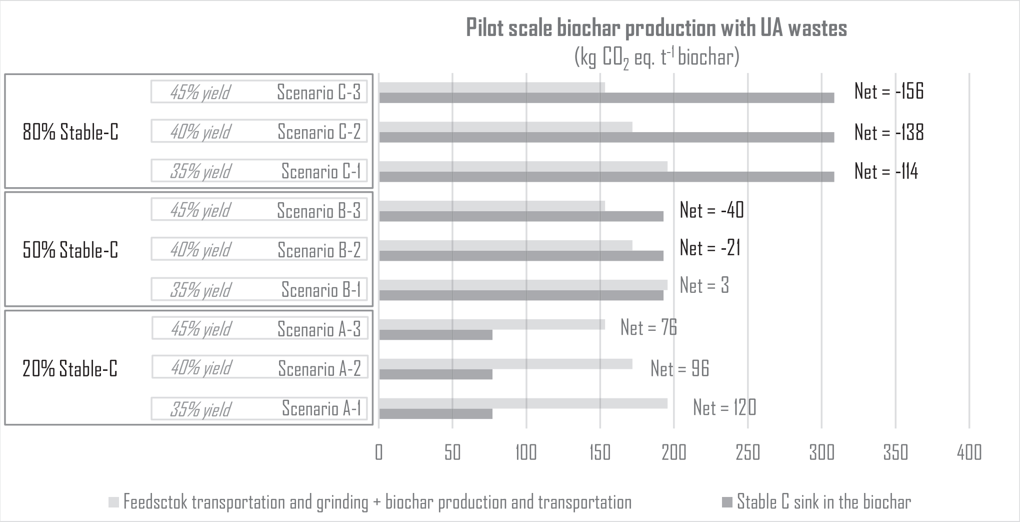

Fig. 3. CO_2 emissions from transportation and production for the production of one tonne of biochar, carbon sink achieved and net carbon emissions for the multiple scenarios under study.

Table 7
Average carbon footprint distribution of the scenarios under study.

	Life cycle stages				
	Dry feedstock transportation	Grinding	Pyrolysis	Biochar transportation	Total
kg CO2 eq.	30.8	39.6	96.8	4.9	172.1
%	18%	23%	56%	3%	100%

30.3%; and the m_{oxygen} is the mass proportion of oxygen to produce one particle of CO_2 with each unit of mass of C fixed in the biochar.

As Fig. 3 shows for scenarios A-1, A-2, A-3 and B-1, the C balance is not favourable as more emissions are emitted during transportation, grinding and pyrolysis than are fixed as stable C within the biochar. So net emissions (emissions from transportation, grinding and pyrolysis minus final stable C) are positive. For these scenarios, it cannot be considered that C is being fixed when biochar is produced. Nevertheless, in case biochar was used as a raw material to produce another product (i.e., insulation materials, mattresses, active carbon), instead of for soil amendment, environmental advantages could be obtained compared to the original raw material used in products. Depending on the final application, biochar could be considered a raw material with a low carbon footprint.

If the final application is considered to be soil amendment, for the rest of scenarios (B-2; B-3; C-1; C-2 and C-3), the CO_2 eq. emissions sink within the biochar are higher than emissions emitted for its generation (see Fig. 3). For these case studies, it can be assumed that there is a carbon sink between 21 and 155 kg of CO_2 eq. t^{-1} of biochar. For the scenario with better results, C-3, the CO_2 sink was 2 times higher than emissions from the pyrolysis process.

As can be observed in Fig. 3, the final stable C into the biochar seems to be a key variable to guarantee that the net emissions of producing biochar are negative. The variation of production yield (a minor production yield implies higher dry feedstock mass transportation and more operation time, see Table 3) between scenarios has a significant but lower influence on result than the final C stable into the biochar (Fig. 3).

The distribution of the carbon emissions for the different stages (Table 7) for the biochar production is very similar to all scenarios (± 1%): 18% transportation of feedstock to pyrolysis plant; 23% grinding process; 56% pyrolysis process and 3% transportation of biochar to the field for its application into soil. The low transportation distances of the feedstock and biochar helps significantly to avoid emissions during these stages, however production stage penalizes seriously the final emissions balance. Reducing the energy losses of the pyrolysis process, which is a small-scale pilot plant, may result on a significant reduction of the emissions emitted during this stage.

3.4. Comparison between urban pilot-scale and large-scale biochar production

Fig. 4 compares the carbon emissions between the biochar production at pilot-scale in urban areas with UA feedstocks and at large-scale with feedstock from conventional crops. As can be observed, total and net emissions for the pilot-scale scenario are lower. It has the potential to sink carbon emissions; however, the large-scale scenario does not.

The large-scale scenario emits 33 kg CO_2 eq. t^{-1} biochar less than the pilot-scale plant during the pyrolysis process. This could be explained by the optimization of heat loses of the pyrolysis plant of the large-scale scenario. Nevertheless, for the transportation stage of feedstocks to the plant, the large-scale scenario emits 93 kg CO_2 eq. t^{-1} biochar more because the feedstock is wet unlike the pilot-scale scenario. In addition, emissions from biochar transportation to field for soil amendment are the double (10 kg CO_2 eq. t^{-1} biochar) than for the pilot-scale scenario, because the transportation distance for the large-scale scenario is the double too. According to results, the urban pilot-scale scenario is interesting from a logistics point of view, but it is penalized by the low efficiency of the pyrolysis plant. Moreover, if for the large-scale feedstock was dry instead of wet for its transportation to the plant

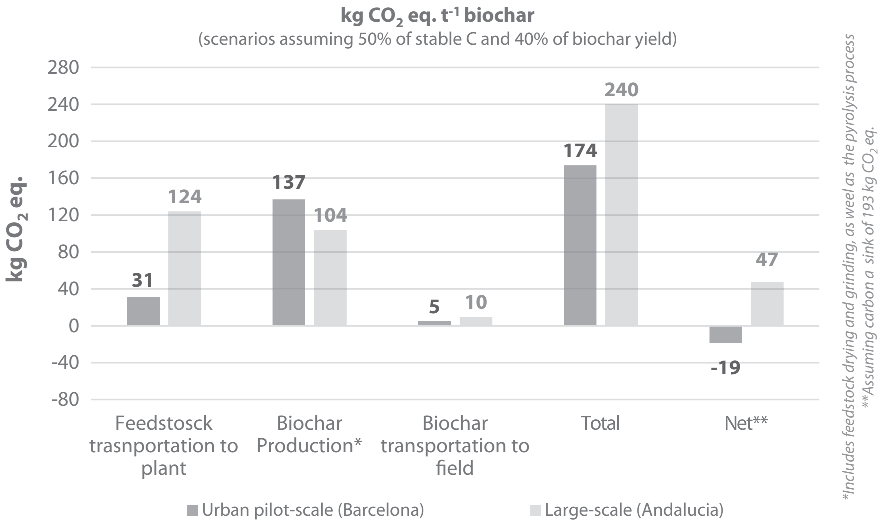

Fig. 4. Carbon emissions from biochar generation at pilot-scale in urban areas (Barcelona) with UA feedstocks and at large-scale (Andalucia) with agricultural feedstocks from conventional food production. (It was assumed a 50% of final stable C in biochar and a biochar yield from production process of 40%).

approximately 93 kg CO_2 eq. t^{-1} biochar could be avoided and the final net emissions could be -43 kg CO_2 eq. t^{-1} biochar.

4. Conclusions

The cellulose, hemicellulose and lignin contents of *Solanum lycopersicum arawak* (tomato variety) stem (28.8%, 8.2% and 19.7%, respectively) show that there is a great potential to valorise these residues by producing biochar. However, low lignin content (6.1%) in leaves does not make them very suitable for biochar production if not mixed with other biomasses with a high lignin content, such as forestry biomasses. The potential biochar yield production from tomato plant biomass can be between 38% and 45% according to TGA results. Nevertheless, the $\%_{\text{Stable-C}}$ into the biochar needs to be quantified in future research. Percentages equal or higher than 50% may be required to ensure C sink with biochar production with UA feedstock with pilot-scale plants. Therefore, C fixed by UA tomato plant feedstock has the potential to reduce emissions to cities, urban agriculture and products. However, these results may be used carefully to avoid double accounting.

The transportation of dry waste biomass for biochar production should be minimized to ensure the production of environmentally friendly biochar. The transportation of the final biochar produced should be minimized as well; nevertheless, its environmental impact per kilometer transported is lower than the transportation of the dry waste required to produce the biochar. Both biochar yield and $\%_{\text{Stable-C}}$ will determine the maximum transportation distances for each type of biochar to ensure that the biochar is fixing and not emitting CO_2 eq. emissions. The higher the biochar yield and $\%_{\text{Stable-C}}$ are, the greater transportation distances that the biochar could be transported.

According to the IBI, BQM and EBC certificates and to the low content of heavy metals in tomato plant biomass, the biochar produced with these feedstocks could be safely used for multiple applications, including soil amendment. Air pollution caused by traffic in urban areas does not seem to affect the results. Nonetheless, further research is required to determine how tomato plant biomass should be mixed with other biomasses, such as forestry biomasses, to reduce ash production during thermal processes. Moreover, the thermal and mechanical properties of biochar may be determined for different biochar samples produced with tomato plant biomass to determine its potential application to produce new products, such as insulation material or mattresses.

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