

Upcycling Sunflower Stems as Natural Fibers for Biocomposite Applications

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One of the big global, environmental, and socioeconomic challenges of today is to make a transition from fossil fuels to biomass as a sustainable supply of renewable raw materials for industry. Growing public awareness of the negative environmental effects of petrochemical-based products adds to the need for alternative production chains, especially in materials science. One option lies in the value-added upcycling of agricultural by-products, which are increasingly being used for biocomposite materials in transport and building sector applications. Here, sunflower by-product (obtained by grinding the stems) is considered as a source of natural fibers for engineered biocomposite material. Recent results are shown for the main mechanical properties of sunflower-based biocomposites and the socioeconomic impact of their use. This paper demonstrates that sunflower stem makes a good candidate feedstock for material applications. This is due not only to its physical and chemical properties, but also to its socioeconomic and environmental rationales.

Keywords: Agricultural by-product; Biocomposite; Natural fiber; Sunflower stem; Waste management

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INTRODUCTION

Over the last few decades, increasing environmental concerns have prompted a surge in research by the composite science community to develop natural-fiber biocomposites. These materials can be completely degraded in soil, or, by composting, do not emit volatile organic compounds, and are softer on the environment than petrochemical resource-based products (Mohanty *et al.* 2000; Lithner *et al.* 2011). Agricultural by-products have several advantages over classical natural fibers: they do not need dedicated agricultural fields, they are already readily available, and they offer valuable environmental compatibility over standard-feedstock fibers (Reddy and Yang 2005). These factors are increasingly central now that biocomposites have found widespread use in all areas of life. The reason for this increasing use of biocomposites is performance at lower cost and reduced density when compared to classic synthetic materials (Reddy and Yang 2005). Nonetheless, some agricultural by-products are already exploited by second-generation biorefineries (Pfaltzgraff and Clark 2014). Therefore, the main objective for the bio-based material sector now is to find new sources of fibers to avoid competition with the growth

of crops for human food or biofuels (Kopetz 2013). In this context, the present work focuses on a promising agricultural by-product, sunflower stems. Sunflower by-products are of interest because they are not currently exploited, their composition enables low-impact extractability from the field, and oilseed biorefineries can achieve greater economic viability by selling their by-products.

Sunflower-based oil ranks fourth in world oil crop production, with nearly 25 million hectares (FAOSTAT 2013). Seed and oil have been the main compounds exploited by industry. In most cases, seed and oil are both extracted from the head, and the stems are left in the fields. No significant industrial use of the stems that are shredded after seed harvesting has currently been proposed, although sunflower stems are exploited for combustion applications, animal feed, and/or fuel production (Chen and Lu 2006). These solutions consume only a small fraction of the sunflower by-product production. We propose to explore a new way of extracting value from sunflower stems by evaluating their potential as a natural fiber feedstock for biocomposite applications. Considering five tons of sunflower stalks per hectare, the potential production of this by-product reaches 125 million tons. In comparison with other natural fibers (not including wood), this potential production tonnage is higher than that of bamboo farming (30 million tons, mostly in Asia and South America), which, alongside cotton, is one of the most heavily produced sources of commercial fiber in the world (Faruk *et al.* 2012). The potential value of sunflower by-products as a biofiber is enhanced by the fact that sunflower is grown worldwide (FAOSTAT 2013). This could create opportunities to build a new worldwide agricultural economy and is a key advantage over other agricultural by-products, like bamboo, that are not available across the world. Furthermore, sunflower by-products are available in large amounts at zero or negligible price in an economic context, where the natural-fiber biocomposites market grew by 15% between 2005 and 2010 (Lucintel 2011). Indeed, the entire composite market is growing. For example, the polymer composites market has increased from 33 billion Euros in 2002 to 41.5 billion Euros in 2005 (Friedrich and Almajid 2013). This surge in the natural fibers market is primarily driven by the automotive and building sectors (John and Thomas 2008). In the automotive sector, EU and US legislations impose specific directives on the end-of-life of vehicles. For instance, the non-recycled fraction of materials will be cut by 5% in 2015 in Europe (European Commission. Directive 2000/53/EC 2000). In addition, natural fibers are expected to provide a 30% weight reduction and a 20% cost reduction compared to classic composites (Bledzki *et al.* 2006). Furthermore, the low density of natural fibers equates to significant energy savings (primarily fuel) and their economic value may be extended to all fields of transportation (railway, marine, aerospace) (Bledzki *et al.* 2006; Friedrich and Almajid 2013). Natural fibers are also exploited in building applications, not only for their low density but also for their thermal insulating properties. Their development was recently stimulated in the USA and in Europe by legislation imposing enhanced energy efficiency of existing buildings by 2020 (European Commission. Directive 2010/31/EU 2010), which yielded a significant market in green retrofit solutions.

This work presents the main results obtained from a project (Demether 2011) whose objective was to produce biocomposites for building insulation by factoring not only chemical and physical properties but also the environmental and socio-economic impacts tied to processing and use (Fig. 1). In view of the results obtained, it is argued that sunflower stems can be useful for other biocomposite-using applications such as automobiles. First, general results are presented corresponding to sunflower by-product properties, highlighting both unpublished and published data by giving associated

references. Note that examples of biocomposite engineering using sunflower by-products can be found elsewhere (Mati-Baouche *et al.* 2014, 2015; Sun *et al.* 2015). In this context, the objective here was twofold: i) to report the main results of the project about the properties of the sunflower stems; ii) to report the general project conclusions on the use of sunflower by-products to give the interested reader a clear picture of what can be expected from this innovative type of biocomposite.

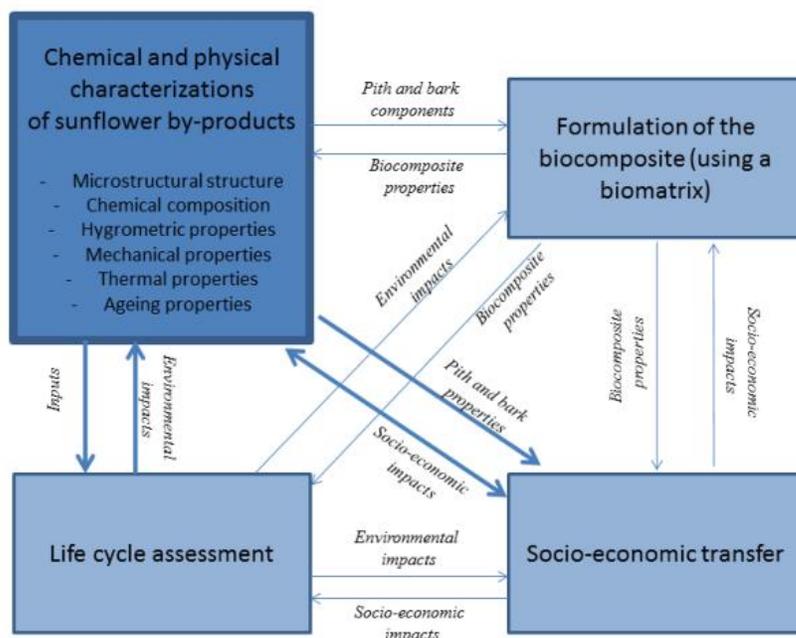


Fig. 1. General flowchart of the design of insulating biocomposite. The article focuses on the main physical and chemical properties of sunflower stems obtained under this project framework.

EXPERIMENTAL

Sample Description

This study characterized the material properties of the stems of LG5474 sunflower species harvested in September 2010 in Perrier, France. Two particular on-stem locations were defined as the bottom and the top of the stalk (Fig. 2). The bottom location was defined as the level of the first node above the roots. Note that no specific (mechanical or chemical) treatment was performed, as it has been shown that specific treatments may alter certain properties (Li *et al.* 2007), as will also be shown by results presented in the discussion that follows. However, as explained earlier, this paper focuses on the properties of fibers, and any investigation into the influence of mechanical or chemical treatments would require a dedicated companion paper. Evidence that these fibers are useable without any particular treatment can be found elsewhere (Mati-Baouche *et al.* 2014; Sun *et al.* 2015).

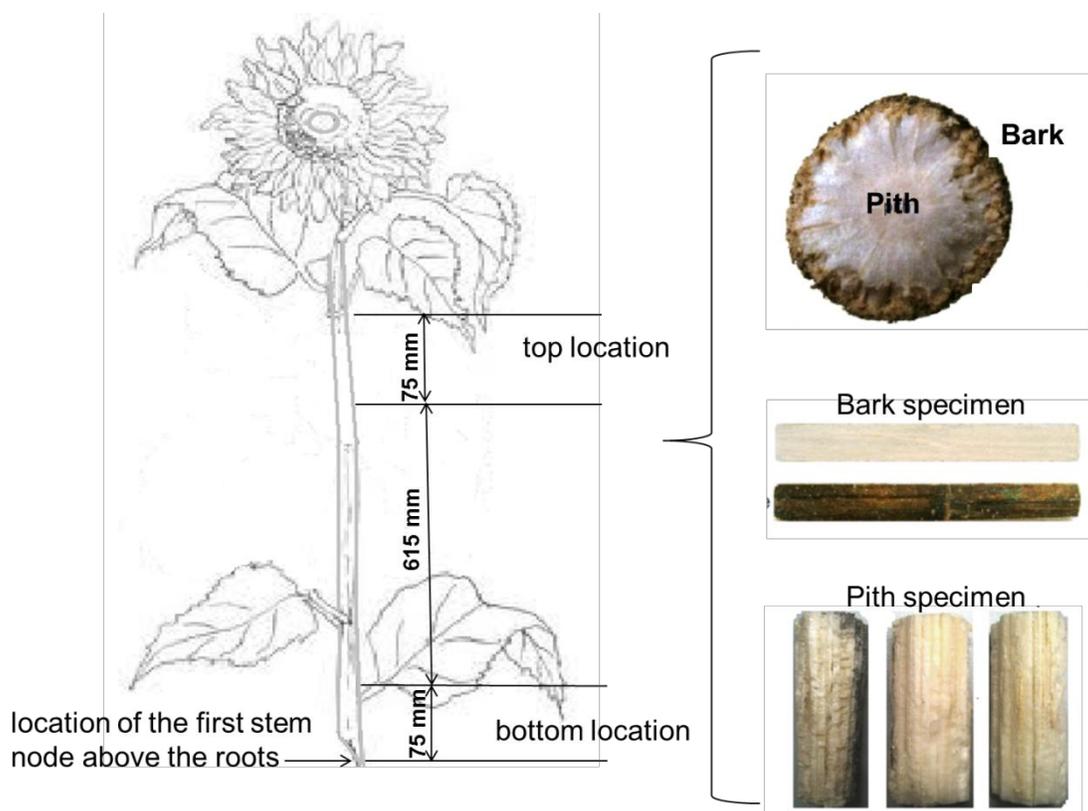


Fig. 2. Sampling zones and specimens tested

Microstructural Analysis

Sections of bark were first separated from the stem, saturated with water, immersed, and kept in three PEG (polyethylene glycol electrolyte) solutions at various concentrations (30%, 60%, and 100%) for 24 h each. A 20 μm -thick sample was cut using a fully automated Leica (Wetzlar, Germany) RM2255 rotary microtome. It was then colored with the so-called double-staining method using safranin (for the presence of lignin) and astra blue (for the presence of cellulose). After coloration, the samples were dried with Joseph paper. They were mounted on a cover-slip with the fast-drying Eukitt (Freiburg, Germany) mounting medium. Finally, micrographs of these cross-sections were obtained using a Zeiss (Oberkochen, Germany) optical microscope. These images were processed with the ImageJ software (National Institutes of Health, USA) to estimate the porosity of the barks extracted from both the bottom and top locations. Macroscopic voids in the pith make it difficult to separate pith and bark. Therefore, the analysis should be carried out on complete stem sections. The analysis was performed using the Skyscan (Anvers, Belgique) CT-Analyzer with two sections of stem extracted from the bottom and top locations. The working length was 30 mm.

Cellulose and Lignin Assays

A biochemical analysis was performed on bark of different stem specimens at different locations (bottom, centre, and top). For the pith, cellulose and lignin assays were applied without distinction of in-stem location. The Henneberg protocol (Henneberg and Stohmann 1860, 1864) was used to quantify the percentage of cellulose (C). Lignin content (L) was evaluated by the procedure of Jarrige (Jarrige 1961).

Hygrometric Analysis

Absorption and desorption tests were performed at various relative humidities (RH) (8%, 33%, and 75%) to deduce both the absorption and desorption coefficients. A desiccant (phosphorus pentoxide) was placed in the oven beforehand. The specimens were then placed in a conditioning chamber (one for each desired value of RH). These chambers were polymer jars in which saturated aqueous salt solutions imposed a certain RH. The RH depends on the nature of the salt. Absorption and desorption coefficients were deduced from the mass-time curves using suitable relationships that depend on specimen geometry. The different solutions corresponding to different RH levels were prepared according to standard ISO 483 procedure (2005). These tests lasted at least three days to ensure that equilibrium was obtained within the specimens. Six bark specimens and five pith specimens were tested for each experimental condition. See Sun *et al.* (2013, 2014) for further details.

Mechanical Analysis

Results for bark specimens were obtained using a Deben (Suffolk, UK) micro-machine equipped with a 2-kN load cell. The cross-head speed was 2 mm/min with a clamping length of 30 mm. Results for pith specimens were obtained by compression tests using an Instron (Norwood, USA) 5543 testing machine equipped with a 500-N load cell. The cross-head speed was 5 mm/min. Ten specimens were tested for each experimental condition.

Thermal Analysis

The thermal diffusivities of the bark and pith specimens were measured with the laser flash method. The specific heat capacity was measured with a C80 Setaram (Caluire, France) calorimeter. Finally, the thermal conductivity of the bark and pith specimens was deduced by multiplying apparent density (equal to the mass divided by the volume of cylindrical specimens) by thermal diffusivity and heat capacity. Another transient technique (Hot Disk from ThermoConcept, France) was used to check the thermal conductivity values on pith specimens and yielded similar results. Six samples were tested for each experimental condition.

Ageing Analysis

Three weather conditions were tested: humidity, temperature, and UV radiation. The humidity and temperature values used for the ageing analysis were 75% and 80 °C, respectively. Specimens were tested for the ageing conditions of 75% humidity, 80 °C, and the combination of both. The ageing condition of 75% humidity was achieved according to the procedure given in the ISO 483 (2005) standard. Conditioning at 80 °C was performed using a Salvislab Thermocenter oven (Rotkreuz, Switzerland). The combined conditions were obtained using a Vötsch (Hanau, Germany) VCL 4003 climatic oven. The UV exposure (1000 h) was performed in the accelerated conditions given by the Atlas MTT (Mount Prospect, USA) SEPAP 12 – 24 chamber, which corresponds to the ageing condition described in the usual standards on this subject (NF-T51-195-5 2008; BS EN 16472 2014).

Spectroscopic Analysis

Fourier-Transform Infrared (FT-IR) measurements were carried out using a Thermo Scientific (Waltham, Massachusetts) Nicolet 6700 FT-IR instrument. The IR spectra (128

scans) were recorded at room temperature on a MTEC (Ames, USA) 200 photoacoustic detector (referenced against carbon black powder; detector chamber was purged with dry helium gas) with a wave-number range of 700 to 4000 cm^{-1} . The spectra were analyzed with Thermo Scientific (Waltham, Massachusetts) Omnic software. Six bark specimens and four pith specimens from the bottom and top locations were tested.

Environmental Assessment

For the comparison of environmental impacts between maize and sunflower, EcoInvent data for crop production (Nemecek and Kagi 2007) was used. The endpoint impacts (Goedkoop *et al.* 2009) associated with the production of maize grain and sunflower seeds in one hectare (Nemecek and Kagi 2007) were compared, *i.e.*, 9279 kg/ha for maize and 3151 kg/ha for sunflower. The farming system considered here was integrated production (IP). Included processes were soil cultivation, sowing, weed control, fertilization, pest and pathogen control, harvesting, and drying the grains. Machine infrastructure and a shed for housing the machine were included. Inputs of fertilizers, pesticides, and seed, as well as their transport to the regional processing centre (10 km), were considered.

RESULTS AND DISCUSSION

Obtained results are detailed and analyzed in the following sections. However, for the sake of clarity, the main results are reported schematically in Fig. 3. The pith and bark properties are compared with those of other natural fibers in Table 1.

Table 1. Main Properties of Bark, Pith, and Other Natural Fibers

	Bark	Pith	Other natural fibers	References
Young modulus (GPa)	[4.6-6.4]	$[0.15-1].10^{-3}$	Pineapple : 1.4 Oil palm: 3.2 Jute: 10 Flax: 80	(Faruk <i>et al.</i> 2012) (Faruk <i>et al.</i> 2012) (Ahmad <i>et al.</i> 2015) (Ahmad <i>et al.</i> 2015)
Specific modulus (GPa.m ³ .Kg ⁻¹)	[0.013-0.018]	$[0.005-0.034].10^{-3}$	Coir : [0.0033-0.005] Jute: [0.00685-0.0206] Flax: [0.0184-0.053]	(Ahmad <i>et al.</i> 2015)
Strength (MPa)	[25-31]	$[3.3-23].10^{-3}$	Coir : 175 Jute : [393-800] Flax: [800-1 500]	(Ahmad <i>et al.</i> 2015)
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	0.12	0.039	Flax: [0.035-0.075] Hemp: [0.040-0.094] Glass wool: [0.04-0.05] Stone wool: [0.035-0.05]	(Kymäläinen and Sjöberg 2008)

Pith and Bark Microstructures

The stem volume constitutes 90% of the sunflower. It is made of two main parts: bark and pith. Intuitively, the bark can be expected to be used for applications requiring mechanical strength, and the pith for thermal insulation purposes, because of its large volume fraction of intragranular pores. Preliminary microscopy observations showed that the pith and bark both change in appearance along the stem (Fig. 3). The number of sclerenchyma fibers in the bark increases going up the stem, while porosity decreases from

59% at the bottom to 53% at the top. The pith shows more macroscopic voids at the bottom of the stem (63%) than at the top (56%).

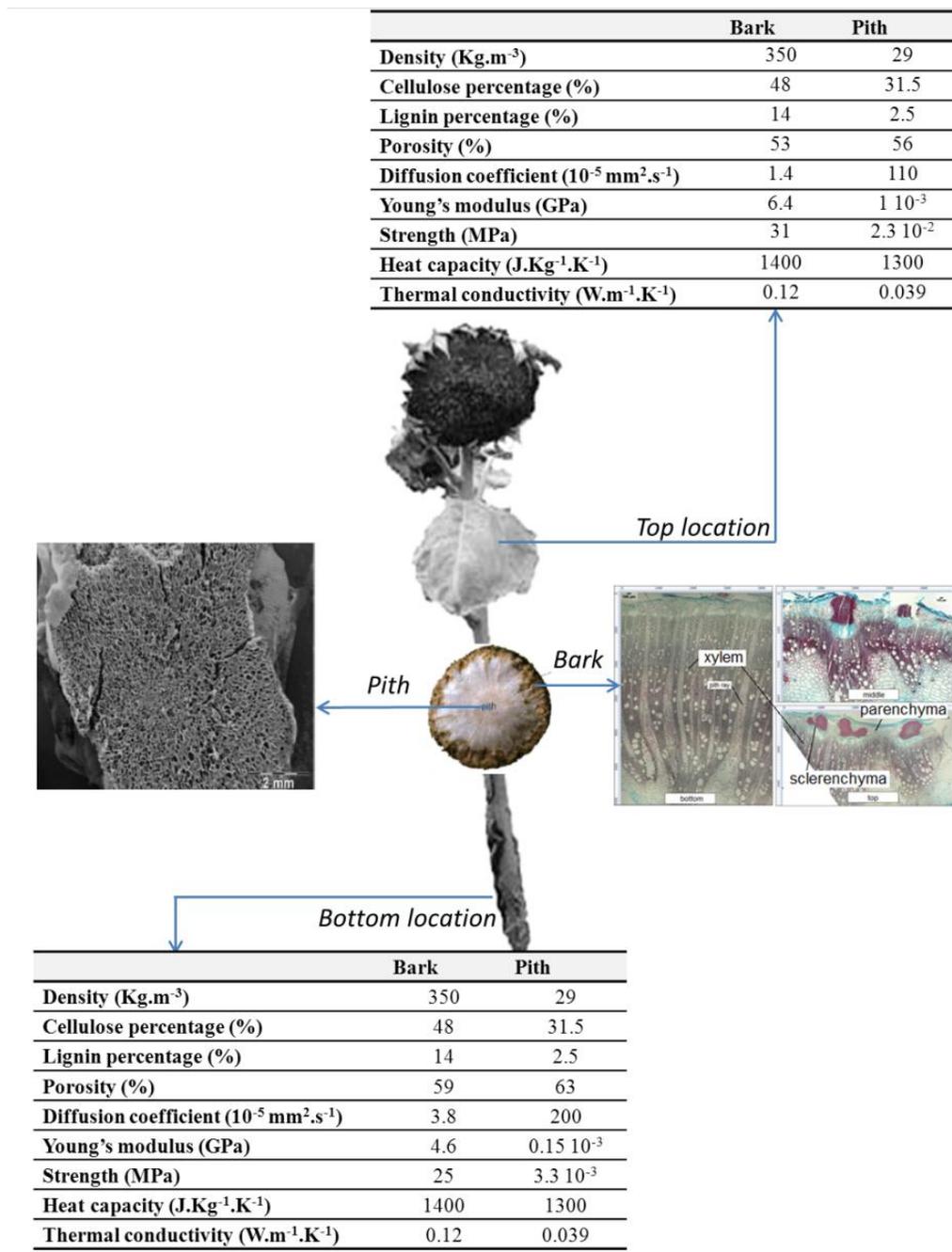


Fig. 3. Main physical and chemical properties of sunflower stems

Biochemical Composition

Biochemical analysis revealed that the chemical composition did not vary along the stem, with a mean composition of 48% cellulose and 14% lignin for the bark, and 31.5% cellulose and 2.5% lignin for the pith. Note that the chemical composition of sunflower stem bark (14% of lignin) is very close to that of jute (13% of lignin) (Summerscales *et al.* 2010). The chemical composition may directly influence the material properties of these

two parts of the stem. However, it does not completely explain the variations in material properties observed along the stem. Therefore, the influence of microstructure along the stem on material properties was examined. Because it is well known that RH significantly influences the material properties of natural fibers, hygroscopic tests were performed beforehand.

Hygroscopic Behavior

The tests results clearly revealed that the diffusion coefficients for moisture of both the bark and pith specimens were higher at the bottom ($3.8 \times 10^{-5} \text{mm} \cdot \text{s}^{-1}$ for the bark and $200 \times 10^{-5} \text{mm} \cdot \text{s}^{-1}$ for the pith) than at the top of the stem ($1.4 \times 10^{-5} \text{mm} \cdot \text{s}^{-1}$ for the bark and $110 \times 10^{-5} \text{mm} \cdot \text{s}^{-1}$ for the pith). This is primarily because of the difference in porosity along the stem. The moisture diffusion mechanism depends directly on cell cavities, as described and explained for other materials such as wood (Times 2002a,b). Two mechanisms govern the moisture diffusion process in sunflower stems: bound water diffusion through the cell walls, and vapour diffusion through the cell cavities. Moisture diffusion through cell cavities is more significant than moisture diffusion through the cell walls. Therefore, the porosity of both the bark and pith specimens is expected to change the value of the macroscopic diffusion coefficient obtained from the hygroscopic tests. In the situation considered in this work, the increase in amount of porosity or decrease in amount of cell wall content of the specimens is expected to increase the value of the moisture diffusion coefficient. Subsequently, the effect of various RH levels was evaluated relative to both the mechanical and thermal properties.

Mechanical Properties

Mechanical tests were carried out to evaluate Young's modulus and the strength of both the bark and the pith. As expected, bark specimens expressed higher Young's modulus values (4.6 GPa at the bottom and 6.4 GPa at the top) than pith specimens (0.15 MPa at the bottom and 1 MPa at the top). It is worth noting that high RH tended to decrease the Young's modulus (a near 10% differential between 0% RH and 75% RH). However, this effect was less significant than the influence of the sample location along the stem. The difference in Young's modulus between bark and pith was in accordance with their chemical composition. Bark has a higher lignin percentage and a lower mean intergranular pore volume fraction than pith. Furthermore, the Young's modulus of both bark and pith increased along the stem, obtaining higher values at the top, which was attributed mainly to the lack of cavities. There was also an increase in the mechanical strength of bark (from 25 to 31 MPa) and pith (from 3.3 to 23 kPa).

The Young's modulus of sunflower stem bark (4.6 to 6.4 GPa) is on par with other by-product fibers, including oil palm (3.2 GPa) or pineapple fibresones (1.4 GPa) (Faruk *et al.* 2012). With respect to other natural fibers extracted from stems, such as flax, hemp or jute, the Young's modulus of sunflower stem bark is slightly lower (lying between 10 GPa for jute and 80 GPa for flax fiber) (Ahmad *et al.* 2015). The trade-off between the Young's modulus and the density is also a key-issue in many applications, for instance, in the automotive industry. In the case of sunflower stem bark, the specific modulus (ratio of the Young's modulus by the density) is between 13 and 18 $\text{GPa} \cdot \text{m}^3 \cdot \text{Kg}^{-1}$, which is very close to the value of the Young's modulus of jute (Ahmad *et al.* 2015). This value enables designers to consider the sunflower stem bark for producing components of vehicles to reduce weight and therefore fuel costs as well.

Thermal Properties

The thermal conductivity also was investigated for both the bark and the pith (Pennec *et al.* 2013). As expected, pith showed a lower mean thermal conductivity ($0.039 \text{ W.m}^{-1} \text{ .K}^{-1}$) than bark ($0.12 \text{ W.mm}^{-1} \text{ .K}^{-1}$). In contrast to the Young's modulus, the thermal conductivity of both the bark and the pith did not evolve along the stem. The variation of the pore volume fraction is thought to be too small to have a significant influence on thermal conductivity. Moreover, both bark and pith demonstrated significant heat capacity values (mean values of 1400 and $1300 \text{ J.kg}^{-1} \text{ .K}^{-1}$ for bark and pith, respectively) approaching levels found in hemp fiber (nearly $1500 \text{ J.kg}^{-1} \text{ .K}^{-1}$). Additionally, preliminary experiments carried out while varying the RH of the samples from 0 to 100 wt% revealed that the thermal conductivity of pith and bark can double because of the absorbed water.

In terms of thermal insulation applications, the pith showed interesting thermal properties. Its thermal conductivity ($0.039 \text{ W.m}^{-1} \text{ .K}^{-1}$) was even better than the thermal conductivity of glass wool ($0.046 \text{ W.m}^{-1} \text{ .K}^{-1}$) and its heat capacity was on a par with hemp. The thermal conductivity of the pith was competitive with other natural fibers. For example, flax's ranges between 0.035 to $0.075 \text{ W.m}^{-1} \text{ .K}^{-1}$, depending on the harvest location and the variety (Kymäläinen and Sjöberg 2008). Hemp's is between 0.040 and $0.094 \text{ W.m}^{-1} \text{ .K}^{-1}$ (Kymäläinen and Sjöberg 2008). Therefore, sunflower pith may be considered as raw materials for thermal insulation applications.

Ageing Results

The biodegradable character of sunflower plants makes them environmentally safe for waste disposal but makes sunflower-based fiber sensitive to weather conditions. The ageing properties were studied by testing the influence of different weather conditions such as humidity, temperature, and UV radiation on the variation in Young's modulus. The Young's modulus of both the bark and the pith were unaffected if only one weather condition was increased (temperature or moisture exposure alone). Increasing both the temperature and moisture exposures ($80 \text{ }^{\circ}\text{C}$ and 75% RH) did not affect the Young's modulus of the bark, but it diminished the Young's modulus of the pith by about 30% after one week (and 50% after two weeks). After UV treatment for 1000 h (equivalent to a 3-year exposure), the oxidation of organic matter was detected by FTIR measurements. Absorption bands at 1703 and 3500 to 2200 cm^{-1} were detected and attributed to the C=O and OH stretching vibrations of carboxylic groups, respectively. These carboxylic acids were most likely from the breaking of polymeric chains.

Environmental Impact

Finally, the environmental impact of exploiting sunflower stems in the rural economy was investigated. Life cycle assessment is a requirement to evaluate the environmental impacts of natural fibers (Joshi *et al.* 2004). The reasonable quantities of water, fertilizers, and pesticides that are needed per hectare seem promising compared to maize, rape, and wheat crops. Using available EcoInvent data for crop production (Nemecek and Kagi 2007), it is possible to assess the impact of sunflower plants over their entire life cycle. Figure 4 presents these results using the ReCipe impact assessment method (Goedkoop *et al.* 2009) for three impact categories, which are human health, ecosystems, and resources. The various effects of sunflower plants over their life cycle were compared against those of maize, which is the most widely grown grain crop. The question of a partial allocation of the agricultural phase to stems depends on their status. As long as sunflower stems are considered agricultural waste, then no impact of the

agricultural phase should be allocated to their production. However, a huge surge in the use of sunflower stems for biocomposite applications would lead to competition for their exploitation, which would prompt a change in the status of sunflower stems and a move them up from “waste” to a valuable “co-product.” In this case, either (i) the part of the environmental impacts of sunflower production should be allocated to the production of the stems, based for instance on a financial allocation; or (ii) the system boundaries should be extended and substitutions should be studied to share agricultural impacts.

Sunflower cultivation has less environmental impact, in terms of water need, fertilizer, and pesticide, than a standard crop production such as maize. Moreover, using existing by-products constitutes an environmental benefit in comparison with other natural fibers, which require a dedicated agricultural field that increases the environmental impacts.

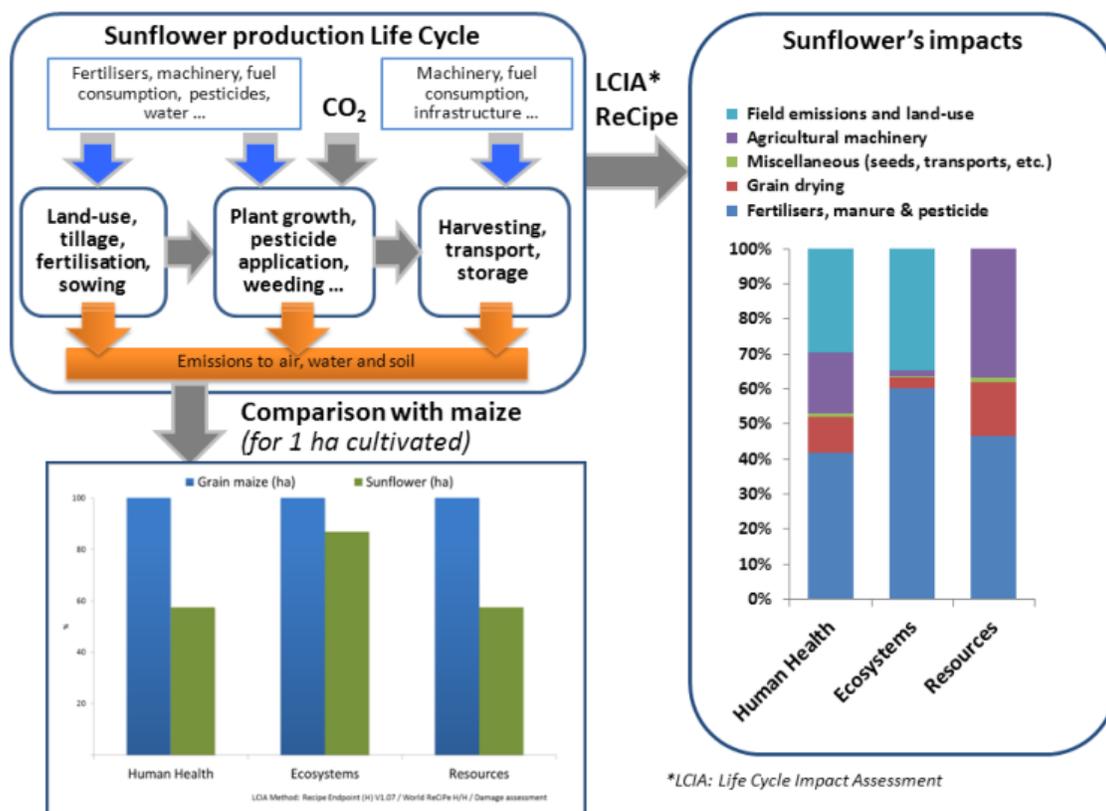


Fig. 4. Environmental analysis of sunflower production

CONCLUSIONS

In Europe and in the USA, legislative and public opinion pressures affecting the use of bio-based materials are rising (Technology Road Map for Plant/Crop Based Renewable Resources 2020 in the USA or the Biomass Action Plan in Europe). The sunflower stems, not yet valued, constitute a promising raw material for a variety of applications. This is mainly due to their mechanical and thermal properties as well as to their environmental impact. Detailed studies will be required in order to characterize the influence of different treatments or industrial processes on the properties of the sunflower

bark and pith, depending on the industrial application. Sunflower also offers a number of socioeconomic assets in a growing natural fiber market of large stocks, low price, and worldwide crop ability. It is also necessary to study in details (like other natural resources), such as how to organise the local agricultural sector for collecting and storing the sunflower stems as well as processes for their conversion into bio-based materials. Further research is therefore needed for moving away from a promising raw material to an effective solution in terms of both physical properties and socio-economic valorization.

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