

Effect of temperature on the release of volatile and odorous compounds in flax fibers

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ABSTRACT: The behavior of flax fibers was investigated at temperatures of 80 °C, 200 °C, 215 °C, and 230 °C for a period of 60 min. First, thermogravimetric and colorimetric analyzes were carried out to characterize the impact of the temperature on the weight loss and the color of the fibers. Then, the release of volatile and odorous compounds from flax fibers was studied using both chemical and sensory approaches. Solid phase micro extraction was done to isolate the volatile organic compounds (VOCs) from the headspace of the sample while gas chromatography-mass spectrometry (GC-MS) and olfactometry (O) were used to determine the volatile and odorous compounds released at each temperature. About 24 VOCs were identified in the volatile fraction of flax fibers with a high occurrence of aliphatic aldehydes, phenols, and furans. Quantification by GC-MS and by the aroma extract dilution analysis method was implemented. The results point to a critical temperature between 215 °C and 230 °C from which the odor of flax fibers becomes more intense, more complex, and with unpleasant features. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43497.

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INTRODUCTION

Flax fibers (*Linum usitatissimum*) are traditionally used for textiles, paper, and agricultural applications. Over the past decade, several studies have shown that among all natural fibers, flax fibers are also suitable for composite materials,^{1–3} owing to their good mechanical properties, low density, and wide availability in Europe.^{4–7} Concerning their composition, flax fibers are linked to each other by a central lamella constituted of pectin, hemicellulose, lignin, and wax. Fibers are made up of two (primary and secondary) concentric cell walls, and the secondary wall is itself divided into three layers. The thick secondary cell wall is made essentially of cellulose and other noncellulosic polysaccharides.^{7–9}

The use of flax fibers as reinforcement in composites has gained popularity due to an increasing requirement for developing sustainable materials for engineering applications mainly in automotive industry. Composites are made of flax fibers coupled with thermoplastic, thermoset, and biodegradable matrices. The fiber content in composites varies commonly up to 40% and different configurations are found (continuous filaments, chopped fibers, mats, ...). However, one of the problems in combining flax fibers with other materials is poor thermal stability which may result in degradation of the fiber components when temperatures above 150 °C are applied during the manufacturing process.^{10–12} This leads to the formation of

low-molecular-weight compounds that can be responsible for undesirable odors. To date, the thermal degradation of flax fibers, considering both the emission of volatile organic compounds (VOCs) and their associated odors, has not been reported. Weston *et al.* (2012) investigated the accelerated hydrothermal degradation of fibers of Phormiumtenax (New Zealand flax) for 55 days at 70 °C.¹³ They showed that VOCs were released during aging including acetic acid, furfural, and a series of short- to medium-chain aliphatic aldehydes. From these results, authors supposed that these compounds could provoke unpleasant odors, especially for furfural. However, it is known that VOCs released in the headspace of a sample do not always induce an odor as it depends on whether the concentration of the compound in the headspace is higher than the human threshold odor concentration or not. Moreover, some compounds at a low concentration may not be detected using conventional gas chromatography (GC) analyses but will all the same participate to the global odor. Last, as odors are produced by a mixture of different compounds, interactions are likely to occur between compounds (masking effect, enhancement, and so on). Consequently, it is not possible to predict the global odor only by the chemical analysis of the VOC emissions in the headspace.¹⁴ For these reasons, additional tools using human detection can successfully characterize the global odor by sensory analysis, on the one hand, or GC-MS (mass spectrometry) coupled with olfactometry (O) to determine the odorous

compounds of a mixture, on the other hand.¹⁵ Using such an approach, Felix *et al.* (2013) carried out a characterization of VOCs and odors focused on wood plastic composites.¹⁶ More than 140 compounds were identified in the headspace of samples by solid phase microextraction (SPME) and GC-MS. In addition, 19 odorous sections were evidenced using GC-MS coupled with olfactometric analysis. In their work, it was shown that hexanoic acid, acetic acid, 2-methoxyphenol, acetylfuran, diacetyl, and aldehydes were the most odorous compounds.

The aim of this work was to simulate the release of VOCs and their associated odors while processing flax fibers under elevated temperatures. To that purpose, the emission of VOCs and odors was investigated under different temperatures using both chemical and sensory analyses. Four temperatures were studied from 80 °C to 230 °C to reproduce the heat treatments applied during manufacturing processes such as extrusion for composite materials. Thermogravimetric analysis (TGA) and colorimetric analyses were done to determine the weight losses and color variations that heat treatments can cause on flax fibers. Simultaneously, the extraction of VOCs released from flax fibers in the headspace was done using SPME. A combination of GC-MS and GC-O analysis was carried out to identify and quantify VOCs and specifically odorous compounds released at each temperature. Finally, results made it possible to distinguish odor profiles for flax fibers for each temperature.

EXPERIMENTAL

Materials

Nonwoven flax fibers were obtained from Dehondt (Notre-Dame de Gravenchon, France), commercialized under the trade name “Lintex M10-F.”

Methods

Thermal Characterization of Flax Fibers. Experiments were conducted using a TGA (Setsys TG-12, Setaram, Caluire, France) to assess the thermal stability and the moisture content of the flax fibers. The measurements were carried out on 12 ± 1 mg samples placed in an aluminum pan and heated from 30 °C to 800 °C with a heating rate of 20 °C/min in ambient air. Four replications were performed.

Colorimetric Analysis. To carry out the analyses, a colorimeter (spectrophotometer CM-5, Konica Minolta, Langenhagen, Germany) was used in transmission mode. Flax fibers of weight 150 ± 1 mg were weighed and placed in an open vial of 20 mL and held in an incubator to be heat-treated for 60 min. Four temperatures were studied (80 °C, 200 °C, 215 °C, and 230 °C).

The aforementioned flax fibers were then packed into a Petri dish to be analyzed. Flax fibers kept at ambient temperature (T_{amb}) without heat treatment were also analyzed. Each analysis was repeated three times.

For all measurements, the $L^*a^*b^*$ system was used to monitor data. L^* corresponds to the percentage of clarity from 0 to 100 (0% being the darkest and 100%, the brightest). Coordinates a^* and b^* give information about the nuances: a^* is the deviation in green–red direction and b^* is the deviation in blue–

yellow direction, where a^* and b^* extend over a scale from -100 to 100 .¹⁷

Analysis of VOCs by SPME and GC-MS-O. For GC analysis, 150 ± 1 mg of flax fibers were weighed and placed in 20 mL headspace (HS)-vials and then introduced into an oven for 60 min at the four different temperatures (80 °C, 200 °C, 215 °C, and 230 °C). The HS-vials were kept open in the oven. After heating, the vials were closed with a PTFE/Silicone septum (Supelco, St Quentin Fallavier, France) and placed in a bath at 80 °C, for 30 min of preincubation and 30 min of SPME fiber exposure (extraction). HS-SPME was used to extract the volatile compounds of the flax fibers. A silica-based SPME fiber coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm , Stableflex) from Supelco (St Quentin Fallavier, France) was used for extraction. All the SPME fibers used were initially conditioned in the injector port of the GC at 250 °C for 1 h. Between each set of extractions, the SPME fiber was held at 250 °C for 10 min.

The VOCs present on the SPME fiber were analyzed by GC using a Perkin Elmer Instrument (Clarus 580 Perkin Elmer) coupled with MS (Clarus 560S Perkin Elmer, Villebon sur Yvette, France) and a sniffing port Sniffer 9000[®] (Brechtbühler, AG, Schlieren, Switzerland). The compounds were desorbed for 5 min with a thermal desorption temperature of 250 °C in the GC injector. Helium was used as the carrier gas at constant flow rate of 1 mL/min. The chromatographic column used for separation was the SLBTM-5 ms fused silica capillary column (5% Phenyl, 30 m \times 0.25 mm \times 0.25 μm , Supelco, St Quentin, France). The oven temperature was programmed as following: initial hold at 40 °C for 3 min, 10 °C/min to 100 °C, then 4 °C/min to 190 °C and finally 15 °C/min to 250 °C held for 5 min.

At the end of the chromatographic column, the effluent was split between the mass spectrometer and the sniffing port (1:2), both being maintained at 250 °C with transfer line.

The MS was operated in the electron impact positive ionization (ionization energy 70 eV; source temperature 200 °C). Full-scan data acquisition was registered over a mass range of 35–550 a.m.u. GC-MS analyses were conducted in duplicates for each sample.

A standard solution of *n*-alkanes (C_6 – C_{16} in ethanol) was injected with the same operating conditions. Thus, the VOCs were identified by comparing the MS spectra to the National Institute of Standards and Technology mass spectral library (NIST) and the calculated Kovats indices (KI) to KI reported in Flavornet, Odour, and Pherobase databases. Moreover, single-referent compounds were injected to confirm identification and to measure the quantity of each identified compound.

For the odor characterization of VOCs, the sniffing port (Sniffer 9000[®], Brechtbühler, AG, Schlieren, Switzerland) with the effluents were enriched with humidified air at 20 mL/min. Two assessors, already well-experienced in GC-O evaluation procedures, proceeded to analysis. Signed consents were obtained from assessors to participate in this study. For each odor stimulus, assessors were asked to record the detection time by pressing the remote control. For each odor stimulus, the “Field of Odors” was used

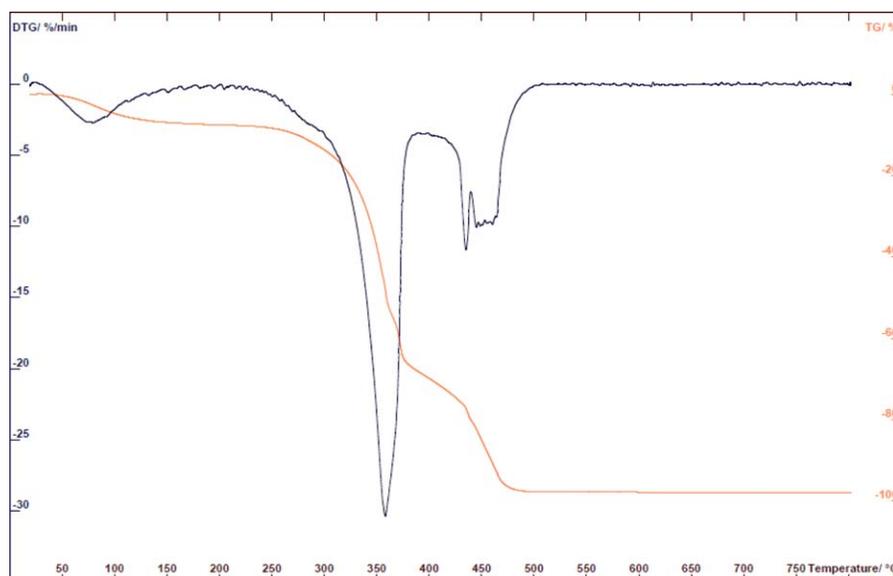


Figure 1. TGA curve from flax fibers with a ramp of 30–800 °C with 20 °C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to give a verbal odor descriptor. This method, proposed by Jaubert *et al.* (1995), is based on 45 pure molecules which permit the characterization of an odor by direct comparison with chemical substances.¹⁸ The name of the substance defines the descriptors, while its odor consists of the reference. Once the panelists have memorized the 45 reference substances, it is possible to obtain an objective description of the smell without personal evaluations. The microphone and the transcription were operated by Dragon Naturally speaking Premium volume 11 (Nuance). Nose To Text Software (Brechtbühler, AG, Schlieren, Switzerland) was used for voice recognition and to collect GC-O data. GC-O analyses were conducted in duplicates for each sample. The aromagrams were traced from 5 to 30 min.

The odorant compounds were identified by comparing the MS spectra to the NIST library, the calculated Kovats indices (KI) to KI reported in Flavornet, Odour, and Pherobase databases and odor descriptions.

Olfactory Quantification of VOCs. To quantify the odor intensity of each extracted compound by SPME and identified by GC-O, the aroma extract dilution analysis (AEDA) method was set up, as was the case in Kim *et al.* (2003).¹⁹ The dilution factor (FD) was determined for each compound found in flax fibers, and it was calculated as follows:

$$FD = d^{n-1}$$

with d , the constant dilution factor (for these analyses, it was 2) and n , the number of successive dilutions required until the assessor no longer perceives the olfactory compound. The split ratios made it possible to simplify the dilutions. Analyses were performed with ratios (0:1), (1:1), (3:1), and (7:1).

RESULTS AND DISCUSSION

Thermogravimetric Analysis

TGA thermograms obtained for the flax fibers are shown in Figure 1.

Three mass losses were observed as reported in the literature.^{20–22} The first weight loss between 50 °C and 100 °C was attributed to the evaporation of water; this loss was equal to 6%. The second peak, with a weight loss of 58% at 360 °C, was related to the degradation of cellulose, hemicellulose, and pectins.^{23–25} The third peak between 430 °C and 520 °C corresponded to a 33% weight loss. This loss could be due to oxidation of lignin and the cleavage of the glycosidic linkage of cellulose.^{20,24} This analysis made it possible to identify and confirm the three mass losses that characterize flax fibers during heat treatment. At the beginning, there was a water loss followed by fiber degradation starting from 200 °C.

Impact on the Coloring of Flax Fibers

Color measurements of the surface of flax fibers were performed at ambient temperature—80 °C, 200 °C, 215 °C, and 230 °C—according to the $L^*a^*b^*$ color scale (Figure 2).

At ambient temperature, flax fibers were characterized by a light-brown color. After treatment at 80 °C for 60 min, the nuances of flax fibers were not modified, that is, the a^* and b^*

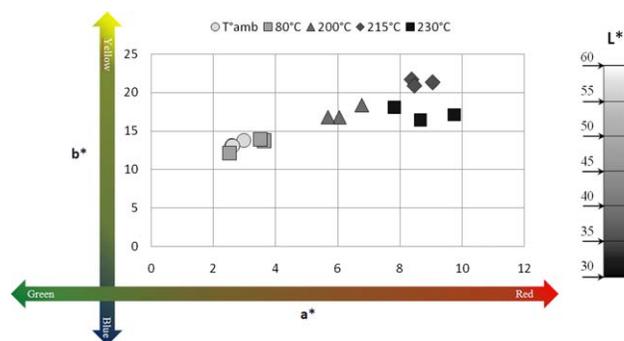


Figure 2. Color variation of the flax fiber at various temperatures for 60 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table I. Identification and Quantification by GC-MS-O of VOCs from Flax Fibers According to the Temperature

Compound	KI cal ^a	Odor descriptor	Identification method	Quantification GC-MS ($\mu\text{g/g}$)—60 min			
				80 °C	200 °C	215 °C	230 °C
n.i.	425	Fatty, butter	n.i.	0.000	0.019	0.054	0.062
Acetic acid	483	Sour	R ^b , MS ^c , IR ^d	n.q.	0.026	0.024	0.216
Pentanal	608	Almond, malt, spice	R, MS, IR	0.000	0.012	0.013	0.056
Hexanal	750	Green, fatty, aldehyde	R, MS, IR	n.q.	0.006	0.007	0.065
Furfural	807	Almond, baked bread, sweet, woody	R, MS, IR	0.000	0.000	0.088	0.695
Furfurylalcohol	836	Burnt, sweet, caramel, bread, coffee	R, MS, IR	0.000	0.008	0.015	0.090
Hexanol	870	Resin, flower, green	R, MS, IR	n.q.	0.000	0.000	0.000
Heptanal	907	Fatty, citrus, rancid	MS, IR	0.002	0.004	0.005	0.058
Butyrolactone	920	Caramel, sweet	R, MS, IR	0.120	0.037	0.051	0.025
5-Methylfurfural	973	Caramel, almond, burnt sugar	R, MS, IR	0.000	0.000	0.000	0.025
Benzaldehyde	978	Almond, burnt sugar	R, MS, IR	0.000	0.000	n.q.	0.085
Hexanoic acid	979	Sweat	R, MS, IR	n.q.	0.000	0.000	0.000
Octanal	1009	Fatty, soap, lemon, green	R, MS, IR	0.003	0.005	0.005	0.056
1-Hexanol, 2-ethyl-	1037	Rose, green	MS, IR	0.056	0.000	0.000	0.000
Guaiacol (phenol-2-methoxy)	1096	Phenolic, smoke, spice, vanilla, woody, medical	R, MS, IR	0.000	0.000	0.000	0.026
Nonanal	1110	Fatty, aldehyde	R, MS, IR	1.817	0.656	0.546	0.467
Nonanol	1138	Fatty, waxy, cucumber	MS, IR	n.q.	0.000	0.000	0.000
Octanoic acid	1177	Sweat, cheese	R, MS, IR	0.148	0.000	0.000	0.000
Dodecane	1206	Alkane	R, MS, IR	0.000	0.000	0.000	0.003
Decanal	1211	Soap, orange peel, tallow	R, MS, IR	0.004	0.016	0.016	0.078
Undecanal	1316	Fresh, fruity, orange	R, MS, IR	0.000	0.118	0.124	0.448
Vanillin	1410	Vanilla	R, MS, IR	0.000	0.017	0.015	0.034
Dodecanal	1414	Lily, fatty, citrus	R, MS, IR	0.002	0.007	0.007	0.014
1-Dodecanol	1482	Fatty, waxy	R, MS, IR	0.086	0.000	0.000	0.000

n.i., nonidentified compounds; n.q. nonquantified compounds.

^aKovats retention index calculated for retention time of peaks in chromatogram.

^bReferences of previous identification of compound in flax fibers.

^cMass spectrum interpretation.

^dRetention index identification.

values had not changed, whereas L^* had slightly decreased from 56 to 49. However, when the temperature reached 200 °C, flax fibers became darker: a^* and b^* increased, indicating an increase in the red and yellow color, while the clarity decreased to 43. When heating to 215 °C, coloring was intensified in the same way. Then, at 230 °C, the value of b^* decreased while a^* continued to increase. At this temperature, the red shade was accentuated and fibers were of dark color with L^* equal to 33. These data show the impact of temperature on the degradation of flax fibers by surface colorimetry. With increasing temperature, we can observe an intensification of the red and yellow colors and a decrease in clarity corresponding to a darkening of the sample. Between 215 °C and 230 °C, we observe mainly a variation in the red color and a drop in clarity.

Identification and Quantification of VOCs

Analyses by HS-SPME-GC-MS of flax fibers in open vial conditions have resulted in identifying and quantifying the major components. VOCs released by the flax fibers were analyzed at

the four aforementioned temperatures. The details of the VOCs identified are indicated in Table I, which includes the names, the calculated Kovats indices, and the identification method used. Many compounds were identified but only the major odorous ones were quantified; 24 in total, of various chemical structures.

Experiments carried out made it possible to identify a large number of VOCs released from flax fibers with a significant temperature effect. Only very few studies have focused on the VOCs emitted from flax fibers. Weston *et al.* (2012) described the volatile compounds released from fibers of *Phormium tenax* (New Zealand flax) during an accelerated hydrothermal degradation (closed vial at 70 °C with water).¹³ They identified 21 components including a majority of aliphatic aldehydes that may have arisen from the oxidation of long chain fatty acids found in lipopolysaccharide material. Aliphatic aldehydes were also detected in our study. For example, hexanal, heptanal, octanal, nonanal, decanal, and dodecanal were analyzed with growing abundance. As

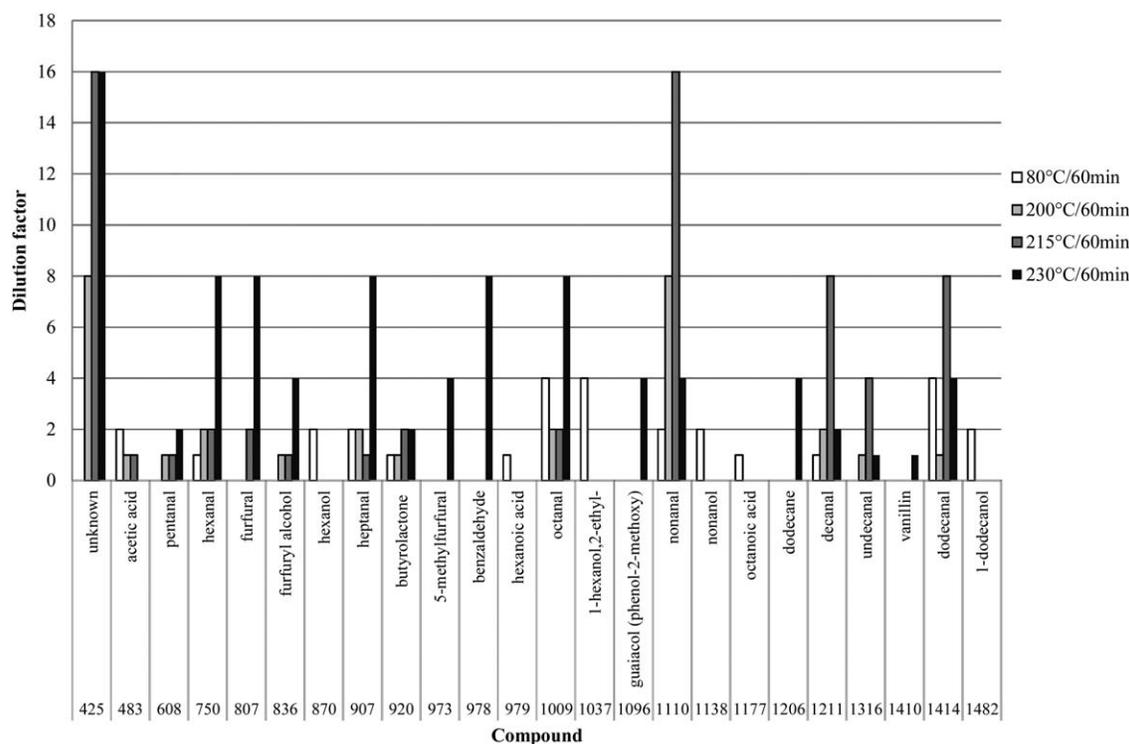


Figure 3. Influence of temperature on odorous compounds released from flax fibers exposed to a heat treatment.

temperatures increase, their quantity increases significantly at 230 °C. In fact, nonanal was obtained from the oxidation of oleic acid and was the major product observed, but its quantity decreases with increasing temperature.

According to Weston *et al.* (2012), the most obvious change in the composition of the VOCs during degradation was the increase in abundance of acetic acid and the appearance of furfural after 2 weeks.¹³ This is in accordance with our results because acetic acid was released at each temperature with an increasing abundance at 230 °C, becoming the major compound at this temperature. At 80 °C, an acetic acid peak is present but coelution skewed quantification. Indeed, the acetic acid resulted from the hydrolysis of acetate groups which were attached to pendant sugars along the chain of the hemicelluloses of the plant fibers. Once released, the acetic acid could further catalyze hydrolysis of the acetate groups and finally also catalyzed hydrolysis of the xylan chain. In this way, the production of acetic acid was a major cause of degradation of the material made from fibers having high levels of hemicellulose. Moreover, furfural was detected from 215 °C with an increase in abundance at 230 °C. According to Lattuati-Derieux *et al.* (2006), furfural was produced until all the hemicelluloses had been degraded.²⁶

Other compounds were also identified and quantified during these experiments. Data were available in the literature concerning wood-derived products and their thermal degradation.^{16,27–31} During this process, biopolymers such as lignin, cellulose, and hemicellulose are degraded by thermal reaction, which induces a sharp modification of the chemical composition according to the temperature. Mainly phenolic compounds and also carboxylic acids (acetic, hexanoic, and octanoic acids) are formed from lignin thermodegradation. In particular,

phenol, vanillin, derivatives of guaiacol, and eugenol were also identified in wood lignin.^{1,27–29,32} Our results suggest that lignin thermodegradation occurs from 200 °C.

Olfactory Quantification

Quantification of the odorous compounds responsible for the odor profile of flax fibers was also carried out. Two assessors, trained to the “Field of Odors,” identified the compounds by sniffing after dilutions of smell by split, following the AEDA method of ranking odorous compounds according to their sensory impact. Figure 3 represents the dilution factor (FD) according to each compound identified at each of the four different temperatures under study. These analyses made it possible to quantify the odorous compounds and thus followed the evolution of the odor of flax fibers with temperature.

At 80 °C, the odor of flax fibers is low and characterized by 14 key compounds belonging mainly to aliphatic aldehydes and carboxylic acids. The odor profile of flax fibers can thus be described as fatty, green, acid, flowery, and also sweet due to butyrolactone. At 200 °C, the odor is more intense but the profile remains mainly fatty with the appearance of a burnt feature because of the impact of furfuryl alcohol. At 215 °C, the odor profile of flax fibers becomes more roasted and caramel-like due to the occurrence of furfural. At 230 °C, 17 key odorous compounds compose the odor of flax fibers. The impact of furfural and furfuryl alcohol is more pronounced and the phenolic and pyrogenic features are boosted by 5-methylfurfural, benzaldehyde, and guaiacol. The intensity of the odor and the presence of such characteristics may induce a negative appreciation of the odor.

As a conclusion, the odor profile changes with temperature. A critical temperature is reached between 215 °C and 230 °C and

generates a more intense and more complex odor with a phenolic and burnt smell. These results on flax fibers may be connected with the odor of composite materials reinforced with flax fibers. The odor of materials is depicted as fatty, sweet, caramel-like, smoked, and roasted. It is likely that the elevated temperature during processing is a prospect to control the odor of composite materials containing flax fibers.

CONCLUSIONS

The emission of volatile compounds and the characteristics of flax fiber odors were analyzed at four temperatures between 80 °C and 230 °C. Analyses by TGA have confirmed a thermal degradation in three steps. The first is attributed to the evaporation of water. The next two steps are caused by the degradation of cellulose, hemicellulose, pectin, and finally, the oxidation of lignin. The second degradation started at around 200 °C. Colorimetry showed a decrease in the clarity of the flax fibers with increasing temperature, mainly between 215 °C and 230 °C. Similarly, a variation of the red shade was accentuated at 230 °C.

Twenty-four compounds were identified and quantified by SPME-GC-MS-O. During the heat treatment, an increase in the number and quantity of VOCs emitted into the headspace was highlighted. VOCs release from flax fiber reaches a critical threshold between 215 °C and 230 °C. From this point, different compounds due to the lignocellulosic thermodegradation were identified, more particularly aliphatic aldehydes, phenolics, and furans. The odor profiles of the sample also changed with temperature and were quantified with the AEDA method. Compounds such as acetic acid and furfural were increasingly present with the increase in temperature. All these data help to understand the behavior of flax fibers at elevated temperatures to control the emission of VOCs and the associated odors during processing and transformation.

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