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Impact of storage conditions on preparation of activated carbon from sheep wool fibres

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Abstract. In the European Union, up to 200 thousand tons (Zoccola et al., 2015) of sheep wool fibres, that are not used for textile fabrication, are a secondary by-product with wide field of application possibilities, including preparation of activated carbon. Taking into account, that wool fibres can be stored for long time, under impact of the local climate conditions (including low temperatures) before their application, for example, under variety of temperature, presence of air and light, different moisture conditions, it is necessary to estimate the impact of wool's storage conditions on the preparation of activated carbon. In the present work, various parameters, such as, temperature, presence of air and daylight as well as humidity, were selected for comparison. After storage of wool fibres under selected various conditions, thermogravimetry/differential thermal analysis (TG/DTA) followed by with Fourier transform infrared (FTIR) spectrometry were used in order to estimate the impact of each parameter on the thermal decomposition processes: release of moisture, sulphur and nitrogen containing compounds and oxidative degradation followed by release of carbon dioxide. It was estimated, that one year of storage under varying conditions does not significantly affect the thermal decomposition properties of the wool fibres. However, minor impact of humidity absorbed from air on wool is observed. Wool samples that were stored at elevated humidity gave higher residual carbon yield (R) in comparison to the fibres stored in dry conditions. The obtained results are used to develop recommendations for preparation of activated carbon from wool fibres and for its application in air filtrating systems.

Key words: sheep wool fibres, thermal decomposition processes, preparation of activated carbon, renewable resources.

INTRODUCTION

Latvian Darkhead is single local origin sheep breed in Latvia (Vecvagars, 2018). There are publications devoted to the genetics and development of this breed (Sjakste et al., 2011; Bārzdina & Kairisa, 2015). However, only recently an interest about application of the Latvian Darkhead sheep wool to various sustainable applications, for example, fabrications of the filters (Voikiva et al., 2020; Podjava et al., 2022; Starkova et al., 2022) has occurred.

Sheep wool, semi-crystallized protein polymer, which consists of various types of amino acids linked through peptide bonds (Allafi et al., 2021) is commonly used for textiles, as organic substrate (Petek et al., 2021), building (Parlato & Porto, 2020), nitrogen fertilizers (Bhavsar et al., 2016), reinforced composites (Lovbak et al., 2023; Sun et al., 2023), and as heavy ion adsorbents from water (Marsalek, 2018). Among the perspective ways of sheep wool modification is preparation of activated carbon (Chen et al., 2013; Pina et al., 2021). Preparation of activated carbon from biowaste materials is widely applied for cotton (Sartova et al., 2019; Gao et al., 2021), wood (Ramirez et al., 2017; Sasmita et al., 2022), as well. However, the main aspect for applying one or other source for preparation of activated carbon, is related with the availability of the raw materials. Therefore, it is important to estimate the application of sheep wool fibres as raw material. In the actual conditions it is expected that cut wool will be collected and prior modification stored for certain time under certain conditions. By keeping the wool in the areas where temperature and air presence conditions correlate with the annual temperature and moisture changes, it may happen, that during storage and transportation wool accumulates some moisture, may change under presence of oxygen in air and might have some structural change due temperature fluctuations. Therefore, it is crucial to estimate impact of these aspects on preparation of activated carbon from sheep wool fibres.

In the present work, the thermal treatment yield is used to compare impact of various storage conditions on outcome of the residual carbon, by using small scale samples. In addition, preparation of larger amount of activated carbon from Latvian Darkhead sheep wool fibres is performed.

MATERIALS AND METHODS

Wool fibres (*Latvian Darkhead*) were purified from the soil, grass and other impurities, washed, dried and carded by *Sunakstes Vilnas nams Ltd*. Surface microstructure of carded sheep wool fibres were analysed by the means of the optical microscopy (OM, *Leica* microscope), while morphology was investigated by a high-resolution field emission scanning electron microscopy (SEM) device *Thermo Scientific™ Helios™ 5 UX*, working distance 7 mm, voltage 15 kV. For SEM measurements, the samples were adhered to aluminium stubs using conductive carbon adhesive tape. Voltage of accelerated electrons was specially selected in order to avoid charging of the samples.

Types of the chemical bonds were characterized with Fourier transform infrared (FTIR) spectrometry, attenuated total reflection (ATR) module, resolutions ± 2 cm^{-1}, range 400–4,000 cm^{-1}, 20 measurements per spectrum, at least 3 measurements per sample, in vacuum, 2.95 hPa. Prior the measurements of the samples a background spectrum measured and subtracted from the sample spectrum.

Table 1. Various storage conditions of carded sheep wool fibres

Parameter	Value	Parameter	Value
Temperature	+20 °C	Air pressure	0.3 bar
	-2 °C		1.0 bar
Light	1,700 lx	Relative	< 30%
	< 10 lx	humidity	~ 30%
			> 30%

Wool fibres were separated into 9 similar portions and divided for the storage under various conditions. Storage in vacuum is selected in order to estimate the impact of oxygen from air in comparison to non-oxygen containing environment. Selected storage conditions are summarized in Tables 1, while investigated samples are described in Table 2.

Table 2. List of wool samples stored under various conditions

No	Conditions	No	Conditions	No	Conditions
1	+20 °C, 0.3 bar, 1,700 lx	4	+20 °C, 1.0 bar, < 10 lx	7	+20 °C, 1.0 bar, ~1,700 lx, RH < 30%
2	+20 °C, 1.0 bar, 1,700 lx	5	-2 °C, 1.0 bar, < 10 lx	8	+20 °C, 1.0 bar, ~1,700 lx, RH ~30%
3	+20 °C, 0.3 bar, < 10 lx	6	-2 °C, 0.3 bar, < 10 lx	9	+20 °C, 1.0 bar, ~1,700 lx, RH > 30%

Before and after storage, thermal properties of the wool fibres were analysed by the thermogravimetry/differential thermal analysis (TG/DTA) equipment (*SEIKO EXSTAR 6300*) connected with FTIR spectrometer. Immediately after finishing the storage process, an aliquot of stored sample, ~1.5 mg, was used for the TG/DTA measurements, up to 1,000 °C, 90 °C min^{-1}, nitrogen flow, ~5 L h^{-1} (*Linde gas*, 99.99%). Mass change, temperature change as well as the temperature difference between the sample and an empty reference crucible was measured. The gaseous polar compounds, released during heating were analysed by means of FTIR spectrometry, *Bruker Vertex 70v* spectrometer with gas cell with Liquid Nitrogen - HgCdTe detector, 600–4,000 cm^{-1}, ± 4 cm^{-1}, gas flow, ~5 L h^{-1}. Prior the measurement, the background spectrum is measured and automatically subtracted from each of the resulting spectra.

Sample mass after the heating in the TG/DTA-FTIR system was compared and type of the samples with the highest outcome of residual carbon was used for preparation of activated carbon. The residual carbon yield (R) value was calculated by dividing the sample mass at the end of thermal processes by the initial mass, according to equation 1:

$$R = \frac{m_c}{m_f} \cdot 100\% \quad (1)$$

where m_f – mass of fibres, mg; m_c– mass of carbon at the end of thermal treatment, mg. It is taken into account, that the initial mass of the analysed sample contains some water molecules and the moisture accumulated during the storage time takes part in the thermal processes. For estimation of standard deviation within one type of the samples, one type

of samples was analysed three times. From the parallel measurements, the standard deviation was estimated to be 5% and applied to the other conditions as well.

Preparation of activated carbon was performed in the custom-made tube furnace, consisting of quartz tube (diameter: 2 cm) and heater. Wool fibres with the mass of around 10 mg were thermally treated in nitrogen flow, applying a similar method as commonly used for preparation of activated carbon from wool (Pina et al., 2018). Fibres were stabilized at 300 °C, pyrolyzed at 750 °C and activated with introducing water vapour in the N_2 flow at 950 °C.

RESULTS AND DISCUSSION

Characterization of the sheep wool fibres

OM and SEM investigations show that the prepared wool samples consist of homogeneously dispersed fibres with scale-like structures on the surface. Diameter of the fibres is estimated to be around 25 ± 3 μm. The OM and SEM images of wool fibres are shown in Fig. 1.

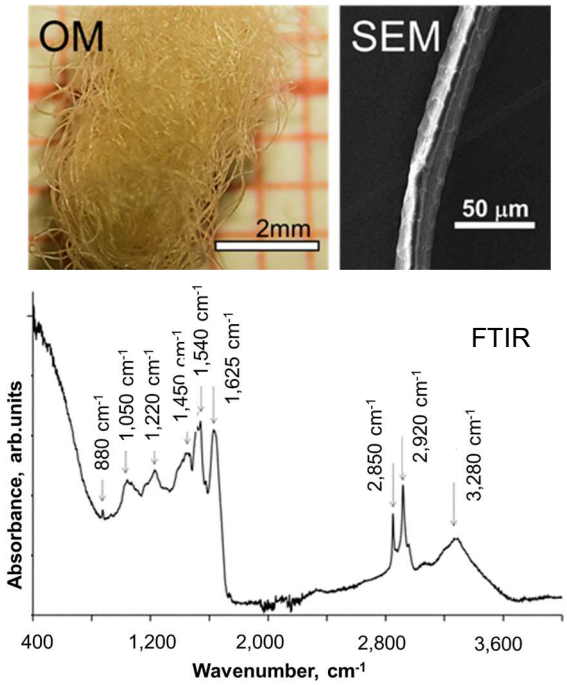

Figure 1. Surface morphology (OM), and microscale morphology (SEM) and chemical bonds (FTIR) of sheep wool fibres.

In the FTIR spectra of wool fibres, the main signals are from CH, C-O, C bonds around 880–1,060 cm^{-1} (Turki et al., 2018; Patla et al., 2019), α-helix, β-sheet, β-turn together with bands of random coil conformations in the amide I around 1,700–1,600 cm^{-1} and amide II in region of 1,560–1,500 cm^{-1} (Kakkar et al., 2014), of CH bonds at 2,850, 2,920 cm^{-1} (Patla et al., 2019), N-H stretching and OH (Patla et al., 2020) bonds around 3,280 cm^{-1} in keratin structure (Wang, 2016).

Estimation of storage impact on amount of carbon residual

An effect of the storage conditions on preparation of activated carbon was estimated by the means of TG/DTA-FTIR spectrometry. An example of the TG/DTA curves and FTIR spectra for sheep wool are shown in Fig. 3. By increasing the temperature up to 1,000 °C, the mass change can be divided into several main steps. In order to distinguish individual processes, a derivative of mass change as mass change rate (red line in Fig. 2) is analysed together with the main groups of released FTIR peaks. The first mass decrease step is observed in range of 40–100 °C (2 min at time scale of Fig. 2 and 3).

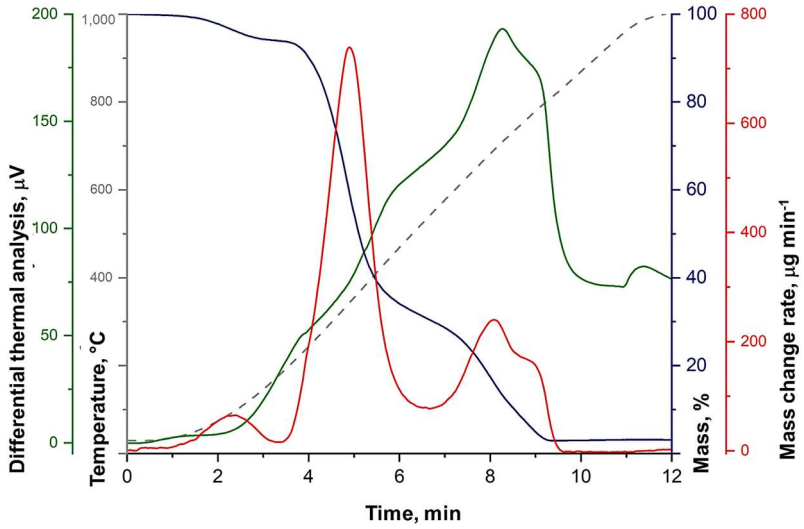

Figure 2. An example of thermal analysis of sheep's wool (dashed line – temperature, blue line – mass change, red line – mass change rate, green line – differential thermal analysis).

By analysis the FTIR spectra of the released gaseous compounds, it corresponds to the splitting off of the water (1,500–1,800 cm^{-1} and 3,500–4,000 cm^{-1} in Fig. 3). Second stage of the mass decrease in the range of about 200–600 °C consist of several exothermic processes, related with release of sulphur and nitrogen containing compounds (4–6 min in Fig. 2 and 3., peaks at 500–1,500 cm^{-1} and peaks of C-H bonds around 2,850–2,950 cm^{-1} in Fig. 3). Green line in the Fig. 2 shows to release of the thermal energy, showing to the presence of exothermic process. Above 600 °C starts the third stage of the mass decrease, correlated with release of carbon dioxide and water (6 min in Fig. 2 and 3., C = O peak around 2,350 cm^{-1} in Fig. 3). Comparing the mass release rate patterns for 9 various storage conditions (Fig. 4), it can be seen, that in all cases the main processes are similar - with 1st stage of releasing the humidity, second - due release of sulphur containing compounds as well as changes in the structure of amino acids and the third - carbonization, pyrolytic decomposition (Rao & Gupta, 1992) and combustion followed by release of carbon dioxide and water. Comparing mass change rate profiles, a correlation between the storage humidity and amount of released moisture can be detected. While the degradation of the amide groups and changes in the fibre internal structure is not significantly affected by presence of daylight, air and decreased

temperature. Therefore, Latvian Darkhead sheep wool can be stored over the climatical circumstances and vacuuming as preservation method is not required for this type of wool.

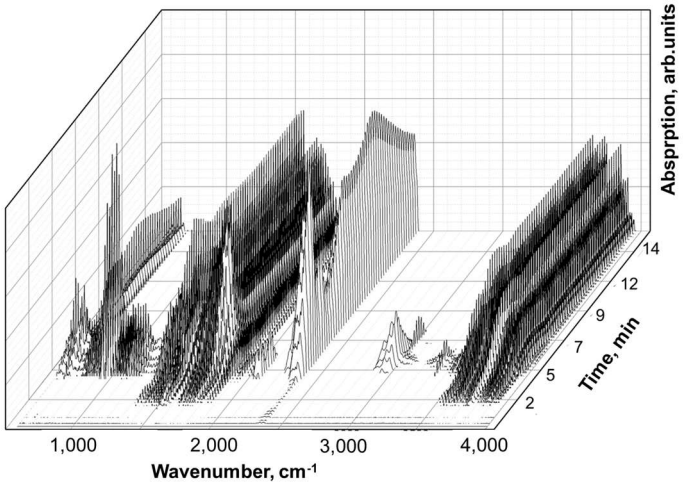

Figure 3. An example FTIR spectra of gaseous polar compounds released during thermal analysis (the time scale equal to one in the Fig. 2).

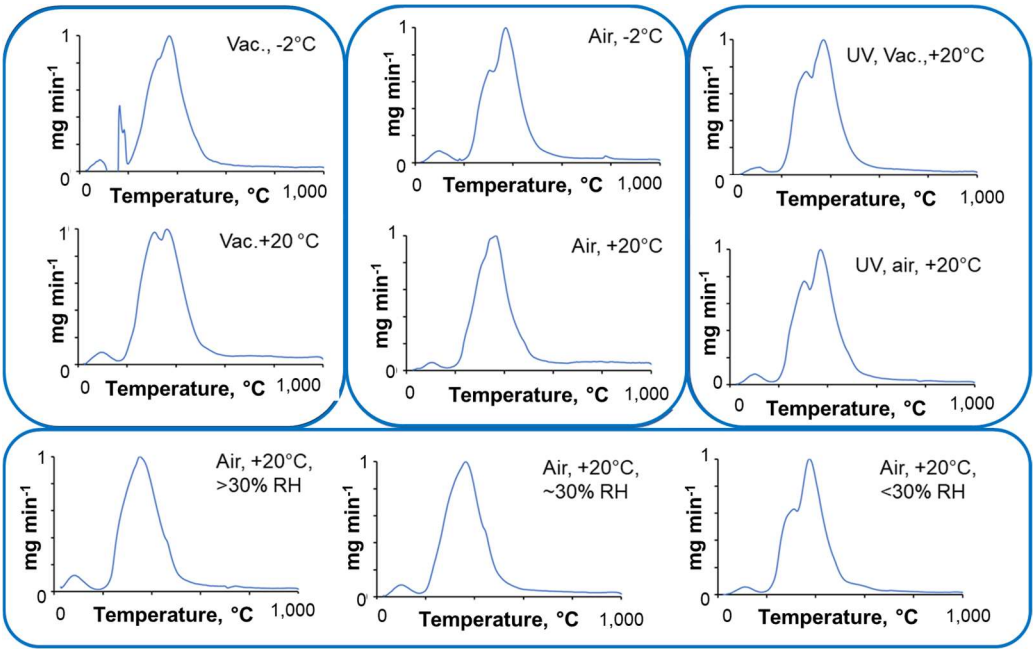

Figure 4. Mass release rate of sheep wool stored under different conditions.

The *R* value is estimated using Eq. (1). By measuring three parallel measurements, the standard deviation of the mass *R* value was estimated to be around 5%. The *R* values depending on the storage conditions are summarized in Table 3.

The R value is estimated using Eq. (1). By measuring three parallel measurements, the standard deviation of the mass R value was estimated to be around 5%. The R values depending on the storage conditions are summarized in Table 3.

Table 3. Residual carbon yield (R) values, estimated during TG/DTA measurements, of the carded sheep wool

No	R value	No	R value	No	R value
1	12 ± 5%	4	15 ± 5%	7	14 ± 5%
2	13 ± 5%	5	11 ± 5%	8	12 ± 5%
3	5 ± 5%	6	10 ± 5%	9	17 ± 5%

An overview of R values and storage conditions is also summarised in Fig. 5. The average from selected types of storage conditions is calculated and set in the graph as indicative value (blue horizontal line in Fig. 4). The standard deviation of this value is set as dashed lines.

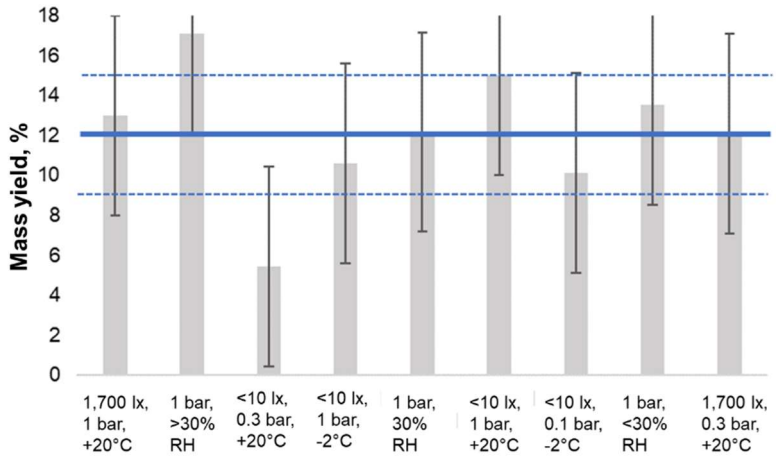

Figure 5. Residual carbon yield (R) values for sheep wool samples and their storage conditions

Two types of the samples are with slightly different values - one stored in vacuum, at room temperature, having lower R value than other samples. And the one stored at elevated humidity, having an increased R value. Presence of water in the thermal treatment process can act as an inhibitor of thermal degradation, meaning, that more energy is consumed for drying the sample and only at elevated temperatures the degradation process starts. The thermal analysis results can be summarized in form, that storage conditions have no significant impact on carbon residues at thermal treatments, therefore, carded sheep wool fibres, stored under various conditions may be used for preparation of activated carbon without specific pre-treatments step. This approach is further applied in present work.

Preparation of activated carbon from sheep wool fibres

Sheep wool fibres have been proved as stable raw material. Wool fibres stored at room temperature in air were used for preparation of activated carbon. Prepared activated carbon shows to fibre-like structures (OM image in Fig. 6) and the surface of the activated carbon is with porous-like structure (SEM image in Fig. 6). These pores can serve for sorption of micro- and nano- sized particles. Analysis of chemical bonds,

performed by FTIR spectrometry (FTIR spectra in Fig. 6) proves, that no polar bonds occur in the spectrum and sheep wool fibres are completely modified.

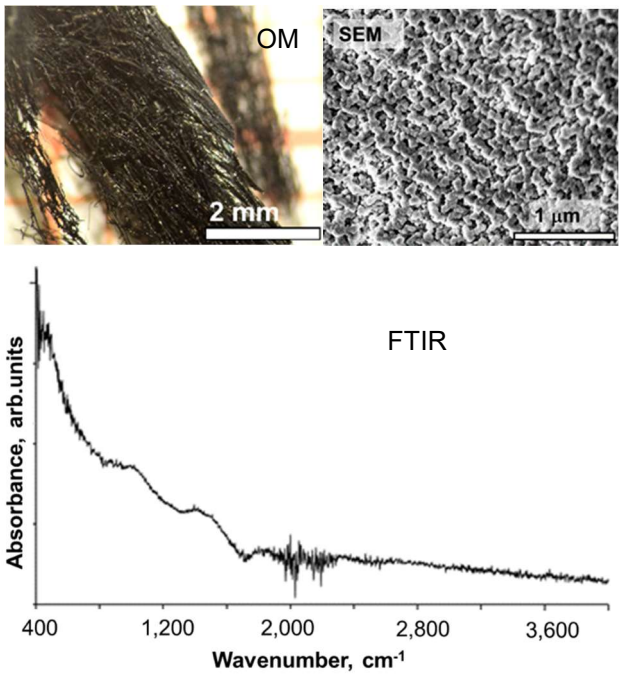

Figure 6. Surface morphology (OM), and microscale morphology (SEM) and chemical bonds (FTIR) of activated carbon from thermally treated sheep wool.

CONCLUSIONS

Long term exposure to various environmental conditions do not significantly affect the thermal decomposition processes and mass of carbon residuals of sheep wool fibres. For the fibres exposed for around a year to various temperature, light, atmospheric pressure and humidity conditions, the thermal decomposition patterns are similar. Performing preparation of activated carbon from sheep wool, a formation of carbon-like material with large surface area is achieved. Therefore, the Latvian Darkhead sheep wool fibres purposed for preparation of activated carbon, do not require additional resources for vacuumed packages and can be stored under ambient conditions.

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