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Thermal behaviour of cork and cork components

Ali Şen[a,*], Jan Van den Bulcke[b], Nele Defoirdt[b], Joris Van Acker[b], Helena Pereira[a]

[a] Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal
[b] Laboratory of Wood Technology, Department of Forest and Water Management, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000 Ghent, Belgium

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ABSTRACT

Thermal behaviour of cork and cork chemical components was studied with coupled differential scanning calorimetry-thermogravimetrical analysis (DSC-TGA) in order to gain insight into the role of the chemical components on the thermal degradation of cork. Cork samples of Turkey oak (*Quercus cerris*) and cork oak (*Quercus suber*) were chemically treated to selectively remove inorganic material, extractives and suberin, to allow characterization of klason lignin and methanolysis-depolymerized suberin. Since *Q. cerris* cork granulates contain phloemic impurities, phloem from *Q. cerris* bark was also subjected to the same treatments as cork. The thermal decomposition of both cork species is similar, starting above 200 °C and increasing with increasing temperature until ashing at approximately 485 °C. TGA curves of both corks are almost identical but a detailed view on the differential thermogravimetry (DTG) and DSC curves shows that the two materials differ from each other. Two exothermal devolatilization and char combustion reactions occur, peaking at approximately 313 °C and 445 °C. These peak temperatures shift to lower temperatures in suberin-free and extractive-free corks giving evidence of the heat retarding effect of suberin and extractives and possible catalytic effect of inorganics in desuberinised cork. Phloem thermal degradation is similar to that of cork although exothermal peak temperatures are higher. Phloem-containing *Q. cerris* cork granulates thus show clear potential for high temperature applications.

1. Introduction

Cork is a biological tissue that is part of the outer bark of trees, functioning as a protective layer. Cork production and industrial processing is at the basis of an important economic sector. At present most of the commercial cork is obtained from the cork oak (*Quercus suber* L.) where it constitutes a thick outer bark layer that is removed periodically in a sustainable manner during the tree's life time [1]. Cork can be obtained also from barks of other species where it is usually associated with phloemic tissue, as in the case of the Turkey oak, *Quercus cerris* [2].

Cork has an interesting set of physical and chemical properties that are at the origin of its use in various applications, as reviewed by Pereira [1]. Although the corks used for sealing wine bottles are the bestknown cork products, other cork materials i.e. insulation or surfacing boards are applied often in demanding performance situations [3]. The thermal behaviour of cork is important regarding both the high temperature range of application of insulation materials as well as the processing conditions for production of cork boards. An example is the thermal treatment with superheated steam at temperatures over 300 °C used in the production of insulation expanded cork agglomerates [4].

Studies on the thermal degradation of cork from *Q. suber* have been reported, mostly using standard summative chemical analysis of heat treated cork samples with different temperatures and times [5–8]. The chemical changes that occur may be summarized as: extractives are volatilized first, hemicelluloses are the first structural components to be degraded, and lignin and suberin are the most stable components [1]. The effect of heat treatment on the structure and mechanical properties of cork were also studied, with a reported expansion of cell volume and strength decrease related to treatment intensity [9,10].

Current knowledge on the thermal transformations of cork from other species is scarce and limited to cork from *Q. cerris*. The chemical composition of *Q. cerris* and *Q. suber* corks is similar, although *Q. cerris* cork has lower suberin and higher lignin content and different suberin monomeric composition [11]. The behaviour of *Q. cerris* cork during isothermal heating was similar to that of *Q. suber* cork: stable until 200 °C and decomposition increased with treatment temperature and time, with hemicelluloses being degraded in the initial steps; however aliphatic extractives and suberin showed more heat resistance than those of *Q. suber* cork [12,13]. The studies

* Corresponding author. Tel.: +351 924001004.
E-mail addresses: umutsen@isa.utl.pt, umutsen23@hotmail.com (A. Şen).

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Table 1
Chemical composition of cork and phloem samples [1,11,12,20,21].

% of dry material	*Q. suber* cork	*Q. cerris* cork	*Q. cerris* phloem
Ash	1.0	2.6	13.0
Extractives	14.0–17.0	7.0–16.7	6.5
Dichloromethane	3.6–7.9	2.5–10.9	1.7
EtOH	4.8–5.8	3.4–3.5	3.6
Hot water	3.1–4.0	1.0–2.4	1.3
Suberin	33.0–40.0	11.8–28.5	5.5
Lignin	21.0–23.0	28.1–32.3	35.4
Klason lignin	19.5–21.0	26.9–29.4	32.4
Acid-soluble lignin	1.2–1.6	1.2–2.9	3.0
Polysaccharides	18.2–21.3	16.5	30.6

were, however, limited and the effective thermal behaviour of the cork chemical components is still unclear.

Another important aspect is that the separation of cork from *Q. cerris* bark yields cork fractions that contain some phloemic material due to the complex structure of the outer bark where the cork tissue is interspersed by phloem [2]. The phloem is of lignocellulosic nature with high ash, low extractives and high lignin and polysaccharides content [11], and therefore should have a thermal behaviour different from cork. Its characterization is therefore also of practical importance for the commercial valorization of *Q. cerris* bark.

The present work aims to unravel the thermal behaviour of cork and of its chemical components by using thermal analysis. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are effective techniques to study the temperature-related decomposition of materials and have been applied to cellulosic and lignified biomaterials [14]. Both techniques are combined in this work to study the thermal decomposition of *Q. cerris* cork. The overall objective is to gain a better understanding of the thermal behaviour of cork from *Q. cerris* that may contribute to the valorization of its bark. Since cork-enriched granulates from *Q. cerris* bark may contain significant amounts of lignocellulosic phloem material [2,11], this was also studied under the same conditions. Cork from *Q. suber* was used as a reference material. Chemically modified samples obtained by component fractioning were also prepared and studied in order to evaluate the contribution of extractives and structural components i.e. suberin, polysaccharides and lignin, on the thermal decomposition of the cork.

2. Materials and methods

Cork samples of *Q. suber* and *Q. cerris* and a phloem sample of *Q. cerris* were prepared. The cork and phloem fractions of *Q. cerris* bark were separated manually to obtain pure samples of each tissue. The three samples were grinded and fractioned to a mesh size of 40–60 (0.475–0.250 mm). The chemical composition of the studied samples is summarized in Table 1.

The samples were chemically treated for selective removal of components. Eight different treatments were analyzed for each of the materials as shown in Table 2. In addition one alpha-cellulose sample obtained from Sigma–Aldrich was also analyzed.

The methods for chemical treatment of cork have been described in detail in Pereira [1,7] and are only briefly reported here. Solvent extractions were made in a Soxtec using successively dichloromethane, ethanol and hot water. Depolymerization and removal of suberin was made on the extractive-free sample by using 3% NaOMe in methanol under reflux. The depolymerized suberin was obtained from the methanol solution after acidification to pH 6, evaporation, suspension in water and extraction with dichloromethane. Klason lignin was the solid residue obtained from sulphuric acid hydrolysis of the desuberinised samples.

All samples with 40–60 mesh powder size were analyzed in a pure oxidative environment with a coupled differential scanning calorimeter and thermogravimetric analyzer (DSC-TGA) at Woodlab-UGent. For the DSC-TGA analysis, 4 mg samples were studied in an open-type platinum crucible to minimize the issue of heat transfer and increase sensitivity for small mass losses (DSC calorimetric precision: ±0.1%, sensitivity: 6.7 μV/mW, TG resolution: 0.002 μg). A four step heating and cooling programme was used with an oxygen flow of 20 mL/min: 5 min stabilization at 20 °C (I), sample drying from 20 to 100 °C with a heating rate of 20 °C/min (II), heating from 100 to 600 °C with a heating rate of 5 °C/min (III), and cooling from 600 to 20 °C with a cooling rate of 10 °C/min (IV). Both heat flow and mass loss were measured simultaneously.

3. Results and discussion

3.1. Untreated corks and phloem

The thermal decomposition of corks and phloem occurred at temperatures above 200 °C and increased with higher temperatures until about 485 °C at which temperature the material was reduced to ash (Fig. 1). This result is in agreement with those from previous studies on *Q. suber* cork [5,7,15], and a similar temperature range was also reported for wood thermal degradation [14].

The TGA curves of the untreated *Q. cerris* and *Q. suber* corks showed quite similar thermal degradations and the mass loss curves are almost superposed. The mass loss was small for temperatures below 250 °C and highest between approximately 250 °C and 350 °C, decreasing subsequently at a lower rate until about 410 °C and more rapidly further on.

The TGA curve of phloem differs from that of cork. Mass loss below 250 °C, although small, is higher than for corks. The main degradation occurs at slightly higher temperatures and corresponds to a smaller mass loss while the final mass loss before ashing occurs in the same temperature range as that of cork (Fig. 1). The higher polysaccharide content in phloem compared to cork is a possible reason for this difference (approximately 30% vs. 20%, Table 1).

The first derivative of the TGA curve (DTG) shows the reaction rates during thermal degradation (Fig. 2). The cork and phloem

Table 2
Samples, treatments and codes of samples.

Samples	Treatment	Code
Q. suber cork *Q. cerris* cork *Q. cerris* phloem	No treatment	Untreated
	Dichloromethane extraction	DCM Ext
	Successive extractions with dichloromethane, ethanol and hot water	Extractive-free
	3% NaOMe extraction of extractive-free samples	Suberin-free
	3% NaOMe extract	Depolym. suberin
	72% and 4% H_2SO_4 treatments	Klason lignin
	Hot water extraction	Hot water-Ext.
	Hot water followed by dichloromethane extractions	Hot water + DCM ext