



Nitrogen-containing gaseous products of chrome-tanned leather shavings during pyrolysis and combustion

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ABSTRACT

Chrome-tanned leather shavings (CTLS) are a type of solid waste generated from the leather industry. In this study, the pyrolysis and combustion of CTLS in nitrogen and air, respectively, were investigated using a thermogravimetric analyser coupled with Fourier transform infrared spectroscopy (TG-FTIR). A heating rate of 20 °C min⁻¹ was applied, with a final temperature of 1000 °C. The pyrolysis process can be subdivided into three stages (drying the sample, fast thermal decomposition and a further cracking process), whereas the combustion process can be subdivided into four temperature stages. The TG/DTG curves for pyrolysis and combustion were similar at lower temperatures. Multiple peaks were observed for combustion in the temperature range of 250 °C to 580 °C. The emissions of CO₂, NH₃, HCN, HNCO, CO, acid and hydrocarbon were identified in CTLS pyrolysis. Similar gaseous products of combustion were found at lower temperatures, whereas CO₂ is the dominant product of combustion at higher temperatures. Combustion was found to be better for disposal of CTLS than pyrolysis.

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1. Introduction

The fabrication of leather from raw skins/hides to finished leather must undergo a series of chemical and mechanical operations, which usually include pre-tanning, tanning and post-tanning (Jiang, et al., 2016). The leather industry has been categorized as one of the worst polluting industries because of the generation of huge amounts of waste (Fela, et al., 2011; Kanagaraj, et al., 2010). It was reported that approximately 1000 kg of wet salted hides would yield only 200 kg of finished leather and generate more than 600 kg of solid waste and byproducts (Cabeza, et al., 1998; Chen, et al., 2008). One type of solid waste generated from the leather industry is chrome-tanned leather shavings (CTLS), which is mainly composed of protein collagen and chrome and poses a serious threat to the environment (Pati et al., 2014). Properly addressing CTLS is an urgent problem.

Incineration is one of the most common techniques used to eliminate combustible hazardous wastes, and it is considered a harmless and efficient disposal method. In China, this is the main technique to treat hazardous waste, but dust emissions and gaseous pollutants are formed by combustion (Mithat, et al., 2003; Addink and Altwicker, 2004). The organic compounds in CTLS can be burned completely, producing gaseous emissions (e.g., SO_x

and NO_x). Pyrolysis and gasification may be the preferred methods to treat organic hazardous waste because they produce lower hazardous gaseous products and particles (Senneca, 2007). Selection of the best pyrolysis and combustion methods is important for the optimal operation and design of incineration plants (Feng, et al., 2011). The evolution characteristics of CTLS pyrolysis and combustion products are therefore investigated in this research.

The thermogravimetric analyser (TG) is used widely in thermal analysis and kinetics studies in both nitrogen and air atmospheres (Senneca, 2007; Liou, 2003; Bingham, et al., 2005; Font, et al., 2005). On the other hand, Fourier transform infrared spectroscopy (FTIR) can be used to evaluate the functional groups and identify the presence of some emissions (Kanokkantung et al., 2006; Qian et al., 2003). In this research, TG-FTIR analysis is used to evaluate pyrolysis and combustion conditions to understand the thermal behaviour of CTLS. The results of weight loss and composition of the produced gases will provide important information to better understand the pyrolysis and combustion characteristics of CTLS.

2. Materials and methods

2.1. Materials

The CTLS used in this study originated from a leather factory in Zhejiang, China. Proximate analysis and ultimate analysis of the samples are shown in Table 1. The Cr content is 2.18%. After being

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Table 1
Ultimate and proximate analysis and HHV of CTLS.

Property	Concentration (wt.%)
<i>Ultimate analysis</i>	
C	38.25
H	5.01
O	24.68
N	12.18
S	1.31
<i>Proximate analysis</i>	
Moisture	9.20
Ash	9.37
Volatiles	67.74
Fixed carbon	13.69
Higher heating value (MJ.kg ⁻¹)	17.2

dried in an oven at 105 °C for 3 h, the original materials were crushed and pulverized to a size of <0.2 mm before they were analysed. Approximately 10 mg of sample material were used for TG-FTIR analysis.

2.2. Methods

A Nicolet Nexus 670 spectrometer and a Mettler Toledo TGA/SDTA851e thermo analyser were coupled with a Thermo-Nicolet TGA special connector. The stainless-steel transfer pipe and gas cell (20 cm optical path length) were heated to 180 °C to minimize secondary reactions. Nitrogen was used as a carrier gas because of its inertia, with a flow rate of 20 ml min⁻¹ during pyrolysis; the air was used as an oxidant during combustion at the same flow rate. If the flow rate is too low, the residence time will increase, and the evolved gas will have a secondary reaction. A high flow rate will reduce the absorbance of evolved gas, which is not conducive to infrared detection. The flow rate was therefore set to 20 ml min⁻¹ based on residence time and the sensitivity of infrared detection. A medium-sized alumina crucible of 70 µl was used as a sample container.

When pyrolysis and combustion of other organic wastes were evaluated at different heating rates (5, 10, 20 and 30 °C min⁻¹), emissions of gaseous products were observed to slow down at lower heating rates. Similar components of gaseous products and change with temperature at different heating rates were found. Based on these results, a heating rate of 20 °C min⁻¹ was applied; the final temperature was 1000 °C. Other specifications for this research included the following: the resolution in FTIR was set to 4 cm⁻¹, the spectrum scan frequency was set to 20 times.min⁻¹, and the spectral region was set to 4000–400 cm⁻¹.

3. Results and discussion

3.1. TG data analysis

The TG/DTG profiles for CTLS as a function of temperature at the heating rate of 20 °C min⁻¹ during pyrolysis and combustion are shown in Fig. 1. The TG and DTG curves are typical for some other collagen materials (Cucos and Budrugaec, 2014; He et al., 2011; Sionkowska et al., 2006).

The pyrolysis process can be divided into three stages based on the DTG profile. The first stage begins weight loss by drying the sample ($T < 250$ °C). Moisture and some volatile substances with a low boiling point were emitted in this stage. The second stage consists of fast thermal decomposition for CTLS between 250 °C and 550 °C; most of the weight loss (approximately 55.2% of the total weight of original samples) occurred in this stage. The weight loss rate reached its highest value at 338 °C (13.88%.min⁻¹).

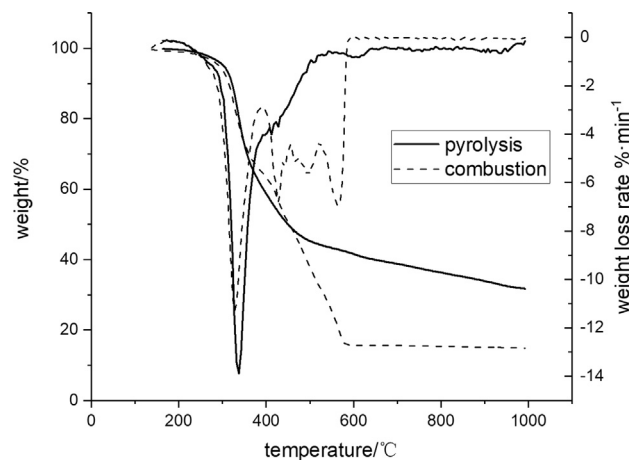


Fig. 1. TG/DTG profiles for the pyrolysis and combustion of CTLS, at a heating rate of 20 °C.min⁻¹.

A single large DTG peak was observed at 330 °C during the pyrolysis of collagen (Cucos and Budrugaec, 2014). A shoulder peak was found at 412 °C that indicates the overlap of a lower peak with the main peak after the sample reached its highest weight loss rate. The last stage was found to have further cracking of the residues in the temperature range of 550 °C to 1000 °C; approximately 11.5% of the total weight was lost at a lower rate in this stage. A total weight loss of 68.3% was achieved when the temperature reached 1000 °C.

The combustion process can be divided into four stages based on temperature (100–250 °C, 250–383 °C, 383–522 °C, 522–1000 °C). A series of parameters calculated from the TG data were used to characterize the combustion of CTLS (Table 2). The characteristics during CTLS combustion were similar to those under nitrogen conditions when the temperature was lower than 320 °C; the TG/DTG curves of pyrolysis and combustion were relatively similar. Multiple peaks were observed, however, for combustion in the temperature range of 250 °C to 580 °C. The highest peak occurred at the second stage, followed by two smaller peaks at the third stage. The weight loss in the second stage was 31.9%. Most of the weight loss (33.6% of the total weight in the original samples) occurred in the third stage. The complete combustion of samples finished quickly approximately 580 °C, which was different from the pyrolysis process. The combustion of the CTLS was nearly complete after the weight loss peak between 522 and 580 °C, and 16.6% of the original sample weight was lost. Results indicate that 600 °C was sufficient for combustion disposal of this waste. The total weight loss of 84.3% was reached at 1000 °C in CTLS combustion. Under oxidizing conditions, the highest peak shifted to a lower temperature (327 °C), and its peak height (11.54%.min⁻¹) was lower than for pyrolysis. For some organic wastes, such as

Table 2
Combustion Characteristic Parameters of CTLS.

Characteristics	CTLS
The initial release temperature of volatile (Tv)	°C 198
The ignition temperature (Ti)	°C 292
The maximum weight loss rate (DTGmax)	%·°C ⁻¹ 0.577
The temperature of DTGmax (Tmax)	°C 327
The burnout temperature (Tb)	°C 586
The lowest weight of sample (TGend)	% 14.86
The temperature of TGend (Tend)	°C 993
The mean weight loss rate (DTGmean)	%·°C ⁻¹ 0.088
The combustible index (Ci)	1.02×10^{-3}
The burnout index (Cb)	1.02×10^{-4}
The combustion index (S)	3.54×10^{-10}

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