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Kinetic model of the thermal pyrolysis of chrome tanned leather treated with NaOH under different conditions using thermogravimetric analysis

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ABSTRACT

The thermal decomposition of chrome tanned leather before and after a soaking treatment with NaOH was studied using thermogravimetric analysis (TGA). The effect of the solution concentration (0.2 M and 0.5 M) and the soaking time (5 min and 15 min) was evaluated. TGA experiments at four heating rates (5, 10, 15 and 20 °C min^{-1}) were run in a nitrogen atmosphere for every treatment condition. A kinetic model was developed considering the effect of the three variables studied, i.e.: the NaOH solution concentration, the soaking time and the heating rate. The proposed model for chrome tanned leather pyrolysis involves a set of four reactions, i.e.: three independent *n*th order reactions, yielding the corresponding products and one of them undergoing a successive cero order reaction. The model was successfully applied simultaneously to all the experimental data obtained. The evaluation of the kinetic parameters obtained (activation energy, pre-exponential factor and reaction order) allowed a better understanding of the effect of the alkali treatment on these wastes.

1. Introduction

Environmental problems posed by chrome tanned leather waste are a widely known issue in the tanning world. Many lines of research are nowadays opened in order to find suitable treatment processes for leather wastes which allow the negative environmental impact to be reversed whilst obtaining valuable co-products to offset the economic cost of the process.

The leather-making process generates big quantities of both solid and liquid waste. The process is divided into four sub-processes: beamhouse, tanning, dressing and finishing. Beamhouse stage involves all operations needed to remove the unwanted components of raw skin. Then, the tanning process stabilizes the raw material, converting hides into a rot-proof material suitable for a wide variety of applications. Dressing and finishing operations give the tanned leather the desired appearance. With solid waste, a distinction is made between those produced in the stages prior to the tanning process and those occurring thereafter. During dressing operations, trimmings, shavings or buffing dust are frequent waste products. Currently, this waste from tanned leather, and also from the footwear industry, is disposed of together with other urban waste. Over 90% of leather tanned worldwide is chrome tanned, generating more than 600,000 t/year of chrome tanned wastes. In Spain, it is estimated that more than 16,000 t/year of tanned-leather wastes are produced (12,800 t/year in tannery industries and around 3800 t/year specifically by footwear industries) (Marcilla et al., 2012). According to Yilmaz et al. (2007), it is reported that the tanned wastes of 0.22 kg/kg of wet salted hides/skins is generated per year in Turkey. The leaching of the chromium in landfills, and the eventual generation of the Cr(VI) cation, which has been classified as carcinogen and consequently can cause serious health risks when in contact with the human body, is one of the main environmental problems (Boopathy et al., 2013; El-Sabbagh and Mohamed, 2011). According to Muralidhara et al. (1982), the leather waste disposed of in landfills resulted in a considerable loss of potential energy (estimated to be 633 TJ annually) and a significant loss of chromium (estimated to be 8.2 Gg annually).

Pyrolysis can be a good alternative to conventional combustion processes in order to recover this type of waste. The pyrolysis process is shown to be technically feasible, economically viable, and can alleviate a leather waste management problem. Tanneries can save an estimated \$7–\$8 million annually by employing this pyrolysis process to conserve energy and chrome in dry tanning wastes (Muralidhara et al., 1982).

Gas and liquid fractions obtained in the process are susceptible to generate useful chemicals after upgrading. In a previous work

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Nomenclature

A	proportionality constant of heating rate
a_i	fitting parameter to consider the effect of concentration and soaking time on the fraction of leather that decomposes through the process i
b_i	fitting parameter to consider the effect of concentration and soaking time on the reaction order of i reaction
C	sodium hydroxide concentration
calc	calculated values
c_i	fitting parameter to consider the effect of concentration and soaking time on the activation energy of i reaction
der	derivative thermogravimetric data
d_i	fitting parameter to consider the effect of concentration and soaking time on the pre-exponential factor of i reaction
E_i	activation energy of i reaction
exp	experimental values
k_i	kinetic constant of i reaction
k_{0i}	pre-exponential factor of i reaction
$m_{i\ exp}$	mean value of experimental data
n_i	reaction order of i reaction
N	number of total points of the curves
OF	objective function
OF_w	objective function of TG data
P	number of parameters to be fitted
R	gas constant
r_i	percentage of the residue formed from fraction W_i
R_i	residue formed through the process i
t	time
T	temperature
v	heating rate
v_i	percentage of the volatiles formed from fraction W_i
V_i	volatiles formed through the process i
VC	variation coefficient
W_i	fraction of the leather that decomposes through the process i

carried out by this research group (Marcilla et al., 2012), flash and slow pyrolysis of tannery wastes were performed. The spectrum of liquid products obtained is complex, formed by around 100 different compounds, most of them coming from protein decomposition.

In addition to being used as a fuel, either alone or mixed with other fuels, the char obtained can also be used as a cheap adsorbent. Besides, the leaching of heavy metals from the char is small compared to the leaching from incineration ashes (Menéndez et al., 2002). Moreover, pyrolysis allows the stabilisation of waste disposed of in landfills.

The understanding of pyrolysis kinetics is especially interesting in the eventual scale up of the pyrolysis process. Developing a model that reproduces the behaviour of decomposition and kinetic constants is crucial to assess the main items in the scaling process such as feasibility and design. Thermogravimetry (TG) is the most used technique to study the kinetics of thermal decomposition of solids (Ninan, 1989), since it is one of the techniques by which kinetic results are less influenced by heat transfer processes. The interpretation of the experimental TG data provides information about the material composition, the number of different processes that take place during the decomposition and the corresponding kinetic constants by modelling and fitting the adequate kinetic model. As Vamvuka et al. (2003) indicated, the thermogravimetric technique has a relative value with respect to establishing reaction mechanisms but it is an essential tool for the determination of the kinetic behaviour and hence for process design and control.

Chemical treatments of leather waste in order to recover the protein and the chromium are other current alternatives for this waste because the process is well-known (Sundar et al., 2011). Alkali hydrolysis has traditionally been used to hydrolyse collagen protein and separate it from chromium oxide in order to reuse the recovered oxide in tanning processes and the hydrolysed collagen as a source of protein products (Holloway, 1978; Taylor et al., 1994; Tahiri et al., 2004; Kolomaznik et al., 2008; Mu et al., 2010; Wionczyk et al., 2011; Estrada Monje and Hernández Moreno, 2014). It is obvious that an alkali treatment of leather reverses the tanning process since during the tanning process Cr (III) compounds react with hides under acidic conditions.

The most studied alkali in leather digestion is sodium hydroxide. Wionczyk et al. (2011) examined the effect of time, temperature and concentration of NaOH solution on the hydrolytic decomposition of leather. They found that increasing the concentration of sodium hydroxide solution from 0.2 M to 0.3 M led to the increase of the rate of both the Cr(III) leaching and the collagen hydrolysis. Tahiri et al. (2004) studied the optimisation of the alkaline digestion of leather waste, based on two parameters, concentration of NaOH solution and reaction time. They concluded that the best operating conditions for the extraction of proteins with sodium hydroxide would be 0.5 M for NaOH concentration and 15 min for reaction time. The developed process allowed the recovery of proteins in the aqueous phase and the metallic salts in the cake.

From the kinetic point of view, the most studied solid waste is agricultural biomass. A wide range of approaches were summarised by White et al. (2011). Other types of waste studied are plastics like ethylene-vinyl acetate (García and Font, 2004), polypropylene (Hirunpraditkoon and García, 2009; Marcilla et al., 2003a,b) and others, used tires (Miranda et al., 2006, 2013; Quek and Balasubramanian, 2012), sludge (Wu et al., 2006) or municipal solid waste (Lai et al., 2012; García et al., 1995). In the 50s and 60s, many different kinetic models were developed, such as Flynn–Wall–Ozawa model or the Kissinger equation (Kissinger, 1957; Ozawa, 1965; Flynn and Wall, 1966) to estimate the kinetic parameters of the solid-state processes from thermogravimetric data based, in general, in isoconversional relationships under dynamic conditions. Nowadays, these models are still being applied (Garcia-Maraver et al., 2015; Kok and Özgür, 2013; Poletto et al., 2012; Slopiecka et al., 2011). However they are devised for single processes.

The information obtained from decomposition processes that take place in a given reactor depends on the experimental equipment and the selected operating conditions, especially when the processes are complex and different decomposition reactions are occurring simultaneously. Moreover, depending on the kinetic parameters of the processes that are taking place, the influence of the operating variables is different and various processes can be masked, which at first glance could be perceived as a single process (García et al., 1995).

Pyrolysis of solid state materials, such as leather, can be classified as a heterogeneous chemical reaction that usually involves a superposition of several pseudo-elementary processes. Leather is formed by many components that show different reactivity and decompose at different rates. Only two papers related to kinetic modelling of tanned leather have been found. On the one hand, Caballero et al. (1998) studied the thermal decomposition of chrome tanned leather waste in strict pyrolysis conditions and