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Dielectric characterization of biodegradable wastes during pyrolysis

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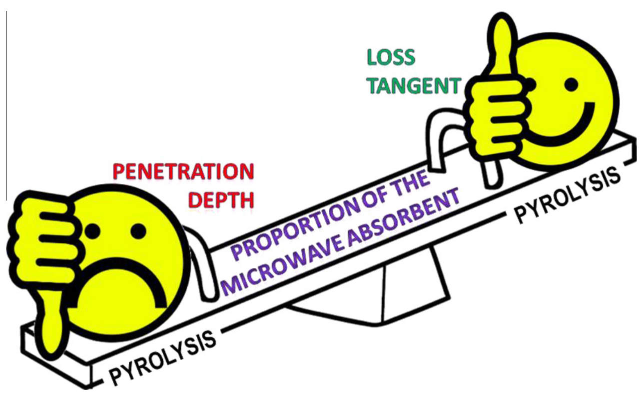
HIGHLIGHTS

- Dielectric properties of an organic waste during pyrolysis have been studied.
- $\tan\delta$ of raw organic waste remains very low up to 400 °C.
- The addition of char reduces the temperature of occurrence of *thermal runaway* effect.
- Low char concentrations enable higher penetration depth and homogeneous heating.

GRAPHICAL ABSTRACT



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ABSTRACT

The lack of dielectric properties data has often been named as one of the reasons that has hampered the simulation of microwave processing of biomass feedstock and process design. In this work, the dielectric behavior of an organic fraction from municipal solid wastes during pyrolysis has been monitored as a function of temperature. Furthermore, the effect of the addition of a microwave absorbent material (carbonaceous char) to the raw biowaste upon the dielectric properties has been investigated for the first time.

The efficiency of the conversion of microwave energy to heat, measured by means of the $\tan\delta$ parameter, is shown in this study to be nearly 20 times higher when the absorbent char is added to the reaction bulk at room temperature and this gap is even greater in the 600–800 °C range. Nevertheless, the results suggest that the addition of increasing amounts of microwave absorbent (up to ca. 40%) impairs microwave penetration, which gives rise to a less homogeneous heating of the bulk. There is therefore an optimum proportion that balances heat conversion and penetration depth.

The results of this study lend support to the use of char as a means to induce thermochemical treatments by microwaves and reduce energy consumption in the process.

1. Introduction

On average, every one of the more than 500 million people living in the European Union (EU) throws away around half a ton of household rubbish a year. This is on top of the huge amount of waste generated from activities such as manufacturing (360 million tons) and construction (900 million tons), while the supply of water and the production of useful energy generate another 95 million tons. Altogether, the EU produces up to 3 billion tons of waste every year [1]. A significant proportion of waste going to landfill is organic material, (i.e. derived from both biomass and

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petroleum sources). Thermochemical conversion processes, involving pyrolysis and gasification, can convert this waste at source into potentially useful chemical feedstocks and fuels after the removal of the more readily recyclable materials, such as metals and glass.

A number of processes are now under development or are at the demonstration stage, whose aim is to provide more cost-effective, environmentally and socially acceptable alternatives to incineration plants. One of these new technologies is microwave pyrolysis based on dielectric heating. This process benefits from the main advantages of using microwaves, such as rapid, volumetric and selective heating, and avoids the need to shred the feedstock and to pre-dry the samples, resulting in a substantial reduction in the costs associated with these steps [2–5]. In spite of these advantages, this technology has not yet reached industrial scale owing to the lack of economic analyses on a large scale and the absence of sufficient data to quantify the dielectric properties of the input feedstocks.

The property that determines the dielectric response of material under the influence of an electric field is the relative complex permittivity, ε^*, which is expressed as a function of a real component known as the dielectric constant (which represents the ability of dielectrics to store electrical energy) and an imaginary component known as the dielectric loss factor (which represents the ability of a material to absorb the electric energy):

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (1)$$

where $j = \sqrt{-1}$ and ε' and ε'' are the dielectric constant and the dielectric loss factor relative to the corresponding dielectric properties of free space.

An estimation of these properties is essential for the effective design and scaling up of microwave heating processes to ensure an accurate prediction of the absorbed power density; i.e. the rate at which the electromagnetic energy is converted to heat in the material. Dielectric properties may vary with composition, frequency, temperature and even material density [6] and, therefore, it is essential to characterize their variation in relation to those parameters.

Several studies have attempted to characterize the dielectric properties of coal [7] and some kinds of biomass [8,9] since it is known that the dielectric loss of these materials at low temperatures is negligible, making them transparent to microwaves. However, when the substrates are subjected to higher temperatures (i.e. temperatures higher than 600 °C), the structures become essentially char, which is known to be a high microwave absorbing material due to the Maxwell–Wagner effect which causes a very high displacement of π-electrons on carbonized structures [10]. It is for this reason that different microwave receptor materials are added to biomass during microwave pyrolysis, so that a high enough temperature is reached to induce pyrolysis [11,12]. However, most published studies are focused solely on the dependence of dielectric properties upon frequency radiation at room temperature [13–16] and ignore the need for a comprehensive study of the whole microwave pyrolysis process. In other words, an in-depth and extensive study of the dependence of dielectric properties on temperature is needed to obtain a better understanding of the dielectric response of organic substrates during microwave pyrolysis and of mixed organic substrates when used with microwave susceptors.

This paper investigates the microwave absorption capability of a biodegradable waste and its mixture with microwave absorbent char on the basis of their dielectric properties, from room temperature up to 800 °C at the commonly used frequency of 2.45 GHz.

2. Materials and methods

2.1. Biowaste preparation and characterization

The biodegradable waste used for this study was an organic fraction from a municipal solid waste, obtained from a landfill in Seville (Spain). The waste was dried, partially cleaned of inerts such as glass or metals and size-reduced to 1–3 mm. This fraction has been labelled as MSWd. The pre-treatment of this organic residue allows a good homogeneity of this fraction. Actually, this fraction has been used in other studies to produce synthesis gas by means of microwave-induced pyrolysis and the composition of the gas was quite homogeneous when repeating the tests [17].

In order to assess the effect of adding char as microwave absorber to the biowaste upon the dielectric response, a carbonaceous solid char was prepared by subjecting the biowaste sample to a temperature of 800 °C in an electric furnace for 1 h in an oxygen-free atmosphere. This has been labelled Char-MSWd. The mixtures of char:biowaste were prepared in weight ratios of 0.3:1 and 0.6:1. These two mixture ratios were considered on the basis of keeping the amount of char as low as possible to induce the microwave pyrolysis. In previous studies [17], we used 0.3:1 ratio; thus, we have used this same ratio in this work. Furthermore, a larger amount (0.6:1 ratio) was considered to study the effect of adding char to feedstock as microwave absorbent.

The moisture, ash content and volatile matter data of the residues were obtained on a LECO TGA-601 device. To perform the ultimate analysis, a LECO-CHNS-932 micro-analyzer and a LECO-TF-900 furnace were used. The micro-analyzer provided data on the carbon, hydrogen, nitrogen, and sulfur percentage composition. The oxygen content was determined using the LECO-TF-900 furnace. The results of proximate and ultimate analyses of the MSWd and char-derived samples are presented in Table 1.

2.2. Measurement of dielectric properties

An inverse methodology to obtain the permittivity of the different biowastes was used (Fig. 1) [18]. This technique is one of the most appropriate; other techniques such as standard coaxial probes may lead to lower precision since air bubbles below the coaxial probe can result in lower values of permittivity; resonant-cavity technique is typically used for low-loss materials (which is not our case) and identifying the resonant frequency and quality factor (intrinsic parameters of this technique) would have been difficult due to the high absorption of the materials. First, each sample (see Sample R in Fig. 1) was introduced and uniformly compacted into a quartz tube (i.d. 5 mm, height 43 mm; MSWd bulk density: 166 kg/m^3; char bulk density: 353 kg/m^3) and heated up to a specific temperature in an oxygen-free

Table 1
Proximate and ultimate analyses of the MSWd and Char-MSWd fractions.

Residue Label		Municipal solid waste MSWd	Char from municipal solid waste Char-MSWd
Proximate analysis (wt.%)	Moisture	2.8	3.3
	Ash[a]	27.7	66.6
	Volatile matter[a]	61.1	1.7
Ultimate analysis (wt.%)	C	45.1	30.7
	H	5.4	0.1
	N	2.1	1.0
	S	0.4	0.7
	O	19.3	0.9

[a] Dry basis.