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Permittivity and chemical characterization of woody biomass during pyrolysis and gasification

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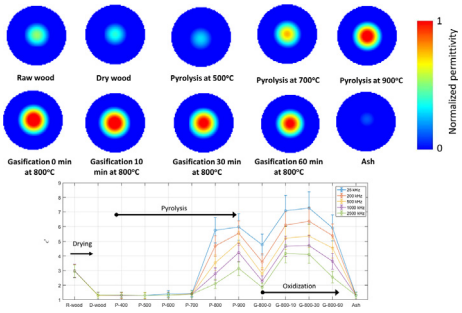
HIGHLIGHTS

- In-vitro biochar permittivity measurements in low excitation frequencies (20 kHz–3 MHz).
- Lab gasification and pyrolysis of woodchips at different times and temperatures.
- Biochar from pyrolysis below 600 °C has a similar permittivity to dry wood.
- Significant increase of permittivity was found at temperatures of 800–900 °C, and in intermediate gasification times.
- Permittivity increase is correlated well with biochar graphitization and with aromatic carbon content.

GRAPHICAL ABSTRACT



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ABSTRACT

Online measurements of key information such as the decomposition stages of biomass gasification/pyrolysis in a fixed-bed reactor is currently limited with existing technologies. In this study a proof of concept for using Electrical Capacitance Tomography (ECT) for monitoring the decomposition stages of woody biomass is done. In practice, ECT measures the permittivity of the material under test. Therefore, the relation between the permittivity of the biomass in terms of the extent of thermal treatment is essential. Pyrolysis and gasification experiments were conducted to different extent of time and temperatures at a lab scale gasifier using wood chips. The permittivity of the samples was measured in-vitro using impedance analyzer at different excitation frequencies (20 kHz to 3 MHz). At a critical pyrolysis temperature of 700 °C the permittivity starts to increase significantly. In addition, for air-aided gasification the permittivity was found to reach its maximum in holding time of 10 or 30 min. Further examination of these samples in an ECT sensor revealed the same trend, implying that the permittivity results can be used for converting ECT reading to decomposition state. Chemical characterizations were done via elemental, thermogravimetry analysis, X-ray diffraction and Fourier transform infrared (FTIR) Spectroscopy. It was found that graphitization of the material is a prominent factor that control the increase of the permittivity. Analyzing quantitatively the aromatic and aliphatic carbon from the FTIR results disclose that it has a strong relation to the permittivity change when the aromatic carbon is higher than 95%. Therefore, in this range, it was possible to correlate these two parameters by an inverse relation which lead to a good match under frequencies higher than 200 kHz.

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1. Introduction

Gasification has been well-recognized as effective process for converting bio-mass residue into valuable products, such as syngas, biochar and heat that could be further used in downstream applications. During gasification process, organic content in the solid waste decreases gradually as it is decomposed and gasified to CO, CO_2, CH_4, H_2 and other gases with smaller quantities. However, gasification is a highly complex process that is difficult to model without very simplifying assumptions, and experiments are limited by the partial information that can be measured. Therefore, the process efficiency can be improved if more theoretical information is recognized. In order to achieve such improvement, the complex fluid dynamics, including reaction rates and reaction zones should be better understood. One step toward this target is detecting the decomposition stages of the biomass during gasification, which is the main goal of this study.

In traditional downdraft fix-bed gasifier the stages that the biomass goes through can be divided into different reaction zones which include: drying, following pyrolysis, then oxidation and reduction, which designed to yield a low tar at optimized conditions [1]. This process is illustrated in Fig. 1. The biomass is usually fed at the top of the gasifier with limited moisture content, i.e. not more than 40% wt. [2], then, heat transfer from the hot gas mixture to the biomass, which stimulate evaporation of the liquid water from the biomass. When drying is completed, the volatile content in the biomass starts to decompose to tar and syngas at intermediate temperatures (i.e. typically 400–700 °C [3]), and the solid goes through a process of charring, which is known as the pyrolysis stage. Following, char is the main component in the solid, and it react with oxygen in exothermic reactions (the oxidation stage), then combustible gaseous are released from the remaining char by endothermic reactions (reduction stage).

One way to distinguish the different zones in a real gasifier is conducting a simulation of the process. But due to the complexity of modeling the multi-scale multi-phase phenomena, it is still not feasible to simulate the full-scale process without very simplifying assumptions, e.g. one-dimensional flow, limiting the amount of gas species, neglect particle-particle interaction and fragmentation, etc. In addition, model calibration is compulsory with specific experimental data that correspond to the same feedstock, gasification agent and gasifier. However, it is a major challenge to retrieve valuable information such as temperate profile, syngas composition profile, and biomass gasification stage from gasification experiments. Therefore, a direct measurement of these properties has an enormous impact not only for monitoring purposes, but also for improving the modeling of the process.

The aim of this study is to provide a proof of concept for using Electrical Capacitance Tomography (ECT) for monitoring different gasification zones. This method is well-known in powder technology for detecting the cross sectional volume fraction profiles in various applications that involve relatively high local volume fraction of particles [4]. These applications include circulating fluidized beds [5] for identifying fluidization state, or the riser mass flow rate, and pneumatic conveying [6,7] for detecting the flow regime (e.g. plug, dune flow, stratified or homogenous) [8], or even distinguishing different phases in multiphase flow of air, water and oil [9,10]. More recently, an untraditional methodologies has been suggested for using ECT for identifying the moisture content in the particles in fluidized bed dryers [11] and for studying the inner structure of flames [12], pointing out the potential use of ECT in reacting flows.

The theoretical principal of ECT which allows these manipulations is the relation between the dielectric properties of the mixture and another property, such as the volume fraction. The objective of this study is to find a correlation between the biomass decomposition states (i.e., raw biomass, dry biomass, biochar after some extent of pyrolysis, and biochar-ash mixture after some extent of oxidation and reduction), and the dielectric properties of the material, which have not been investigated systematically before for ECT application.

In order to tackle this problem a brief introduction is brought here for dealing with the most common implementation of ECT: recognizing the volume fraction. For this application, the permittivity is varied in terms of air content at different spatial locations at the cross section. The permittivity composes from a real and imaginary parts:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1}$$

And if the so-called Maxwell model is considered, this relation is known as:

$$\varepsilon_m' = \frac{\varepsilon_1'(2\varepsilon_1' + \varepsilon_2' - 2c_v(\varepsilon_1' - \varepsilon_2'))}{2\varepsilon_1' + \varepsilon_2' + c_v(\varepsilon_1' - \varepsilon_2')} \tag{2}$$

where ε_m', ε_1' and ε_2' are the real permittivity of the mixture, air and fully packed solid particles, respectively. And c_v is the volume fraction of the dense phase. Additional relations between the bulk density and the material permittivity can be found in [13–15]. However, when using ECT and measuring the capacitance, the mixture permittivity is unknown, and the relation between the permittivity and the measured capacitance is given by the Maxwell equation:

$$C_M = \frac{Q}{V_c} = \oint \varepsilon(x, y)\nabla\cdot\phi(x, y)ds \tag{3}$$

where C_M is the measured capacitance, Q is the charge, V_c is the potential difference between the electrode pair, and ϕ is the potential distribution. Unfortunately, Eq. (3) is nonlinear and very complex to solve analytically. Therefore, it is more practical to describe the forward problem in an ECT device, which is defined as the relation between the measured capacitance and the permittivity distribution within the sensor [16]:

$$\lambda = Sg \tag{4}$$

where $\boldsymbol{\lambda}$ is the normalized capacitance composed from a $mx1$ vector correspond to m electrode pair measurements, $\boldsymbol{S}$ is mxn matrix which is called the sensitivity matrix, giving a sensitivity map for each electrode pair, and $\boldsymbol{g}$ is the normalized permittivity, which compose from $nx1$ vector, and n is the number of cells in the mapping area. From this forward problem, the so called inverse problem needs to be solved, which is finding the permittivity from the capacitance measurements. Thus, if the inverse problem is solved, Eq. (2) can be used for evaluating the volume fraction. However, the accurate solution of the inverse problem is complicated, and only an estimated solution can be implemented, which were developed by different authors and are revised for their accuracy in [16]. In addition, there are different ways in the

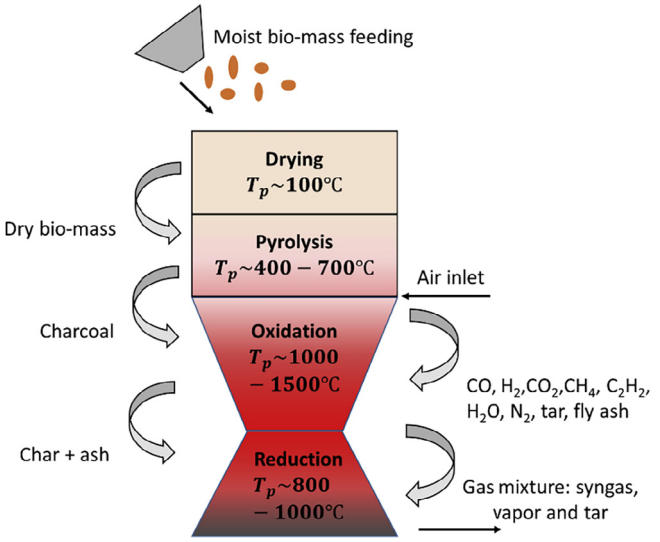

Fig. 1. Illustration of gasification zones in a typical downdraft gasifier including particles temperatures and conversion stages.