Biomass and Bioenergy 108 (2018) 330–337

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Research paper

# Assessment of biomass alterations during hydrothermal pretreatment by in-situ dynamic mechanical analysis

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ARTICLE INFO

*Keywords:*
Thermal degradation
Viscoelasticity
Lignocellulosic biomass
Poplar
Steam explosion

ABSTRACT

This work proposes an original innovative in-house device able to characterize the evolution of viscoelastic properties of lignocellulosic products during hydrothermal pretreatment (water-saturated conditions up to 190 °C). The main objective is to assess the cooking phase before steam explosion. We designed and built a novel experimental device for analyzing the dynamic mechanical analysis of the biomass soaked in water or acidic water. The device allows the sample to be loaded/unloaded during the test with an accurate measurement of deformation and force despite the severe conditions. This system can perform the mechanical test on immersed samples under controlled pressure (up to 1.5 MPa) and temperature (up to 190 °C). Experiments were performed with poplar via harmonic and periodic tests. The experimental data collected on poplar allows the characteristic time constants of the thermo-chemical reactions to be obtained as a function of the operating conditions.

## 1. Introduction

The main objective of the pretreatment of biomass, a key step in the production of lignocellulosic biofuels, is to increase the availability of polysaccharides to enzymes attack [1–3]. In order to obtain a relevant pretreatment, the operating conditions of the process should insure a good compromise between the initial characteristics of the biomass, the kinetics of its degradation during the cooking phase, and the efficiency of the subsequent enzymatic treatment.

The evolution of the viscoelastic behavior of biomass during the cooking phase is complex and involves several phenomena. At short treatment times, the main effect is the reduction of apparent stiffness due to thermal and hydric activation of viscoelastic behavior. The coupled effect of these two parameters is quite well documented in the literature for tests performed at atmospheric pressure [4–8].

In the case of saturated samples above 100 °C, the direct assessment of viscoelastic behavior must be performed under pressure, which requires specific devices to be designed. A search of the literature reveals that devices designed from creep tests [9–11], relaxation tests [12], and harmonic analysis [13] are suitable for that purpose. From this literature review, it is obvious that such levels of temperature under water saturation not only activate the viscoelastic behavior, but also induce significant chemical degradation [13]. In such conditions, one must keep in mind that the characteristic mechanical time must be distinguished from the treatment time for the data analysis to be relevant. The only possibility is to perform harmonic or periodic tests during cooking; the time of one cycle is tied to the mechanical time, whereas the total time represents the residence time (or cooking time).

The main objective of this work is to present an innovative, in-house, device able to perform such tests up to 190 °C under water-saturated conditions. This device is then used to characterize the viscoelastic behavior of water-soaked poplar during steam treatment of up to 1 h, at various temperature levels. This device uses the same principle of the device WAVE$^T$ (Environmental Vibration Analyzer for Wood) developed a decade ago [13,14] to perform harmonic tests under saturated steam up to 130 °C.

However, due to the requirement of performing tests under the industrial conditions used in acidic cooking before steam explosion, a completely new device was designed. For this purpose, we used the concept of two chambers, one measurement chamber and one cold chamber with the scientific instrumentation. These two chambers are connected without any friction due to the concept of controlled leakage between these two chambers.

This new original facility, named WAVE$^T$ v2 (version 2), can perform dynamic mechanical tests (periodic and harmonic protocols) of biomass under water-saturated conditions up to 190 °C. The saturated water pressure at this temperature equals 1.3 MPa, which requires 1.5 MPa of working pressure, as a portion of non-condensable gas is needed in our measurement principle. To achieve these specifications, only the patented design of WAVE$^T$, which allows the accurate

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https://doi.org/10.1016/j.biombioe.2017.11.014
Received 29 June 2017; Received in revised form 15 November 2017; Accepted 19 November 2017
Available online 08 December 2017
0961-9534/ 

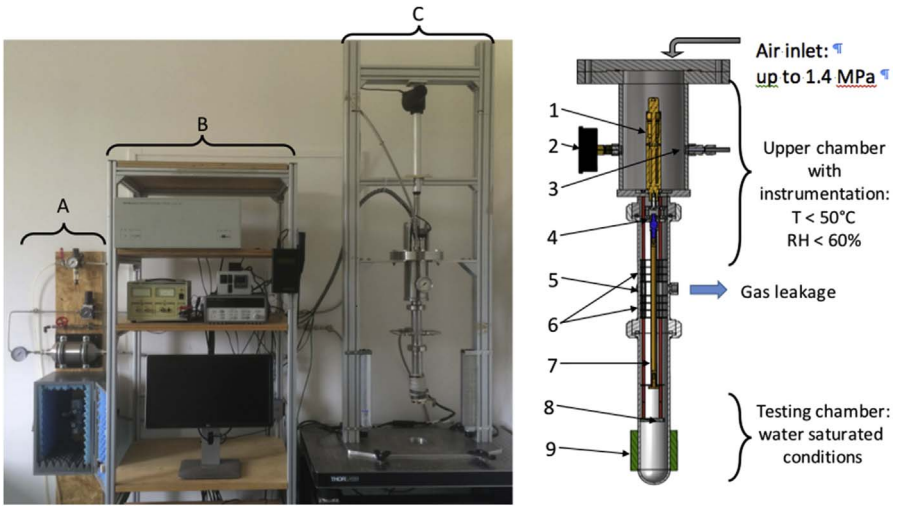


**Fig. 1. Left:** Global view of the experimental setup (A, inlet air pressure and outlet air flow control; B, control and data acquisition instruments; C, test bench on an anti-vibration table). **Right:** Schematic view of the double chamber test bench (1, actuator; 2, manometer; 3, safety valve; 4, load cell; 5, gas leakage; 6, series of fins; 7, moving rod; and 8, electric heater).

instrumentation to be protected from the severe cooking conditions, was kept in the present design. All remaining parts were redesigned to increase the working range (190 °C instead of 130 °C, 2.0 MPa instead of 500 kPa), involving a much smaller chamber diameter, thicker tube walls, new sample holder, new actuator, and an electrical heating instead of a double jacket.

In the following section, this new device is presented in detail. A series of tests performed on poplar are then presented and analyzed. These tests are focused on the thermal activation of the mechanical properties as well as on the evolution of the mechanical behavior during cooking. This second piece of information allows the characteristic time constants of the thermo-chemical reactions as a function of temperature to be obtained.

## 2. Materials and methods

### 2.1. Materials

The complete system WAVE$^{T}$ v2 is depicted in Fig. 1. Close observation of the experimental setup allows the double-chamber test bench to be distinguished, along with its inlet air pressure and outlet airflow control mechanism, and the instruments and data acquisition equipment. The whole device is controlled by an in-house Labview application (National Instruments). From the schematic of the double-chamber test bench (right side), one can distinguish from bottom to top: i) the testing chamber, the hot chamber working under water saturation conditions, ii) the intermediate zone designed to maintain the two contrasted conditions and iii) the upper zone, the cold chamber, housing the actuator and the sensors.

The core of this device is an in-line mechanical system composed of the actuator, a load cell, and the charge rod. For the actuator, we use either the compact Newport LTA-HS, for high displacement and travel range (50 mm travel range and 50 N of load capacity for 100 nm minimal increment), or the LTA-HL for better precision increment and higher force loads (25 mm travel range and 120 N of load capacity for 50 nm minimal increment). This type of actuator includes two key functions needed for mechanical tests: the excellent displacement precision required during mechanical tests and the large travel range necessary to fit the sample geometry. The load cell is a Measurement Specialties XFTC 310 (full scale range of 100 N and both linearity and hysteresis less than ± 0.5% of full scale).

The wood samples are subjected to deformation by harmonic (sinusoidal) and periodic load under compression (relaxation and creep). This apparatus is therefore able to determine the evolution of mechanical properties (apparent stiffness and viscoelastic behavior) as well as deformation (shrinkage) of wood samples in water-saturated conditions up to 190 °C. A resistive heat frame (370 W) controlled by a PID regulator (Eurotherm 3216) controls the temperature of the test chamber. Heating rates up to 10 K min$^{-1}$ can be achieved.

The key feature of this experimental device is to maintain very contrasted environments in the two chambers connected by a mechanical transmission without friction between the load rod, the load cell, and the actuator: the bottom test chamber, with elevated temperature and pressurized steam; and the top measurement chamber with conditions suitable for the accurate scientific instrumentation.

The system that is designed to separate these atmospheres is summarized in Fig. 2. An inlet flow of pressurized cold and dry air enters at the top face of the cold chamber, where all instruments are located (Fig. 2a). This flow forces its passage through the small gap between the load rod and a collection of fins from a distance of about 1 cm, which forms a succession of small volumes along the air flow (Fig. 2b). The large value of the Péclet number existing at all fin passages eventually inhibits any diffusion of vapor toward the top chamber. The airflow leaves the device at mid-length by a controlled leakage. The inlet gas pressure must be higher than the saturated water-vapor pressure in the hot chamber to ensure that diffusion acts to limit the water vapor flux between the hot chamber and the leakage position. Fig. 2c depicts the temperature and RH data acquired for one test during which the test chamber, with saturated water vapor, was gradually heated up to 180 °C. The leakage was adjusted during this test to successfully maintain reasonable temperature and humidity values in the top chamber ($T < 30$ °C and RH $< 60\%$). This test proves that the chamber separation works perfectly even though they are mechanically connected without friction.

### 2.2. Wood samples

In this work, we performed all tests with poplar samples under compression and in the radial direction. The poplar samples were selected from a seventeen-year-old Euramerican poplar I-214 (*Populus deltoides* × *Populus nigra*). They were cut into $8^3$ mm$^3$ cubic samples from a same long stick of section 8 × 8 mm$^2$ sections. These samples are therefore aligned along the longitudinal direction of the wood, which reduces the variability among samples. Duplicate samples were dried at 103 ± 2 °C until reaching a stable mass to determine the anhydrous mass and hence the initial moisture content of the samples. The same moisture content was assumed on all samples, which allowed their dry mass to be determined from their air-dry mass. The samples were soaked for 24 h prior to the test with several vacuum cycles in distilled water. The samples were therefore fully saturated at the beginning of the test and remained saturated during the entire test due to the additional water condensing on the sample during the heating-up