Fuel 115 (2014) 644–651

Contents lists available at ScienceDirect

Fuel

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

Heat capacity measurements of various biomass types and pyrolysis residues

Capucine Dupont [a,*], Rodica Chiriac [b], Guillaume Gauthier [a], François Toche [b]

[a] CEA, LITEN, Laboratory of Technologies of Biomass, France
[b] Université Lyon 1, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Villeurbanne, France

HIGHLIGHTS

- Heat capacity was measured on 21 biomass types and on fast pyrolysis chars.
- The influence of biomass type was moderated with relative differences below 20%.
- Linear increase was observed for biomass under the range of temperatures tested.
- Linear increase was observed for chars except in the range 353–513 K.
- Exothermal phenomenon of char recombination seemed to occur in the range 353–513 K.

ARTICLE INFO

Article history:
Received 24 June 2013
Received in revised form 22 July 2013
Accepted 23 July 2013
Available online 5 August 2013

Keywords:
Heat capacity
Biomass
Char
Pyrolysis

ABSTRACT

This study aims at measuring heat capacity on a large range of biomass types and on pyrolysis chars obtained under conditions representative of industrial reactors for further use of these data in thermal conversion models. As expected, linear increase could be observed with temperature for the 21 biomasses tested between 313 K and 353 K. The relative difference of heat capacity between the different biomasses was significant but lower than 20%, with values ranging from 1300 to 2000 J kg^{-1} K^{-1}. The sample form, either in block or powder, did not seem to have any influence. Values of about 1000 J kg^{-1} K^{-1} were measured on chars, whatever the pyrolysis temperature. These values are in the same order of magnitude as those extrapolated from literature correlations. As expected, linear increase could be observed with temperature, except in the range 353–513 K, in which an exothermal phenomenon of recombination seems to occur inside the char.

1. Introduction

Biomass-to-energy processes have recently gained growing interest due to the energy crisis. Indeed, there is a high potential of available lignocellulosic biomass, i.e. wood, energy crops and agricultural by-products [1]. Thermal processes, i.e. combustion, gasification and pyrolysis, appear as particularly suitable to convert this kind of biomass [2]. All these processes consist in a first step of pyrolysis, during which biomass is converted under the effect of heat only into gas and a solid carbonaceous residue called char.

Developing models of biomass thermal conversion is of great importance for reactor design. In such models, one crucial issue is the description of heat transfers inside biomass particles during pyrolysis, as these phenomena can limit the transformation under typical reactors conditions, for instance in gasifiers [3]. This description requires the knowledge of the thermal properties of biomass as well as their evolution with conversion [4]. One of these properties is heat capacity.

Experimental studies on heat capacity can be found in literature on biomass species of interest for current industrial applications: woody species [5,6], together with cellulose, which is the main constituent of biomass and the main product used for pulp applications [7–11] or agricultural biomass for food applications, such as peanut [12], cassava, yam, plantain [13] or cumin seed [14]. To our knowledge, agricultural by-products were considered only by Mothée and De Miranda [15] with measurements on coconut fibre and bagasse and there are no available heat capacity data on energy crops or wood from Short Rotation Forestry (SRF) and Short Rotation Coppice (SRC).

There is very little information about the evolution of biomass heat capacity with conversion. Only Gupta measured thermal properties of softwood and softwood bark chars obtained after pyrolysis under high heat fluxes conditions at 553 K [16].

* Corresponding author. Tel.: +33 438780205.
E-mail address: capucine_dupont@hotmail.fr (C. Dupont).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.07.086

These heat capacity measurements were generally performed either with adiabatic calorimeter such as in [10] or with Differential Scanning Calorimetry (DSC) such as in [13,16]. Many studies on food biomass were carried out by the method of calorimetry by mixtures but this technique is not accurate [14]. DSC seems to be a very accurate tool. However, it uses small volumes of solid, and therefore small masses of biomass, typically of a few milligrams, as biomass density is very low. The resulting heat flow is very low and one may doubt about the measurement significance. Moreover, as biomass and a fortiori char are heterogeneous, the issue of representativeness may also be raised when such small samples are used. Hence the calorimeter, which requires higher masses of solid, typically of a few grams, seems to be the reference tool for biomass heat capacity measurement.

Biomass heat capacity is known to be influenced by both temperature and biomass moisture. There is a general agreement on the linear increase of biomass heat capacity with temperature, that goes from 5 K to 423 K depending on the studies. Note that biomass heat capacity can be measured only up to temperatures of about 423 K, as biomass begins to decompose when temperature is higher than 423 K [17]. Regarding char, Gupta found that the heat capacity followed a linear increase from 313 K to 413 K and then a smoother increase characterised by a second-order polynomial between 413 K and 713 K [16]. This is in agreement with the findings of Raznjevik on charcoal [18].

The influence of moisture has been studied in a systematic way for several food biomass species. As for temperature, the increase of biomass moisture is generally found to lead to a linear increase of heat capacity [12,19–21]. According to the purpose of Njie et al. [13], measurement on dry biomass is sufficient to predict the heat capacity of moist biomass. Indeed, the heat capacity of moist biomass seems to be satisfactorily predicted by the summative contributions of dry biomass and water content except for very moist biomass (>60%).

The influence of the form of the sample, either bulk or pellets, has been studied only in a few papers. According to Vargha-Butler, the smaller the particle size, the lower the heat capacity for the four coals tested [22]. In contrary, no influence has been observed between minor millet grains and flours [23]. Wood pellets heat capacity was measured by Guo, but not compared with other forms of the same wood [21].

Based on these experimental data, pyrolysis models generally use one unique value or one correlation versus temperature obtained for wood whatever the biomass type. Regarding chars, as the available data are scarce, one unique value or average correlation is chosen for all chars, whatever the pyrolysis conditions, although it is well-known that chars produced under different conditions may have different properties, both in terms of composition and morphology [24]. Ragland et al. [25] assumes that the heat capacity of char is roughly equal to the heat capacity of pure graphite, but with no experimental data to support this affirmation. Other authors use measurements obtained on charcoal [26], as this solid has similarities with char and as it has been much better characterised for the last fifty years, for instance in [18,22,27,28].

Based on this background, this study aims to contribute to the completion of the existing data by measuring heat capacity versus temperature on:

- A large range of biomass types considered as potential feedstock for gasification process. This panel includes various woods among which Short Rotation Forestry and Short Rotation Coppice, in the form of blocks and powder, as well as agricultural by-products and energy crops.
- Pyrolysis chars obtained under conditions representative of those encountered in industrial reactors, i.e. high heating rate at the particle surface and temperatures up to 1073 K.

2. Materials and methods

2.1. Feedstock preparation

Biomass samples were selected to be representative of species potentially useable as feedstock in thermal processes. They were classified as follows:

- Wood: beech, angelim, faveira, maçaranduba, hazelwood, black pine, mixture Scot pine + spruce, poplar.
- Short Rotation Forestry/Coppice: SRF of poplar and eucalyptus, two SRC of poplar (numbered 1 and 2).
- Perennial crops: miscanthus, switchgrass.
- Agricultural by-products: wheat straw, rice husk, olive pomace, corn stover.
- Energy crops: triticale, tall fescue.
- One sample of cellulose Avicel was also selected for comparison with literature data.

All samples were ground below 200 μm in order to reduce samples heterogeneity and to make comparison possible. For this latter

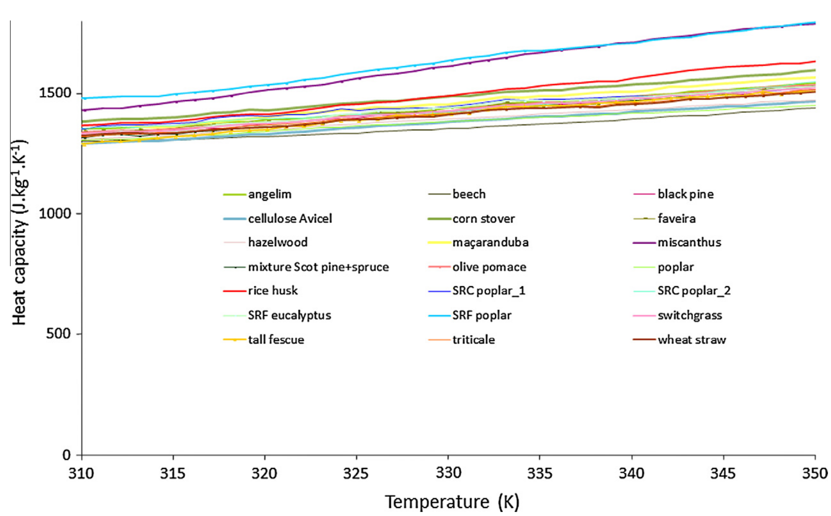

Fig. 1. Heat capacity of biomass samples versus temperature.