Predictions of biochar yield and elemental composition during torrefaction of forest residues

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HIGHLIGHTS

- Torrefaction of two forest residues is studied using a thermogravimetric analyzer.
- Torrefaction kinetics of spruce and birch residues is established.
- A model is developed to estimate the biochar yield and elemental composition.
- Distributions of initial, intermediate and final solid products are reported.
- This method is useful for the design and optimization of industrial torrefaction processes.

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ABSTRACT

In this work, a direct prediction method coupled with a consecutive reaction model is developed to estimate the biochar yield and elemental composition in a biomass torrefaction process. Norway forest residues were chosen as feedstock and torrefied at different temperatures under nitrogen atmosphere in a thermogravimetric analyzer. Obtained data were modeled to predict the mass loss during torrefaction. Distributions of initial, intermediate and final solid products as well as torrefaction kinetic parameters are reported. Thereafter, a direct method to predict the elemental composition of biochar is introduced. The results show that the decomposition of initial biomass to form an intermediate solid has higher conversion rate than the degradation of the intermediate. Moreover, the predictions reproduce well the experimental thermogravimetric curves and show composition trends similar to the literature data. This method is useful for the design and optimization of industrial torrefaction processes with predictable biochar yield and elemental composition.

1. Introduction

Torrefaction is a promising thermochemical pretreatment method to upgrade biomass to a homogeneous and hydrophobic fuel with increased heating value, better grindability, and superior combustion characteristics (Chen et al., 2015; Chew and Doshi, 2011; Ciolkosz and Wallace, 2011; van der Stelt et al., 2011). During torrefaction, raw biomass fuel is heated at 200–300 °C in an inert atmosphere to produce a solid product called biochar, which accounts for about 50–90% mass and 60–95% energy of the raw biomass (Chen et al., 2015). Other torrefaction products include a condensable mixture (containing mostly water, organic compounds and lipids) and non-condensable gases (including

hydrogen, carbon dioxide, carbon monoxide and hydrocarbons) (Bach and Skreiberg, 2016). In the last decades, plenty of researches have been conducted to assess the physical, chemical and fuel properties of torrefied fuels from various biomass sources and under different torrefaction conditions (Chen et al., 2013b; Lu et al., 2012; Mišljenović et al., 2014; Tran et al., 2016; Uemura et al., 2013). Energy applications of torrefied fuels such as combustion, gasification, iron-making and pyrolysis have been also intensively studied (Chen et al., 2013a, 2012; Khalil et al., 2013).

The torrefaction technology is developing rapidly for market introduction and commercial operation with a number of demo plants around the world (Cremers et al., 2015; Wilén et al., 2013). For industrial applications of the technology, it is important to understand the thermal degradation behavior of biomass during torrefaction as well as to predict the yield and fuel properties of biochar product in order to control and optimize the process. To address this need, several regression analysis studies (Almeida

et al., 2010; Medic et al., 2012; Tumuluru et al., 2010) have been performed to predict the yield, heating value, energy yield, and composition of biochar. However, these regression empirical models were based on only a few experimental points, thus their reliability and accuracy in further industrial applications might be limited. In addition, the studies provided no information about the torrefaction kinetics (e.g. activation energy) and the distribution of the products during the torrefaction process (e.g. how intermediate product is formed and degraded). For these requirements, Prins et al. (2006a) proposed a consecutive reaction model to predict the solid mass loss during willow torrefaction in kinetically controlled conditions (i.e. employing thermogravimetric analysis technique). Nevertheless, detailed distribution of solids and the predicted fuel properties of biochar were not included in the study. Based on this mechanism, Bates and Ghoniem (Bates and Ghoniem, 2012) further developed a method to estimate the elemental composition of biochar (e.g. C, H, N, and O contents) indirectly through that of released volatiles, which consist of 9 different species, detected by a gas chromatograph (GC) and a high performance liquid chromatograph (HPLC). This indirect method is interesting but it requires well capturing and precisely analyzing all the volatiles, from which any leakage can lead to an inappropriate prediction of biochar composition. To address the aforementioned issues and provide a more accurate prediction, it is necessary to develop a direct prediction method, which is the objective of this work.

In this study, forest residues (Norway spruce and birch branches) were torrefied in a thermogravimetric analyzer at different temperatures. The consecutive reaction model from (Prins et al., 2006a) was employed to study the torrefaction kinetics of the forest residues. The degradation and formation of solids during the torrefaction process as well the kinetic parameters (activation energy and pre-exponential factor) of each reaction are presented. In addition, a method to directly predict the elemental composition of biochar product is reported.

2. Materials and methods

2.1. Materials

Norway spruce and birch branches were collected from a local forest in Trondheim (Norway) to represent forest residues. In the Nordic countries, these branches are usually discarded after wood harvesting, thus they are relatively cheap feedstocks. The collected branches were 2–2.5 cm in diameter. Before cutting and washing, the bark was removed from the core branch in order to avoid possible interferences caused by impurities, contaminants and composition differences. The bark-free branches were then dried at $103 \pm 2\,°C$ in an oven for 24 h, and ground in an IKA MF 10 cutting mill (from IKA®-Werke GmbH & Co. KG) with a closed bottom. A Fritsch Analysette 3 Pro vibrator was used to select particles less than 125 μm for thermogravimetric analysis. The fuel characterization of the dried feedstocks used in this study is tabulated in Table 1.

Table 1
Fuel characterization of forest residues.

Feedstock	Proximate analysis[a]			Ultimate analysis[b]				HHV[c]
	Ash	VM	FC	C	H	N	O	
Norway birch	0.64	89.74	9.63	47.62	6.38	0.37	45.63	19.52
Norway spruce	0.68	85.18	14.14	49.58	6.39	0.39	43.64	20.32

VM: volatile matter, FC: fixed carbon
[a] Dry basis.
[b] Dry and ash free basis.
[c] Higher heating value, dry basis, in MJ/kg.

2.2. Thermogravimetric method and procedure

Torrefaction of the forest residues were carried out in a thermogravimetric analyzer (SDT Q600 TGA, TA Instruments). For each run, an amount of 10 mg sample was weighed and loaded in an alumina crucible, and a nitrogen flow rate of 100 mL/min was supplied for the experiment. The experiment started from room temperature. The sample was heated to 105 °C and held at this temperature for 30 min for further drying. Thereafter, it was heated to preset torrefaction temperatures (220, 240, 260, 280, 300 °C) and held isothermally for 2 h. It is worth noting that different but slow heating rates were applied for different torrefaction temperatures in order to archive the same non-isothermal period, which took a constant time of 5 min for all samples to reach the preset torrefaction temperatures. To ascertain the analysis quality, the thermogravimetric analyzer was periodically calibrated, and the tests suggested high repeatability of TGA curves in the experiments.

2.3. Modeling

2.3.1. Distributions of solid products

Prins et al. (2006a) proposed a model consisting of two series-reactions to simulate the solid mass loss during torrefaction on the basis of data collected from thermogravimetric analysis (TGA) experiments at different temperatures in isothermal mode. In this model, it is assumed that raw biomass A is converted to an intermediate solid B and volatiles V1. The intermediate solid B reacts afterwards to form final solid C and additional volatiles V2. The four reaction rate constants (k_1, k_{V1}, k_2, k_{V2}) were determined by fitting predicted curves to the experimental mass loss curves.

$$\qquad (1)$$
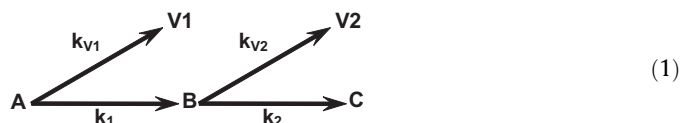
Assuming that all reactions are first order, the rate constant equations for the solids (A, B, C) and volatiles (V1, V2) can be written as:

$$\frac{dm_A}{dt} = -m_A \cdot (k_1 + k_{V1}) \qquad (2)$$

$$\frac{dm_B}{dt} = k_1 \cdot m_A - m_B \cdot (k_2 + k_{V2}) \qquad (3)$$

$$\frac{dm_C}{dt} = k_2 \cdot m_B \qquad (4)$$

$$\frac{dm_{V1}}{dt} = k_{V1} \cdot m_A \qquad (5)$$

$$\frac{dm_{V2}}{dt} = k_{V2} \cdot m_B \qquad (6)$$

where m_i is the mass of any pseudo-component ($i = A, B, C, V1, V2$) and its rate constant obeys the Arrhenius law: $k_i = A_i e^{-\frac{E_i}{RT}}$, in which A_i and E_i are respectively the activation energy and pre-exponential factor of the component i, R is the universal gas constant, T is the absolute temperature.

The degradation/formation of the components can be obtained by integrating Eqs. (2)–(6). The cumulative mass yield of the components can be calculated as a function of time, from which the biochar yield (Y_S) and the total volatiles yield (Y_V) are the sums of appropriate components:

$$Y_S = Y_A + Y_B + Y_C \qquad (7)$$