



# Diversity of chemical composition and combustion reactivity of various biomass fuels



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## HIGHLIGHTS

- Chemical composition and combustion kinetics were measured simultaneously in a TGA.
- Straw char pellets had the largest variability for combustion properties.
- Wood char pellets had the smallest variability for combustion properties.
- The differences in predictions between the two applied reaction models were small.
- The accuracy of kinetics for different pellets strongly affected model prediction.

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## ABSTRACT

A simple and fast method for measuring simultaneously the chemical compositions and combustion reactivities of biomasses and evaluating their heterogeneity was developed using a commercial thermogravimetric analyzer. Wood, straw, and bark pellets were selected as the biomass fuels. Compared to the variations observed for volatiles and char contents, the variations of moisture and ash contents for the three types of biomass were large in an individual pellet. The straw char was more reactive than the bark char and wood char, probably due to the high ash content of the straw, which is especially rich in potassium. Furthermore, the variations of the characteristic temperatures and kinetics in an individual pellet increased from the wood char to bark char to straw char. The experimental results for char combustion can be described by the two simple reaction models: the volumetric model and the shrinking particle model. For each type of biomass, the differences in predictions between the two reaction models were much smaller than the differences in the accuracy of the measured kinetics for the different particles. For the kinetic parameters, the activation energy  $E$  and the natural logarithm of apparent pre-exponential factor  $A^*$  ( $\ln A^*$ ) showed a linear correlation in the two applied models ( $A^* = e^{(0.2140E - 8.713)}$ ), while the measured activation energies of the two applied reaction models were also linear ( $E_{\text{shrinkingparticle}} = 0.8136E_{\text{volumetric}}$ ). The performed analyses revealed that 10 biomass samples could ably characterize the conversion of a batch of biomass char particles and the average kinetics of the reactions. In addition, the distribution of conversion rates of the different chars in a batch at a specific time or temperature could be estimated from the standard deviation of the average value for the kinetics.

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## 1. Introduction

Biomass is one of the most utilized renewable resources worldwide [1–3]. Its importance for the energy and chemical industries is expected to increase to enable the transition from fossil fuels to renewables, so as to meet various climate goals and to create a more sustainable society in the long term [4]. Compared with the concentrated highly energy-dense fossil fuel resources, biomass

is widely spread geographically and in its original form has a low energy density owing to its high moisture content, low bulk density, and high oxygen content [5]. Furthermore, biomass is very heterogeneous in nature and its properties vary within plant species and even within the same plant [6]. Studies on the biomass diversity of physical property and chemical composition have been widely reported in the open literatures [5,7–9]. The biomass diversity makes it difficult to characterize biomass and to define representative properties that can be used to describe the conversion behavior in, for example, a biomass boiler for heat and power production or a gasifier for gas production.

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In contrast to coal, most of the chemical energy in biomass is stored in the volatiles rather than in the char [10]. Nevertheless, the chemical energy stored in the char is significant. Thus, the process of char conversion in a boiler or gasifier plays an important role in plant design. For this reason, extensive efforts have been made to generate representative kinetic data and reaction models for various types of biomasses. Di Blasi et al. summarized different reaction models and showed that the kinetics varied by several orders of magnitude [11,12]. Dall'Ora et al. studied the influence of pyrolysis conditions on char reactivity and morphology. Adánez et al. extrapolated the kinetics obtained at low temperatures to conditions at high temperatures by a combined method [13]. Wornat et al. pointed out that the heterogeneity from particle to particle, in char properties, particle shape, and combustion reactivity, is an overwhelming feature of biomass char [14]. Related work performed within our research group has shown that the properties of the ash vary significantly, even from pellet to pellet in a single batch of straw pellets. Thus, it is reasonable to assume that char kinetics is also particle-specific and even varies according to the location within a single particle. However, to authors' best knowledge, studies on the biomass diversity of char reaction kinetics are rare. These raise two questions related to engineering calculations. The first question is how to choose a conversion model and related kinetic data to predict conversion rates in an industrial reactor. The second question is how to obtain appropriate kinetic data and determine in an efficient way its variability in a batch of biomass.

In the present work, these two questions are approached by selecting three important biomasses that are widely used in northern Europe and that have different characteristics: stem wood, bark, and straw. To ensure representative samples and a model-friendly shape, the biomass material was dried, grained, and pelletized by a uniform commercial process. Generally, in a dryer the moisture content in the raw material was reduced from approximately 50% to around 8–12%. After that the dried raw material was ground to a specific but rather broad particle size distribution, usually less than 4 mm, in a hammer or ball mill, and then screened to remove oversized and fine particles. Subsequently, the prepared material was forced by rollers through the holes of a hot die to form dense 6–8 mm diameter and 5–30 mm long pellets and finally allowed to cool [1,15,16]. In the grinding and densification steps, the material moisture content is further reduced to around 5–10% [5,7,17,18]. Before and after the whole pelletizing process, the biomass bulk density can increase from initial 40–200 kg/m<sup>3</sup> to final 400–800 kg/m<sup>3</sup> [7,19]. Though the whole pelletizing process, the effects of original moisture content, fiber structure, and local density variations on the reaction kinetics and other ash-related issues were minimized. By modifying the common thermogravimetric method of the fuel proximate analysis, in a single test, we could measure the chemical compositions, derive the fuel kinetic data, and obtain the variabilities of these properties, which are subsequently applied to the engineering calculations.

## 2. Experimental

### 2.1. Materials

Wood, straw, and bark pellets were used in the present study. The dimensions of selected pellets are shown in Fig. 1. All the pellets had a diameter of approximately 8 mm. The average lengths of wood, straw, and bark pellets are 17.5, 17.8, and 17.0 mm, respectively, and each selected pellet weighs about 1.0 g. The typical proximate and ultimate analyses of biomass fuel, which were obtained using the standard method, are listed in Table 1. The compositions of the three types of biomass were quite similar, with high contents of volatiles and oxygen and low carbon content, although the straw



Fig. 1. Dimensions of selected biomass pellets: measurements of diameter and length were done by a vernier caliper.

and bark had higher ash content. The moisture content was in the range of 8–11 wt.%, which meets the standard for commercially produced pellets [7,8]. In addition, the sulfur content was very low. The lower heating value decreased from bark (19.30 MJ/kg, dry basis) to wood (18.70 MJ/kg, dry basis) to straw (16.13 MJ/kg, dry basis), which meant that the bark had the highest values for energy and mass density, while the straw had the lowest values.

### 2.2. Apparatus and methods

The biomass pellets were analyzed using a thermogravimetric analyzer (Leco, TGA701). The chemical compositions and combustion reactivities of the three types of biomass pellets were determined and compared. For each analysis, 10 selected samples (each biomass pellet weighed  $1.0 \pm 0.1$  g) were loaded into 10 ceramic crucibles, respectively, and heated from room temperature to the final temperature set in the apparatus according to the designed temperature program. The applied temperature program and gas environment are shown in Table 2, which is modified based on the common thermogravimetric method of proximate analysis. This modified method is more suitable and faster for biomass analysis, because biomass usually has a high content of moisture and is rich in some inorganic compounds that have low temperatures of evaporation. More importantly, the kinetics of char combustion can also be obtained in the same analysis. Initially the samples were dried in crucibles without covers at a rate of 20 °C/min by raising the temperature from room temperature to 150 °C in N<sub>2</sub>. The sample weight loss during the drying step was designated as the reference value for the moisture content of the biomass. Thereafter, the dried samples were heated in crucibles with covers at a rate of 40 °C/min to 850 °C and held for approximately 5 min at 850 °C in N<sub>2</sub>. The sample weight loss during the pyrolysis step was designated as the reference value for the volatiles content of the biomass. Subsequently, the remaining char samples were cooled in crucibles with covers to 200 °C (below the ignition temperature of char) in air. Finally, the char samples were heated in crucibles without covers at a rate of 5 °C/min to 700 °C and held for approximately 20 min at 700 °C in O<sub>2</sub>. The residual sample weight from the combustion step was designated as the reference value for the ash content of the biomass.

### 2.3. Combustion of biomass char

In the biomass char combustion step, the ignition and burnout characteristics can be determined from the weight loss curves,

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