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Coupling of a distributed activation energy model with particle simulation for entrained flow pyrolysis of biomass

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ABSTRACT

This study evaluated the applicability of the distributed activation energy model (DAEM) while incorporated in a particle model designed for entrained flow pyrolysis of biomass. For that purpose, two types of biomass (spruce sawdust and coconut shell) were pyrolyzed in a thermogravimetric analyzer to obtain the intrinsic kinetic parameters. These kinetic parameters were then incorporated in the particle model. For comparison, entrained flow pyrolysis of those samples was also conducted at different temperatures (1073 and 1273 K) by varying particle size (150–250 μm and 500–600 μm). The modeling results were also compared with the literature data. The prediction using DAEM kinetics was improved when pyrolysis heat of reaction was included in the model. Based on the findings, a method was proposed to use the intrinsic kinetic parameters for particle simulation to determine the conversion profile of biomass pyrolysis under laminar entrained flow condition.

1. Introduction

Pyrolysis is a rather complex and rapid process that occurs with temperature increase prior to gasification of the char. In the past few years, significant attention is paid to understand the reaction kinetics and underlying mechanism of pyrolysis. Generally, pyrolysis kinetics is studied in literature by non-isothermal experimental methods. There are several methods available for kinetic analysis of biomass; these range from simplistic (single reaction model) to the most complicated models (three parallel *n*th order distributed activation energy model (DAEM) [1]). Based on the model requirements, different modeling strategies are adopted. To determine intrinsic kinetics of the pyrolysis process, particle size is kept very small to avoid any heat transfer effect and pyrolyzed under low heating rate [2]. The parameters generated by these models can be used to estimate the conversion time for pyrolysis. This is also an important input for simulating particles under pyrolysis condition. Depending on the operating conditions, a biomass particle can be affected by several other factors such as heating rate (heat transfer), pyrolysis heat of reaction, and in some cases mass transfer. For biomass particle sizes ranging from 100 μm to 1000 μm, Dupont et al. [3] showed pyrolysis as a heat transfer affected process under high heating rate because of low thermal conductivity of biomass. During this process, they observed negligible internal mass transfer by comparing the characteristic times. Even though some researchers [4] included the mass transfer in pyrolysis modeling, it was understood that this phenomena would only affect the process when the particles are larger (>1.5 mm) [5]. Also, their study was not conducted for a high heating rate process (200–10000 K/s). Similar studies [6–8] are available in literature which addressed low heating rates (6–10 K/s). In most cases, they compared their simulation values with the experimental results by Pyle and Zaror [9] under fixed bed condition in the temperature range of 623–780 K with particle size between 0.6 and 2.2 cm.

On the other hand, industrial gasifiers use a very high heating rate for gasification process where pyrolysis takes place in a fraction of a second. To simulate those processes, pyrolysis in laminar entrained flow reactor is an attractive technique. Few recent studies [10–12] reported particle simulation with experimental comparison in such condition (particle motion and high heating rate). In those studies, particle model was developed to determine the conversion time and solid yield for pyrolysis to compare with the experimental results. The solid structure change due to sudden release of volatiles was observed by scanning electron microscope imaging [10,11]. However, the complex process was not incorporated in the model. Also, these studies did not include the release of gas and tar from particles. Nevertheless, the determination of accurate weight loss profile and conversion time for biomass pyrolysis is of utmost importance from practical viewpoint. It was found that the particle model without considering the heat of reaction for pyrolysis was good enough for predicting the char yield from experiments. To account for the weight loss profile and characteristic time for pyrolysis of biomass particles, apparent kinetics was used in this model instead of intrinsic kinetics. Usually, apparent first-order kinetics determined under a high heating rate results in significantly lower values of kinetic parameters (31–48 kJ/mol) [13,14] compared

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to the parameters determined under slow heating rate with advanced kinetic models (150–250 kJ/mol) [15–17]. Therefore, the intrinsic kinetics is known to be inappropriate to use for particle simulation of pyrolysis under entrained flow condition as they are not evaluated under exact similar condition. However, it would be beneficial to use those parameters for particle model as slow heating rate experiments are easy to perform and the kinetics estimated by the process is more reliable due to precise measurements.

Therefore, the aim of this study was to assess the incorporation of the intrinsic kinetic parameters determined by *n*th order DAEM algorithm [17] in a particle simulation of entrained flow pyrolysis process of two types of biomass. It is to be noted that this work focuses strictly on description of the pyrolysis conversion time, heat transfer, and weight loss profiles, but not on structural change of the solid and the tar–gas phase reactions. For comparison, some experimental and modeling data were adopted from Umeki et al. [10] with the current experiments. In the end, a modeling strategy was proposed based on the findings to include intrinsic kinetics in particle simulation considering heat of reaction.

2. Experimental

2.1. Sample

Spruce sawdust (*Picea abies*) and coconut (*Cocos nucifera*) shell powder were used for thermogravimetric analysis and entrained flow pyrolysis. For thermogravimetric analysis, particle size was kept below 90 μm, which was used for intrinsic kinetics determination. On the other hand, entrained flow pyrolysis was performed on the particle size ranges of 150–250 μm and 500–600 μm. The particle size distribution of the samples is presented in Fig. 1. It is well known that smaller particle size is suitable for entrained flow reactors. For coal, this size is as small as 150 μm whereas for biomass it can be around 300–400 μm due to its low density [18]. Drift et al. [18] showed that reduction of particle size to 200 μm induces a need for 0.05 kW(electric) per kW(thermal), which is more than 10% based on primary energy. These particle sizes were chosen assuming largest possible particles would be used under entrained flow condition to minimize the energy penalty and, furthermore, to verify the particle model over a wide range of particle size.

Table 1 shows the proximate and ultimate analysis of the samples under consideration. However, it should be remembered that the values of volatile matter measured in would be different from the volatile matter released during the entrained flow pyrolysis experiments. This difference is due to the acceleration of the primary pyrolysis during entrained flow pyrolysis of biomass which leads to low char yield [13,19].

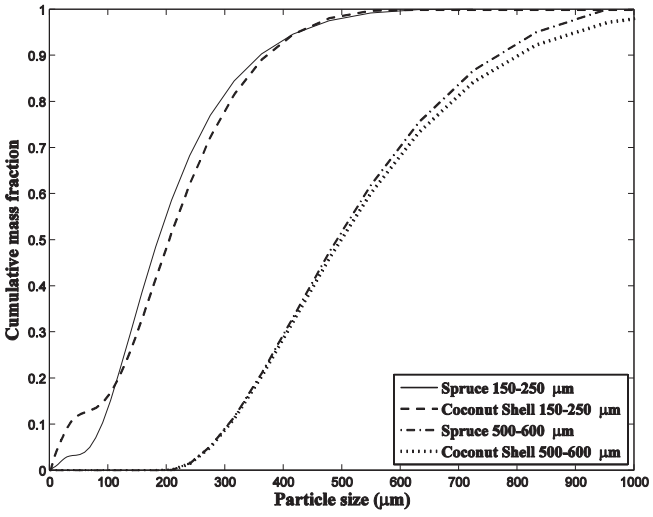

Fig. 1. Particle size distributions of the biomass samples.

Table 1
Proximate and ultimate analysis of the samples.

	Spruce	Coconut shell
Proximate analysis (wt%, (daf))		
Volatile matter	72.71	74.27
Fixed carbon	27.29	25.73
Ultimate analysis (wt%, (db))		
C	44.5	49.67
H	6.55	5.89
N	0.05	0.26
S	0.1	0.95
O[a]	48.36	42.53
Ash	0.5	0.7

2.2. Experimental procedure

To determine the intrinsic kinetics of the samples, non-isothermal pyrolysis was conducted at three different heating rates (5, 10 and 20 K/min) in a thermogravimetric analyzer (Model STA 449 F3 Jupiter®, NETZSCH-Gerätebau GmbH, Germany) with two repeats. A shallow (2 mm depth) alumina crucible was used for this purpose under a constant N_2 flow of 0.02 L min^{-1}. Blank runs at the respective heating rates were subtracted from the sample runs to remove any instrument artifact.

An entrained flow reactor of 2 m (effective reaction zone—1.885 m with 50 mm inner diameter) length was used to investigate the conversion of the solid particles during rapid pyrolysis. The experiments were designed to be compared with the modeling results. This study considers two temperatures (1073 K and 1273 K) for experimental and modeling purposes. The feed rate varied between 10 and 30 g/h for different samples and particle size. The experimental setup is shown in Fig. 2. To feed the particles in an entrained state, 1.0 L/min at a standard state was maintained while feeding the particles through the narrow injector. Secondary gas was also supplied from the bottom of furnace but entered the reactor from the top with a flow rate of 4.0 L/min at a standard state. As the Reynold's number in the reactor was in the range of laminar flow, it was denoted as laminar EFR reactor. The reactor length was varied from 0.65 to 1.885 m by different length of water cooled injectors. At the bottom of the reactor, solid residue was collected by a flask at the bottom after cooling. Solid conversion was determined by measuring the solid retained at the bottom along with ash tracing method [20]. Further details of the experimental setup and reactor can be found elsewhere [21].

3. Modeling strategy

3.1. Pyrolysis kinetics

The pyrolysis kinetics at slow heating rates were measured by the *n*th order distributed activation energy model (DAEM) algorithm developed and applied on several solid fuel by Kirtania and Bhattacharya [17,22]. The model uses a single set of reactions for estimating kinetics. The benefit of this assumption is that it can condense to a single reaction in case of high heating rate. The integral equation for the model is represented by Eq. (1).

$$\frac{w}{w*} = \int_0^{\infty} \left\{ 1 + (1-n) \int_0^t k_0 \exp\left(-\frac{E}{R_g T} \right) dt \right\}^{\left(\frac{1}{1-n}\right)} f(E) dE, \text{ where } n \neq 1 \quad (1)$$