**ARTICLE IN PRESS** 

#### Fuel xxx (2015) xxx-xxx

ELSEVIER

Contents lists available at ScienceDirect

## Fuel

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

Please cite this article in press as: Gable P, Brown RC. Effect of biomass heating time on bio-oil yields in a free fall fast pyrolysis reactor. Fuel (2015), http://

# Effect of biomass heating time on bio-oil yields in a free fall fast pyrolysis reactor

### Preston Gable, Robert C. Brown\*

Bioeconomy Institute – Iowa State University, 1140 BRL, Ames, IA 50011-3270, United States

НІСНІСНТУ

• The effect of pyrolysis heating time on bio-oil yield was studied.

• The analysis shows that pyrolysis continues well beyond the 1–2 s frequently assumed.

• All biomass components contribute to this extended pyrolysis time.

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ARTICLE INFO

#### Available online xxxx

- 25 Keywords:
- 26 Biomass
- 27 Heating time
- 28 Free fall reactor29 Devolatilization
- 30 Bio-oil
- 31

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#### ABSTRACT

The goal of this study is to evaluate the role of biomass heating time on bio-oil yield during fast pyrolysis in a free fall reactor. Biomass heating times were controlled using several configurations for conveying solids from the bottom of the free fall reactor. In all tests reactor wall temperature was 550 °C, sweep gas flowrate was 18 L/min, and heated reactor length was 2.77 m, which set the minimum biomass heating time of approximately 1.4 s (particles falling downward in sweep gas). Analysis of products included solid, liquid and gas mass yields; proximate analysis of the solids; and water-soluble sugar and carboxylic acid content of the liquid. These experiments showed that biomass continued to pyrolyze well beyond the few seconds frequently assumed to be adequate to achieve fast pyrolysis. Bio-oil yield increased with biomass heating times even for times exceeding 40 s. Analysis of liquid products suggests that hemicellulose, cellulose, and lignin all contributed toward the longer than expected pyrolysis times.

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#### 1. Introduction

Fast pyrolysis is the rapid heating, followed by rapid cooling, of a finely ground biomass feedstock in the absence of oxygen to produce predominately liquid product that can ideally be a drop-in replacement for current liquid fuel applications such as heat, power, transportation fuels, and specialty chemicals. Technoeconomic analyses of a variety of biomass conversion pathways indicate that fast pyrolysis is among the most cost effective of these technologies [1–9].

Fast pyrolysis is often thought to be essentially complete in just a few seconds [10]. Computational studies performed by Kersten et al. [11] evaluated several intrinsic kinetic schemes proposed in the literature. They found that fast pyrolysis at 500 C is expected to be complete in 2–12 s. To our knowledge no experiments have been performed to investigate this question under conditions of

http://dx.doi.org/10.1016/j.fuel.2015.10.073 0016-2361/© 2015 Elsevier Ltd. All rights reserved.

dx.doi.org/10.1016/j.fuel.2015.10.073

high heat rates (>100 C/s) characteristic of fast pyrolysis. Fluidized bed and auger reactors, the two most common configurations for fast pyrolyzers, do not lend themselves to measurements of devolatilization times for pyrolyzing biomass. Typically biomass remains in a fluidized bed until it is converted to char sufficiently fine to be elutriated from the reactor [12]. Auger reactors move biomass through the pyrolysis zone at rates that are much longer than the one to two seconds usually assumed for completion of fast pyrolysis [13]. Micropyrolyzer systems are usually operated in conjunction with a gas chromatograph-mass spectrometer (GC-MS), making dynamic measurements of pyrolysis impractical. Thus, an investigation of biomass devolatilization times during fast pyrolysis requires a reactor that allows some level of control over biomass heating time after it has been rapidly heated to pyrolysis temperature.

This study investigates fast pyrolysis in a free-fall reactor, designed to rapidly heat biomass to the desired pyrolysis temperature as it falls through a long, vertical column followed by controlled biomass heating time in a heated catch pot at the bottom of the column. We have found that biomass continues to 81

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<sup>\*</sup> Corresponding author.

*E-mail addresses*: pagable@iastate.edu (P. Gable), rcbrown3@iastate.edu (R.C. Brown).

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pyrolyze in the heated catch pot, contrary to our original expectation that essentially devolatilized biomass (char) would exit the
bottom of the column [14]. The present study is to understand
the effect of biomass heating time on bio-oil yields from pyrolyzing
biomass.

#### 87 2. Materials and methods

88 The reactor system used in this study, shown in Fig. 1, was designed to allow for continuous operation. Biomass was fed into 89 90 the system using an Acrison BDFM volumetric feeder with the abil-91 ity to meter feedstock at rates ranging from 0.25 kg/hr to 2 kg/hr. 92 The reactor was 3.05 m tall. The reactor was built from 11/4" Sched-93 ule 40 316 L stainless steel pipe providing an inside diameter of 94 0.035 m. The drop tube portion of the reactor was heated using 95 Watlow high temperature ceramic radiative heaters while the remaining parts of the reactor were heated using high temperature 96 97 heat tapes. All heaters and exposed surfaces were insulated using 98 high temperature ceramic insulation.

Particle heating time is equal to the reactor height divided by
the particle velocity. In the absence of sweep gas, the particle
velocity is equal to the terminal velocity of the particle in free fall.
In the presence of co-flowing sweep gas, the particle velocity is the
sum of the terminal velocity of the particle and the velocity of the
sweep gas. In the former case, particle heating time was about
2.5 s, decreasing to 1.4 s in the presence of sweep gas.

106 Temperature was controlled via manipulation of individual 107 heater zone set points. These heaters were controlled via thermo-108 couples placed on the exterior surface of the reactor underneath 109 the corresponding heater. Sweep gas volumetric flow rate was manipulated by altering the amount of sweep gas introduced at 110 111 the top of the reactor. Particle heating time was mainly a function of the heated length of the reactor and the time that the biomass 112 113 was heated in the system.

Two methods were used to capture solids exiting the bottom of the vertical heating zone of the reactor. The static solids catch method simply allows the solid particles to accumulate in a catch pot for the duration of the test as illustrated in Fig. 2(a), a method previously used by Ellens and Li [14,16]. In some experiments the catch pot was heat traced to the pyrolysis temperature allowing the collected solids to continue to pyrolyze, giving a biomass heating time that was effectively infinite. In other experiments a conical quench section was interposed between the bottom of the vertical column and the catch pot, shown in Fig. 2(b). At the bottom of the quench section, cold nitrogen gas at approximately -196 °C was injected to quickly cool the biomass heating time was approximately 1.4 s.

An alternative solids collection system allowed control of biomass heating time at the bottom of the vertical reactor. This was accomplished by interposing a cooled auger between the bottom of the heated vertical reactor and the unheated catch pot. By controlling the rotational speed of the auger, the heating time of the biomass could be controlled, ranging from five to forty seconds. This configuration is illustrated in Fig. 2(c).

Six experiments were performed specifically to understand the relationship between the yields of pyrolysis products and biomass heating time (see Table 1). The biomass chosen for these experiments was ground red oak sieved to 250–850 µm (average of 500 µm). One experiment was conducted with both the heated and cooled static solids catch systems and four tests were performed using the conveyed solids catch system operating at different auger speeds. Previous experience with this reactor indicated as high level of repeatability between tests. Thus, uncertainty in the data for the several experiments was determined by repeating one of the test condition in triplicate, determining their standard deviation and 95% confidence interval and using this confidence interval to estimate the uncertainty in the other tests.

Pyrolysis operating conditions were identical for the six tests, 148 the only variable altered in the tests being the particle heating 149 time. The lower 2.77 m of the 3.05 m reactor was heated to 150 550 °C wall temperature, which was accomplished with six inde-151 pendent electric heaters controlled by a thermocouple placed on 152 the exterior wall of the reactor. Nitrogen gas at room temperature 153 was used as a sweep gas at a flow rate of 18 L/min. While 18 L/min 154 is high for a free fall reactor, this rate was used to dilute produced 155 vapors and to promote volatilization and tertiary reactions. The 156 sweep gas created a cold flow velocity of 0.42 m/s. Therefore, the 157 average particle terminal velocity was calculated to be 1.13 m/s. 158





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2

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