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Full Length Article

# Understanding of formation mechanisms of fine particles formed during rapid pyrolysis of biomass

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ABSTRACT

Fine particles formed during pyrolysis are the precursors of particulate matters (PM) after combustion and/or gasification. This study aims to conduct a preliminary research on the characteristics of fine particles. The rapid pyrolysis of raw and acid-washed biomass was conducted in a drop tube furnace (DTF) with a wall temperature 1073–1473 K and varied residence times. Components of fine particles formed during rapid pyrolysis were determined by investigating their morphologies and element contents. Particle size distributions (PSDs) of fine particles were also measured by granulometry technique. The results showed that the yields of fine particles increased significantly with increasing pyrolysis temperature. PSDs of fine particles formed at different conditions varied from each other, and trimodally distribution was identified for fine particles derived from pyrolysis of raw biomass at 1473 K. Those independent fine particles consisted of abundant small fragments, and slight soot and ash particles. The size of soot and melting ash particles increased with residence time and temperature, and the size ranges of small fragments broadened as residence time increased.

## 1. Introduction

Biomass has been regarded as a renewable fuel because the amount of carbon dioxide generated during combustion is equal to that absorbed during biomass growth [1–3]. PM emitted from biomass utilization constitutes significant environmental and health hazards, thus, restrictions on PM emissions have been imposed by many countries to control air pollution [4,5]. Formation of fine particles during pyrolysis is a rather complex and important subject and deserves a thorough investigation because those fine particles are the precursors of PM after combustion and/or gasification, nevertheless, no clear literature available has comprehensively investigated those fine particles.

Rapid pyrolysis is a complex process accompanied with the formation of various kinds of particles. Biomass and other solid fuels usually experience violent fragmentation and generate abundant irregular-shaped small fragments during rapid pyrolysis [6–8]. Friedemann and co-workers identified particle fragmentation with plenty fine particles during coal rapid pyrolysis by means of direct optical observation with a high-speed camera [9]. Senneca et al. conducted a rapid pyrolysis under severe heating conditions (104 K/s) and obtained relatively coarse fragments and sometimes a multitude of fine particles [10]. Cui et al. found that the exfoliation occurred at the outer zone of the char particles dominated the fragmentation during rapid pyrolysis of anthracite coal [6]. In their later studies, the fragmentation of biomass chars was attributed to the internal overpressure caused by drastic volatile release [11]. Additionally, contribution of particle shrinkage and thermal stress to biomass particle fragmentation was proposed by Sreekanth et al. [12].

It should be emphasized that in all of the aforementioned literatures, attention merely concentrated on the char matrix and ignored the characteristics of small fragments (yield, PSDs, etc.). Compared to coarse char matrix, the small fragments are much more abundant and have even more crucial influence on the PM emission and radiative heat transfer [13,14].

Attention was also paid to other potential fine particles probably formed during pyrolysis in earlier studies, such as mineral ash particles and submicron soot particles [8,15–18]. Zhang et al. [19,20] found roughly same amount of submicron mineral particulates (smaller than 0.1 μm) formed during pyrolysis compared to combustion, indicating that most of the mineral PM would form during pyrolysis. Fragmentation of char during pyrolysis has important effects on PSDs of ash particles in combustion, because the minerals in small fragments are

*Abbreviations:* DTF, drop tube furnace; PSDs, particle size distributions; PM, particulate matters; SD, saw dust; WS, wheat straw; DS, density separation; RS, rice straw; XRF, X-ray fluorescence; SEM – EDX, scanning electron microscope with energy-dispersive X-ray spectroscopy; TEM, transmission electron microscope; DE, deconvolution of PSDs; CenterMax value, location for peak maximum height

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**Table 1**
Characteristics of raw and acid-washed biomass samples.

| Samples | SD | SD-AC | WS | WS-AC | RS | RS-AC |
|---|---|---|---|---|---|---|
| *Proximate analysis, wt%, dry (d) basis* | | | | | | |
| VM | 90.92 | 91.02 | 85.08 | 88.13 | 78.93 | 82.53 |
| FC | 7.74 | 8.98 | 8.52 | 11.87 | 10.98 | 17.07 |
| Ash% | 1.34 | 0 | 6.40 | 0 | 10.09 | 0.40 |
| *Ultimate analysis, wt%, dry (d) basis* | | | | | | |
| C | 42.39 | 48.26 | 44.04 | 42.26 | 43.07 | 42.03 |
| H | 5.64 | 4.97 | 4.92 | 5.02 | 4.13 | 5.00 |
| O* | 49.40 | 44.00 | 44.01 | 49.95 | 41.06 | 50.09 |
| N | 0.79 | 0.63 | 0.35 | 0.84 | 0.35 | 1.18 |
| S | 0.44 | 2.14 | 0.28 | 1.93 | 0.30 | 1.30 |
| *Contents of inorganic species in biomass, mg/g biomass, dry (d) basis* | | | | | | |
| Na | 0.1447 | | 0.4582 | | 3.7636 | |
| Mg | 0.3618 | | 1.4016 | | 2.3308 | |
| K | 0.3229 | | 1.4656 | | 7.1942 | |
| Ca | 2.3115 | | 4.8064 | | 4.1268 | |
| Al | 0.9018 | | 3.8400 | | 0.16850 | |
| Si | 2.6612 | | 18.2080 | | 32.4494 | |
| Fe | 0.5896 | | 2.9376 | | 0.3199 | |
| *Ash flowing temperature, K* | | | | | | |
| FT | 1429 | | 1372 | | 1425 | |

* Calculated by difference.

usually insufficient to coalesce into coarse ash particles [21,22]. Besides, abundant submicron soot particles form rapidly during pyrolysis [23,24]. Soot particles are regard as an undesirable product because of the environmental pollution and the loss of carbon combustion efficiency [25–28]. Knowledge about the PSDs and yield of small fragments and soot formed during pyrolysis is desired to help understanding the

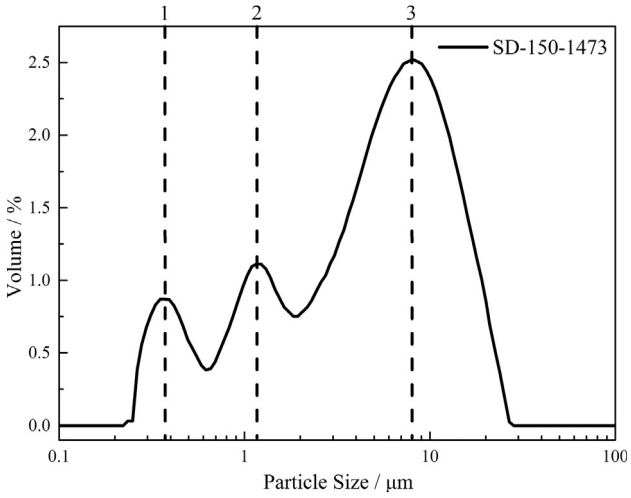


**Fig. 2.** PSDs of SD-150-1473.

PM formation in combustion, because part of the carbonaceous fragments and soot will not burn out during combustion and turn into fly ash [29–31].

Recently, several papers have investigated the PM precursors by indirect methods. Gao et al. [32] and Chang et al. [33] found the significant effect of devolatilization on the formation of ultrafine particles by comparing coal-derived PM and char-derived PM. However, no further direct investigation of fine particles was available in previous literatures.

This study mainly aimed to determine the component and PSDs of fine particles formed during rapid pyrolysis of biomass, and to

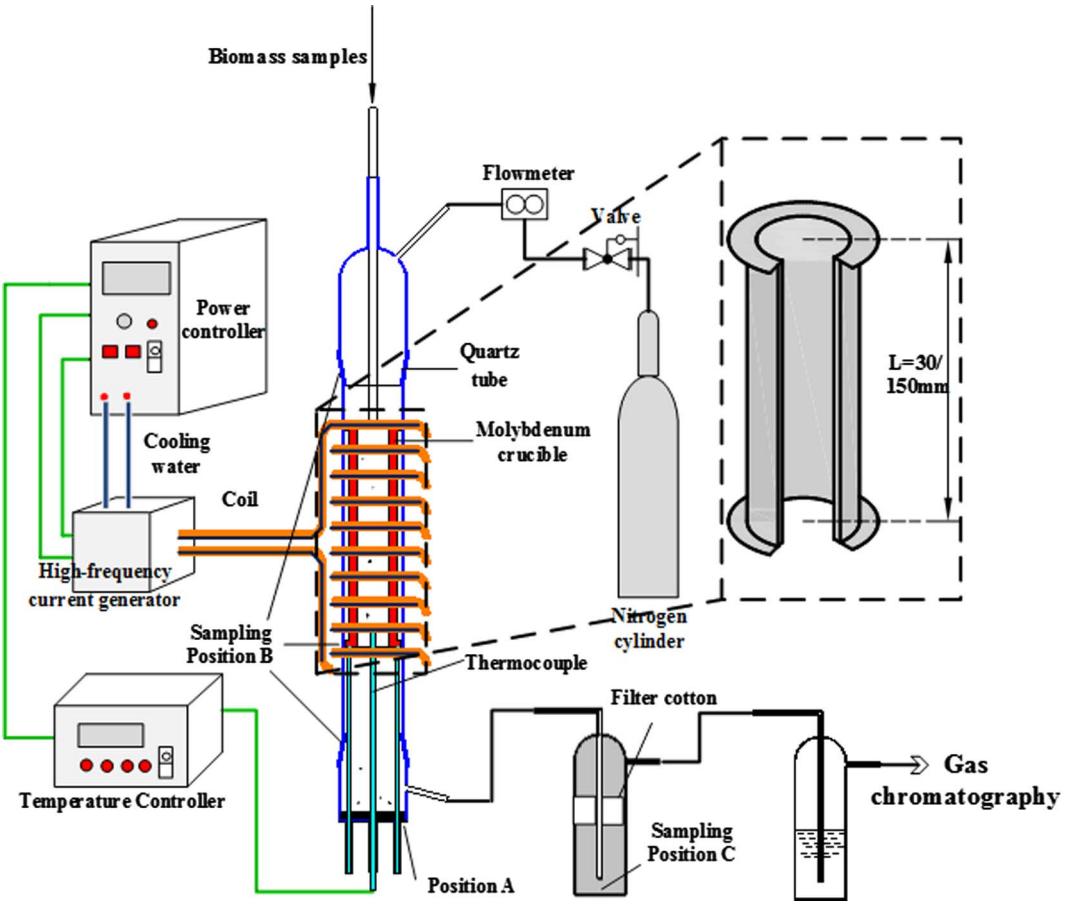


**Fig. 1.** Laminar drop tube furnace (DTF) schematic diagram.