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Particle formation during pressurized entrained flow gasification of wood powder: Effects of process conditions on chemical composition, nanostructure, and reactivity

Henrik Wiinikka[a,b,*], Pal Toth[a,c], Kjell Jansson[d], Roger Molinder[a], Markus Broström[e], Linda Sandström[a], JoAnn S Lighty[f], Fredrik Weiland[a]

[a] *RISE Energy Technology Center AB, Box 726, SE 941 28 Piteå, Sweden*
[b] *Energy Engineering, Division of Energy Science, Luleå University of Technology, SE-971 87 Luleå, Sweden*
[c] *University of Miskolc, Institute of Thermal Energy, B1 404 Miskolc-Egyetemváros, 3515 Miskolc, Hungary*
[d] *Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden*
[e] *Thermochemical Energy Conversion Laboratory, Department of Applied Physics and Electronics, Umeå University, SE-901 87 Umeå, Sweden*
[f] *Department of Chemical Engineering, University of Utah, Salt Lake City, UT, United States*

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ABSTRACT

The influence of operating condition on particle formation during pressurized, oxygen blown gasification of wood powder with an ash content of 0.4 wt% was investigated. The investigation was performed with a pilot scale gasifier operated at 7 bar(a). Two loads, 400 and 600 kW were tested, with the oxygen equivalence ratio (λ) varied between 0.25 and 0.50. Particle concentration and mass size distribution was analyzed with a low pressure cascade impactor and the collected particles were characterized for morphology, elemental composition, nanostructure, and reactivity using scanning electron microscopy/high resolution transmission electron microscopy/energy dispersive spectroscopy, and thermogravimetric analysis. In order to quantify the nanostructure of the particles and identify prevalent sub-structures, a novel image analysis framework was used. It was found that the process temperature, affected both by λ and the load of the gasifier, had a significant influence on the particle formation processes. At low temperature (1060 °C), the formed soot particles seemed to be resistant to the oxidation process; however, when the oxidation process started at 1119 °C, the internal burning of the more reactive particle core began. A further increase in temperature ($>$ 1313 °C) lead to the oxidation of the less reactive particle shell. When the shell finally collapsed due to severe oxidation, the original soot particle shape and nanostructure also disappeared and the resulting particle could not be considered as a soot anymore. Instead, the particle shape and nanostructure at the highest temperatures ($>$ 1430 °C) were a function of the inorganic content and of the inorganic elements the individual particle consisted of. All of these effects together lead to the soot particles in the real gasifier environment having less and less ordered nanostructure and higher and higher reactivity as the temperature increased; i.e., they followed the opposite trend of what is observed during laboratory-scale studies with fuels not containing any ash-forming elements and where the temperature was not controlled by λ.

1. Introduction

Under directive 2009/28/EC, the European Union member states have taken on binding national targets for raising their share of renewable energy in all forms of transport to 10% by 2020 [1]. Pressurized entrained flow gasification has been used since the 1950s to produce fossil motor fuels from coal and have proven to be a promising technology for the production of renewable motor fuels from biomass as well [2]. Gasification involves the production of raw syngas which is first upgraded to clean syngas through the removal of particles and tars before being converted to a liquid in downstream catalytic processes. Cleaning raw syngas is essential in avoiding fouling and clogging as well as catalyst poisoning in the downstream synthesis plant [3,4].

In order to demonstrate that it is possible to produce syngas from pulverized biomass powder, a 1 MW pilot scale pressurized entrained flow biomass gasifier (PEBG) was commissioned in 2011 in Piteå, Sweden [5]. Initial work focused on the gaseous com-

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[*] Corresponding author at: RISE Energy Technology Center AB, Box 726, SE 941 28 Piteå, Sweden.
E-mail address: henrik@etcpitea.se (H. Wiinikka).

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position of the syngas and demonstrated that syngas produced from wood powder had potential for further upgrading to motor fuels [5]. Further work investigated gaseous trace compounds [6] and quench water characteristics [7] in detail. Gasification of other fuels (both liquid and solid) [8–10] were also studied. Weiland et al. [11] investigated both theoretically and experimentally how the product gas composition and efficiency of the PEBG gasification process was affected by changing different process parameters, such as the operating pressure and the stoichiometric ratio (λ). The experimentally obtained efficiency of the process was 5–10% lower compared to the theoretical thermodynamic maximum. One reason for this behavior could be the formation of unconverted soot or other carbonaceous submicron particles.

Particles formed during the operation of the PEBG gasifier sampled from the quench water [7] and from the syngas after the bubbling quench [12,13] have been investigated with respect to their concentration, size distribution, morphology, and composition. During the gasification of wood powder with low ash content both fine soot particles with a primary particle size between 30 and 50 nm and large soot particles with a primary particle size between 100 and 300 nm were produced. Traces of K (<2 wt%) and polyaromatic hydrocarbons (PAHs) could also be found in these soot particles. When fuels with higher ash content were gasified, several other types of particles with higher concentration of inorganic elements were also observed [12]. Furthermore, the results also indicate that inorganic elements and especially metallic zinc interacts in the soot formation process creating a particle with shape and microstructure significantly different from a classical soot particle [12].

The influence of λ (0.25–0.35) and process temperature (1000–1400 °C) on gas product distribution and soot formation during air-blown biomass gasification in a bench scale, electrically heated, atmospheric, entrained flow reactor was investigated by Qin et al. [14]. The unconverted C only formed soot particles when the process temperature exceeded 1000 °C. Maximum soot yield was obtained at a process temperature of 1200 °C. When the process temperature increased further, or when λ increased, the soot yield decreased significantly from its peak value.

Qin el al. [14] also found that the soot produced during gasification of wood at high process temperatures (1400 °C) was more reactive than soot produced at low temperatures. Septien et al. [15] later reported that soot produced through the pyrolysis of wood at high process temperatures (1400 °C) displayed higher ordering and higher reactivity than soot produced at a low process temperature (1200 °C). They attributed this to the higher ash content of the soot produced at high temperature (2.5 wt%) compared to that of the soot produced at low temperature (0.7 wt%). Further elemental analysis indicated that the ash consisted mainly of K which is known to have a catalytic effect on thermochemical conversion. Qin et al. [14] also reported a higher reactivity for soot with an ash content of 2.3 wt% compared to soot that has an ash content of 1.8 wt%. The observation regarding the reactivity of soot produced during the pyrolysis or gasification of biomass is in contrast with what is usually observed when using well-defined fuels such as acetylene, [16] benzene, [17] and dodecane [18]. Here, the reactivity of the soot was found to be determined by its structural properties, which in turn were determined by the type of fuel from which the soot originated [17] and by the formation temperature [16,19]. Soot with a high reactivity displayed an amorphous, less ordered structure while soot with low reactivity displayed a graphitic, more ordered structure [16–18]. Soot formed at low temperatures was less ordered [16,18] and more reactive [16] than soot formed at high temperatures. The same correlation between soot reactivity and structural ordering were observed by Jaramillo et al. who studied the reactivity of a model C [20]. The ordering of the structure could be quantified by measuring the length and curvature (tortuosity) of the graphitic sheets using high resolution transmission electron microscopy (HRTEM) [17,18,20]. The effect of ordering on reactivity was attributed to the differences in accessibility of C layer edge sites for the oxidant molecules [17]. In line with these results, it was recently found that the incorporation of soot nanostructure, as an indicator of soot maturity into soot models increases the fidelity of model predictions [21].

Table 1
Physical and chemical composition of the fuel.

Particle size distribution	
d_{50} (μm)	140
d_{90} (μm)	240
Proximate analysis (wt% as received)	
Moisture	7.7
Volatile	77.9
Fixed carbon	14.0
Ash	0.34
Ultimate analysis (wt% dry)	
C	51.3
H	6.4
N	<0.10
Cl	<0.02
S	0.02
O (by differences)	41.8
Major ash forming elements (mg/kg dry)	
Si	28
Al	12
Ca	979
Fe	8
K	389
Mg	149
Mn	91
Na	40
P	34
Zn	7

In this work we return to the formation of particles during gasification of biomass in the PEBG. The main objective of the present work was to investigate the effect of operating parameters of the gasifier on the formation of particulates with regards to concentration, composition, morphology, nanostructure, and reactivity. A reader who is unfamiliar with the general fuel conversion process during entrained flow gasification is referred to the description in [11] for detail information. The information presented here contributes to the knowledge base of high temperature biomass gasification in general and the characteristics of particles derived from biomass gasification in particular. The results may also be used in the optimization of operating parameters and as an aid in the design of downstream upgrading equipment.

2. Experimental

2.1. Pressurized entrained flow gasifier

A short description of the PEBG gasifier used in this work is given below. A more detailed description has been published previously [5]. The gasifier was designed to operate in slagging mode at high temperature (1200–1500 °C) and consisted of a lock hopper system which introduced fuel and O_2 into a burner inserted through the top of a refractory lined reactor with an inner vertical wall length of 1.67 m and a diameter of 0.52 m. Downstream of the gasifier, water spray nozzles and a bubbling quench cooled the raw syngas to <100 °C and separated it from smelt and particles. The raw syngas was then directed through a series of sampling points before being flared.

The process temperature inside the gasifier was measured using 5 thermocouples (type S) protected by ceramic encapsulation. The maximum temperature possible to record with the thermocouples was 1550 °C. One thermocouple was mounted at the top of the re-