# Insights into Mechanisms of Screw Feeder Plugging by Heated Pine Forestry Residues Using in situ and Correlative Microscopy

Josephine Gruber*, Yining Zeng†, Steven Rowland•, Daniel Carpenter•, and Bryon Donohoe*
*Biosciences Center, National Renewable Energy Laboratory, Golden, CO, USA
†Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, CO, USA
•National BioEnergy Center, National Renewable Energy Laboratory, Golden, CO, USA

## Abstract

The conversion of biomass feedstocks into bio-fuels using fast pyrolysis is a promising form of renewable energy. Feed screws that convey biomass to pyrolysis reactors, however, often encounter plugging. Indirect heating of the feed screw occurs due to contact with the pyrolysis chamber, resulting in a heating gradient ranging from ambient temperature (22˚ C) to the temperature of the reactor (500˚ C). Given major cell wall macromolecules, such as lignin, cellulose, and hemicellulose, begin to degrade within this temperature gradient and produce bio-oils and volatile resin acid compounds, we hypothesized that indirect heating during feed screw conveyance is sufficient to cause the premature degradation of biomass, characterized by increased surface roughness and changes in overall particle morphology and production of bio-oils cause particle agglomeration leading to feed screw plugging. Correlative analysis between optical in situ hot stage microscopy, confocal Raman spectroscopy, and SEM analysis revealed that heating as low at 375˚ C caused significant increases in surface roughness, with large fissures forming between and within cell walls. Additionally, droplets of bio-oil were observed on particles, especially in bark and cambium samples. This work suggests engineering a solution to cool the feed screw could prevent particle agglomeration and reduce plugging incidents, increasing biomass processing efficiency.

## Introduction

As availability and carbon emissions associated with fossil fuel dependence and combustion become of increasing concern, more industries are looking toward lignocellulosic biomass feedstocks, such as pine forestry residues, as a renewable and more environmentally conscious energy alternative [1-3]. Fast pyrolysis in a fluidized bed reactor is widely regarded as the most efficient conversion method; however, feed screws used to convey feedstocks to the reactor often experience plugging that is attributed to indirect heating of the material that can range from 22˚ C (ambient temperature) and 500˚ C (operating temperature of the reactor) [1,2].

In studies of hardwoods and other biomass types, heating from 350-500˚ C causes severe degradation of cell wall macromolecules and carbonization that leads to the rupture of the cell wall and lumen, resulting in particle shrinkage [4,5]. Surface texture changes that occur within this regime include the formation of large pores on the particle surface associated with volatilization of cell wall macromolecules and surface wrinkling caused by the breakdown of the cell wall structure, both of which increase total particle surface area and interparticle friction [4-6]. Additionally, the production of highly viscous bio-oils may occur as major cell wall macromolecules begin to break down at temperatures as low as 200˚ C . The temperature regime within the feed screw may be sufficient to produce these bio-oils, which could coat surrounding particles and cause agglomeration [2,7,8].

We hypothesize that temperatures within the feed screw will be sufficient to cause major changes in particle morphology and surface texture that increase interparticle friction and produce viscous bio-oils that contribute to agglomeration that causes feed screw plugging.

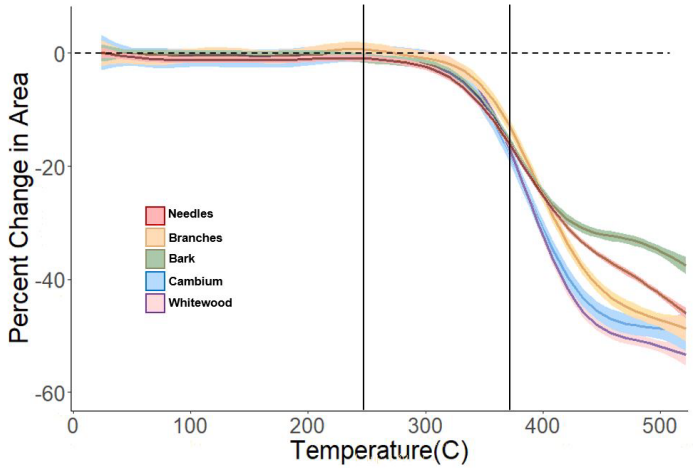


**Figure 1.** Generalized additive models (GAM) of relative changes in particle size of each anatomical fraction (needles, branches, bark, cambium, and whitewood) based on optical *in situ* micrographs captured during heating. Particle heating modeled screw feeder conditions (ranging from ambient temperature (22˚ C) to reactor temperature (500 ˚ C) with an estimated heating rate of 5 ˚ C/min). Relative changes in particle size indicate certain anatomical fractions (branch and cambium) swell slightly near 250 ˚ C and all anatomical fractions decrease rapidly in size between 300 ˚ C and 400 ˚ C, with *a* maximal rate of change near 375˚ C.

## Methodology

- Pine residues were collected, separated into needles, branches, bark, whitewood, and cambium fractions, and milled to 2mm courtesy of Idaho National Lab.
- Optical in-situ hot-stage microscopy was observed via time-lapse imaging as particles were heated from 22˚ C to 500˚ C . Particle surface area was measured per frame and used to determine temperature regions of major morphological change. Samples were heated to 250˚ C and 375˚ C and analyzed by confocal Raman spectroscopy and SEM.
- Samples were photobleached to reduce autofluorescence before confocal Raman analysis. Signal integration times were optimized to obtain a minimum of 80% intensity and subject to 30 accumulations for optimal SNR.
- Heated particles already analyzed by confocal Raman were coated with 15nm of iridium and imaged via SEM at 20kV to analyze particle morphology and surface texture.

## Results

- Image analysis revealed significant changes in particle size between 300-400˚ C, with a maximal rate of change near 375˚ C. Branch and cambium samples showed evidence of swelling near 250˚ C. Both of these regions were investigated further by confocal Raman spectroscopy and SEM to investigate the evolution of bio-oils and the breakdown of cell wall macromolecules (Figure 1).
- Minor changes in surface texture were observed in particles heated to 250˚ C, with the presence of cracks separating cells and fissures within cell walls becoming more evident. At 375˚ C, particle surfaces are dramatically rougher. Large cracks in and between cell walls predominate (Figure 2).
- All anatomical fractions show decreased signal in cellulose regions (orange), suggesting cell wall degradation is occurring. Cambium samples also showed reduced lignin signals (blue), as well, and needle samples show decreased resin acid signal in the 1660cm$^{-1}$region, although the signal is highly variable between replicates (Figure 3).
- SEM revealed the presence of bio-oil droplets on particle surfaces. Bio-oil was most abundant in bark samples and cambium samples. Interestingly, observed bio-oils were commonly located near fissures in the cell wall caused by heating (Figure 4).

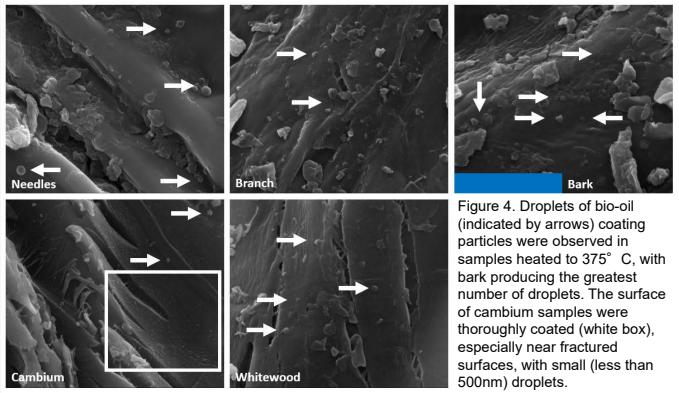


Figure 4. Droplets of bio-oil (indicated by arrows) coating particles were observed in samples heated to 375˚ C, with bark producing the greatest number of droplets. The surface of cambium samples were thoroughly coated (white box), especially near fractured surfaces, with small (less than 500nm) droplets.

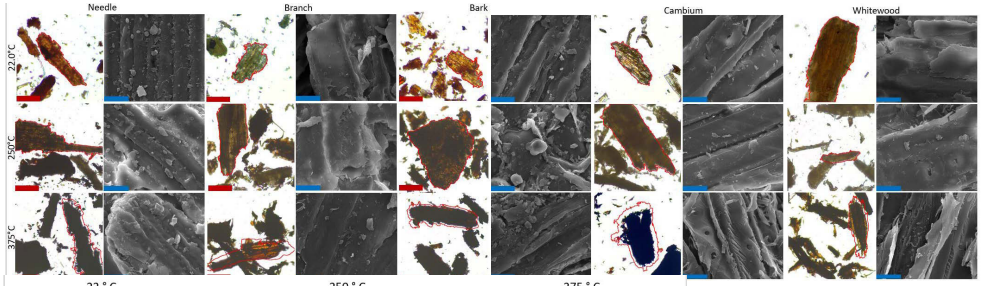


**Figure 2**. Optical and electron micrographs of particles heated to 22ºC, 250ºC, and 375ºC with corresponding SEM micrographs of the same regions. Red outlines in optical micrographs indicate the particle size and shape prior to heating. Red scale bar on optical micrographs is 200µm, blue scale bar on SEM micrographs is 20 µm. Particle analysis indicates surface topology becomes corrugated, with fissures opening between cells and within cell walls contributing to overall roughness of the particle surface. Fissures are the most prominent in bark, cambium, and whitewood samples.

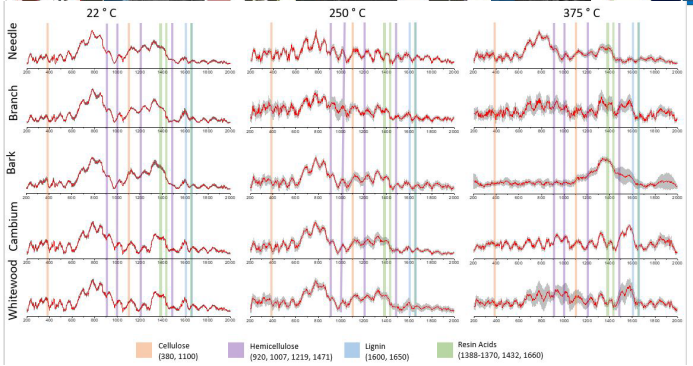


**Figure 3**. Confocal Raman spectra. Each spectra is an average of three replicate measures taken per sample, with shading indicating standard error. Bands of interest associated with cell wall macromolecules (cellulose – orange [9], hemicellulose – purple [10], and lignin – blue [9]) and volatile resin acids (green) [11] identified in feed screw material via molecular beam mass spectrometry (MBMS) (Rowland, Dunning, & Carpenter, unpublished).

## Conclusions

- Loblolly pine biomass particle morphology changes during feed screw conveyance as particles reach 300˚ C, where particles begin to reduce in size and major fissures form on the particle surface as the cell wall begins to break down at 375˚ C.
- Droplets appear on the surface of particles heated to 375˚ C, thoroughly coating bark and cambium fractions. Further chemical analysis will be required to characterize the composition of these droplets.
- Increased surface roughness and possible evolution of bio-oils caused by premature heating during feed screw conveyance may increase interparticle friction and cohesion.
- Engineering cooling systems for the feed screw would avoid premature heating and prevent plugging, increasing overall reactor productivity

### Future Work

- Quantitative analysis of changes in particle surface texture using stereometric SEM reconstruction to characterize true height changes across particle topology
- Targeted confocal Raman spectroscopy of bio-oil droplets on particle surfaces identified by SEM to characterize and confirm droplet chemistry

### References

1. Bridgwater, A. V. (1999). Principles and practice of biomass fast pyrolysis processes for liquids. Journal of analytical and applied pyrolysis, 51(1-2), 3-22.
2. Mohan, D., Pittman Jr, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: a critical review. Energy & fuels, 20(3), 848-889.
3. White, E. M. (2010). Woody biomass for bioenergy and biofuels in the United States: A briefing paper.
4. Haas, T. J., Nimlos, M. R., & Donohoe, B. S. (2009). Real-time and post-reaction microscopic structural analysis of biomass undergoing pyrolysis. Energy & fuels, 23(7), 3810-3817.
5. Bonelli, P. R., Della Rocca, P. A., Cerrella, E. G., & Cukierman, A. L. (2001). Effect of pyrolysis temperature on composition, surface properties and thermal degradation rates of Brazil Nut shells. Bioresource technology, 76(1), 15-22.
6. He, N., Yoo, S., Meng, J., Yildiz, O., Bradford, P. D., Park, S., & Gao, W. (2017). Engineering biorefinery residues from loblolly pine for supercapacitor applications. Carbon, 120, 304-312.
7. Huang, F., Singh, P. M., & Ragauskas, A. J. (2011). Characterization of milled wood lignin (MWL) in loblolly pine stem wood, residue, and bark. Journal of agricultural and food chemistry, 59(24), 12910-12916.
8. Oasmaa, A., Kuoppala, E., Gust, S., & Solantausta, Y. (2003). Fast pyrolysis of forestry residue. 1. Effect of extractives on phase separation of pyrolysis liquids. Energy & Fuels, 17(1), 1-12.
9. Agarwal, U. P. (2006). Raman imaging to investigate ultrastructure and composition of plant cell walls: distribution of lignin and cellulose in black spruce wood (Picea mariana). Planta, 224(5), 1141.
10. Zeng, Y., Yarbrough, J.M., Tucker, M. P., Vinzant, T. B., Decker, S. R., & Himmel, M. E. (2016). In situ label-free imaging of hemicelluloses in plant cell walls using stimulated Raman scattering microscopy. Biotechnology for Biofuels, 9(1), 1-16.
11. Nuopponen, M., Wilson, S., Jaaskelainen, A. S., Sundberg, A., & Vuorinen, T. (2004). A UV resonance Raman (UVRR) spectroscopic study on the extractable compounds of scots pine (Pinus sylvestris) wood. Part I: Lipophilic compounds. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 60(13), 2953-2961. I. Effect of extractives on phase separation of pyrolysis liquids. Energy & Fuels, 17(1), 1-12

*This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE), and the Bioenergy Technologies Office (BETO) as part of the Feedstock Conversion Interface Consortium (FCIC) . The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.*

*Microscopy & Microanalysis Meeting 2020*
*Virtual Conference*
*8/3-8/7*
NREL/PO-2700-77375