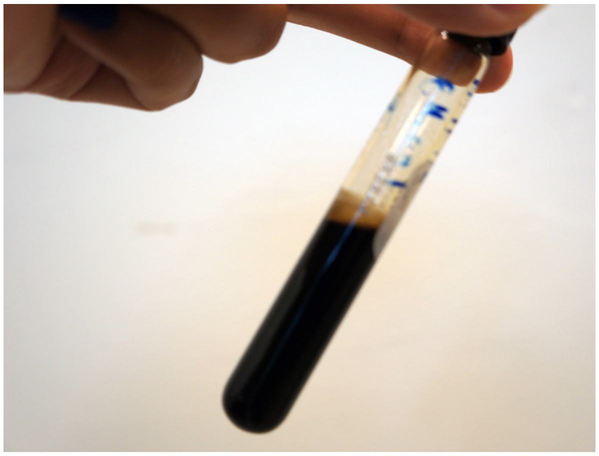

# Bio-Oil: An Introduction to Fast Pyrolysis and its Applications

WASHINGTON STATE UNIVERSITY EXTENSION FACT SHEET • FS140E

## Introduction

The United States has targeted biofuels generated from domestic biomass supplies as a significant contributor for future liquid fuel supplies. Reliance on domestic fuel production opens the door for a wide range of opportunities for natural resource managers, farmers, and other landowners who will be instrumental in developing the industry, its technologies, and its utilization of agricultural crop residues and forestry biomass. Washington State specifically is rich in crop residue and forestry biomass—two forms of biomass that lend themselves to a variety of conversion processes, but in particular, bio-oil production via fast pyrolysis.

This factsheet discusses bio-oil produced via fast pyrolysis, its applications, and associated biomass feedstocks. The purpose of this factsheet is to increase the knowledge on bio-oil sources, manufacturing, and utilization for natural resource managers, such as forest and farm owners. This publication is a rudimentary introduction to increase the acumen of the public and decision-makers who are interested in the development of the biofuel industry to support developing economies. Recent breakthroughs in conversion of biomass to useable oil products will provide opportunities for biomass values to become realized in Washington State. As technology and opportunities arise, factsheets such as these are primers for natural resource managers and interested stakeholders to make decisions and serve as an introduction to the technology.

## Biomass Materials

Biomass can be in woody and non-woody forms, and is defined as non-fossilized organic material made from plants, animals, and other living organisms. Common sources of biomass used in energy products can come from a wide range of sources, commonly regarded as waste products, such as municipal solid wastes, crop residues, sawdust, and forest biomass left as slash from logging operations. Biomass can also be grown as agricultural crops, such as giant cane (*Arundo donax*) or poplar trees. Biomass can be intentionally harvested from forest-health management practices, such as tree-thinning.

The majority of biomass on earth is available as wood forest materials. For example, almost one half of the 42,515 acres in Washington State is forested. Trees, like other plants, capture the sun's energy through photosynthesis and store the energy through chemical bonds in the form of carbohydrates. This energy is then released when those bonds are broken, such as when you light a fire or ignite a gasoline engine. While forest biomass is widely available, accessing, transporting, and processing biomass feedstock economically is a challenge.

Forest biomass is most commonly accessed through logging and timber harvests. Logging leaves behind large amounts of unutilized slash and residue, causing significant fire hazards. Forest-health treatments such as tree stand thinning, also provide easily accessible biomass that otherwise has no commercial value. Overstocked forests need thinning to reduce fire and pest threats. Additionally, thinning overstocked stands promote vigorous growth when trees

### Washington State Biomass

Experts have developed two key resources to assess and evaluate biomass sources for Washington State:

- *Biomass Inventory and Bioenergy Assessment, An Evaluation of Organic Material Resources for Bioenergy Production in Washington State* (Frear et al. 2005) provides an extensive review and assessment of 45 potential biomass resources, in addition to providing a county level inventory (see https://fortress.wa.gov/ecy/publications/publications/0507047.pdf).
- The *Washington Forest Biomass Supply Assessment* (Perez-Garcia et al. 2012), a report from the Washington State Department of Natural Resources, details the total volume of forest biomass from different forest management sources and assess the economic availability of the biomass (see http://www.dnr.wa.gov/Publications/em_finalreport_wash_forest_biomass_supply_assess.pdf)

are released from spatial and resource constraints. Adding economic value to forest-health treatments, such as thinning, would greatly increase the amount of effort put into maintaining healthy forest stands through providing long-term forest growth, and overall health of forest ecosystems (Badger and Fransham 2006).

### What is Bio-oil?

Although biomass is a fuel, its solid form makes it impractical for some applications, for example, as a transportation fuel. Converting solid biomass into a liquid fuel can greatly increase its applicability. Bio-oil is the liquid fuel resulting from biomass in a process known as fast pyrolysis. The oil is a brown liquid that is free flowing, however, over time it can increase in viscosity, resulting in a limited shelf life. Bio-oil has also been referred to as pyrolysis oil, pyrolysis liquid, wood liquid, wood oil, liquid smoke, wood distillates, pyroligneous acid, and liquid wood.

The brown liquid is highly oxygenated and typically containing 15 to 30% water. Oxygenated means that its molecules contain a large fraction of oxygen atoms. Although it is called oil, it does not readily mix with petroleum products. Bio-oil is acidic (its pH can range from 2 to 4) and can be corrosive. The oil contains hundreds of different chemical compounds; common organic components include acetic acid, methanol, aldehydes, ketones, alkyl-phenols, alkyl-methoxy-phenols, sugars, and lignin-derived compounds. Low levels of nitrogen- and sulfur-containing compounds are sometimes found in bio-oil, but give off little sulfur and nitrogen pollutants when burned (Mohan et al. 2006).

## Pyrolysis and Bio-oil Production

Pyrolysis is the thermal degradation of organic matter (biomass) in the absence of oxygen from air. It produces biochar, ash, permanent gases, and volatiles. Cooling and condensation of the volatiles produces bio-oil. The oxygen-free medium, usually nitrogen, is important to avoid burning the volatiles and permanent gases, consuming the products. This is the difference between pyrolysis and combustion. When oxygen is present, the volatiles and gases ignite.

Pyrolysis has been used to generate many products since the times of ancient Egypt. Early products were used to caulk boats and embalm and mummify human remains. Pyrolysis is the process used to make wood into charcoal briquettes that are used in outdoor cooking. The coal industry uses pyrolysis to process coal into coke, a much more refined coal product, which is burned in industrial furnaces (Mohan et al. 2006).

Biochar is the solid carbon product that is left over from pyrolysis. Slow pyrolysis heats biomass over hours, and even days. The process converts up to 35% of the biomass into char. Current research is testing ways to use biochar as a soil amendment to improve soil characteristics and sequester large amounts of carbon to offset some greenhouse gas emissions. Granatstein et al. (2009) provides an overview of biochar production and its feasibility as an agricultural input in Washington State. It has the potential to offset greenhouse gas emissions by acting as a carbon sink, a place where carbon is sequestered and not released into the atmosphere.

Compared to slow pyrolysis, which produces a high yield of biochar, fast pyrolysis produces mostly bio-oil, along with small amounts of biochar and permanent gases, like hydrogen, carbon monoxide, and carbon dioxide. Bio-oil is the desired product and has higher market value potential. Fast pyrolysis heats up biomass rapidly in the absence of oxygen and condenses the products into liquid forms (bio-oils). Often the biomass is heated for just a few seconds to temperatures around 500°C. Up to 75 percent by weight

### Methods for Producing Biochar and Advanced Bio-fuels in Washington State

Washington State University faculty from the Department of Biological Systems Engineering and the Center for Sustaining Agriculture and Natural Resources, along with Washington State Department of Ecology and industry leaders, has created an extensive four-part series of the current state of the science of producing bio-fuels.

Part one, *Methods for Producing Biochar and Advanced Biofuels in Washington State Part 1. Literature Review of Pyrolysis Reactors.* (Garcia-Perez et al. 2010), details pyrolysis technology and reactor types (see https://fortress.wa.gov/ecy/publications/publications/1107017.pdf).

Part two, *Methods for Producing Biochar and Advanced Biofuels in Washington State Part 2: Literature Review of Biomass Supply Chain and Processing Technologies (From Field to Pyrolysis Reactor)*. (Garcia-Perez et al. 2011), covers the supply chain and preprocess technologies (see https://fortress.wa.gov/ecy/publications/publications/1207033.pdf).

Part three, *Methods for Producing Biochar and Advanced Bio-fuels in Washington State Part 3: Literature Review of Technologies for Product Collection and Refining* (Garcia-Perez et al. 2011), describes bio-oil recovery, collection, uses, and considerations for industrialization of the technology (see https://fortress.wa.gov/ecy/publications/publications/1207034.pdf).

The final part of the series, *Methods for Producing Biochar and Advanced Bio-fuels in Washington State. Part 4: Literature Review of Financial Analysis* (Garcia-Perez et al. 2012), describes the financial and business analysis of a biomass economy utilizing pyrolysis as the means to produce energy products (see https://fortress.wa.gov/ecy/publications/publications/1207035.pdf).

(75 wt %) of the biomass is converted to bio-oils. Typically, about 10 to 15 wt % of biochar and 10 to 15 wt % of permanent gases are also produced (Bridgewater et al. 1999). The byproduct gases can be burned to provide a source of thermal energy to dry and prepare incoming biomass, as well as maintaining the temperature of the pyrolysis reactor. Thus, the reactions can be self-sustaining, requiring a minimum amount of energy input to keep the process running.

Different reactor configurations used to carry out fast pyrolysis have been explored and are still in the early stages of development. Only a few of the reactor types are in demonstration and commercialization scale; most are still laboratory scale units (Ringer et al. 2006; Garcia-Perez et al. 2010). At their basic design, pyrolysis reactors consist of a chamber where all oxygen can be removed while receiving the prepared biomass. Usually an inert (non-reactive) gas, such as helium or nitrogen, is used to replace oxygen. Inside the chamber, the biomass travels through a very hot media (such as sand), or is otherwise exposed to very high temperatures where the biomass is converted into vapor and biochar. Sand is often used to promote mixing and improves heat transfer to the biomass particles. Volatiles are condensed and collected inside a heat exchanger where the volatiles are separated from the permanent gases. After biomass is converted and the bio-oil is collected, other byproducts, including the permanent gases or hot medium can be recycled to generate heat for the process. Figure 1 illustrates the range of reactor designs and attributes.

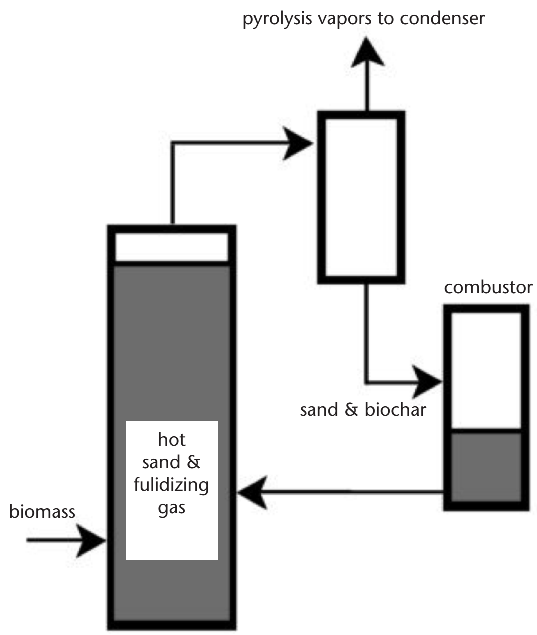


***Figure 1a. Circulating Fluidized Bed Reactor. The arrows show the pathway of the biomass material as it converts to gas, bio-oil, and char through the reactor (adapted from D. Mohen et al. 2006). Bubbling fluidized bed and circulating fluidized beds/transport reactors use heated sand in motion to transfer heat to the biomass. In both reactor types, the particle size of the biomass needs to be small (about 2-3 mm). These reactors are appropriate for small-sized biomass particles such as sawdust or smaller. The biomass is pushed through heated sand in the absence of oxygen to produce char, volatiles, and permanent gases. The volatiles are quickly condensed and collected as bio-oils. Both reactor types are simple designs and can accommodate a large amount of biomass of small particle sizes. The difference between bubbling fluidized bed and circulating fluidized bed reactors is that the circulating fluidized bed allows the sand to be removed, in order to burn the char formed and produce energy for the process. The sand is then recycled back to the reactor. To scale up production, these designs offer the ability to create large sized reactors. Source: Adapted from D. Mohen et al. (2006).***

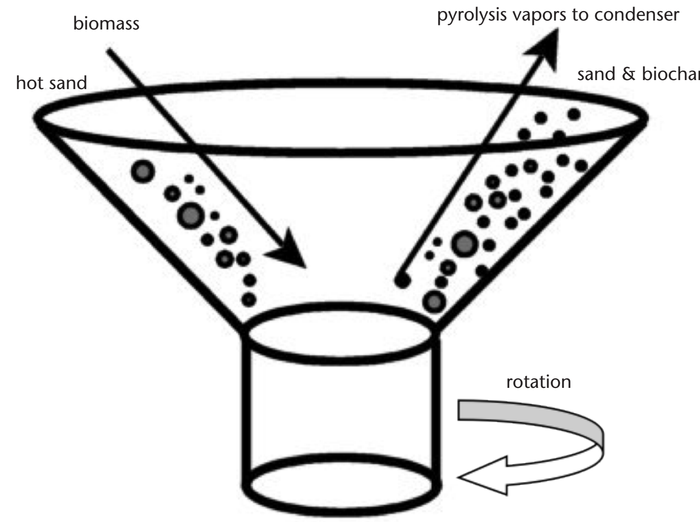


***Figure 1b. A rotating cone reactor introduces biomass particles and hot sand at the base of the cone. Through the spinning centrifuge action, the particles and sand are moved up the cone where pyrolysis occurs. Volatiles are collected and condensed in a very short amount of time adding to the efficiency of the design. As with the previously described processes, small sized particles are needed for this reactor. The produced char and sand can be reheated and introduced back into the reactor. This reactor needs to be relatively small and is difficult to scale up, but has produced consistent yields of bio-oil. The centrifugal spinning carries the gas to the condenser and does not require a carrier gas to take the pyrolysis vapor products to a condenser (like other reactor types). Source: Adapted from D. Mohen et al. (2006)***

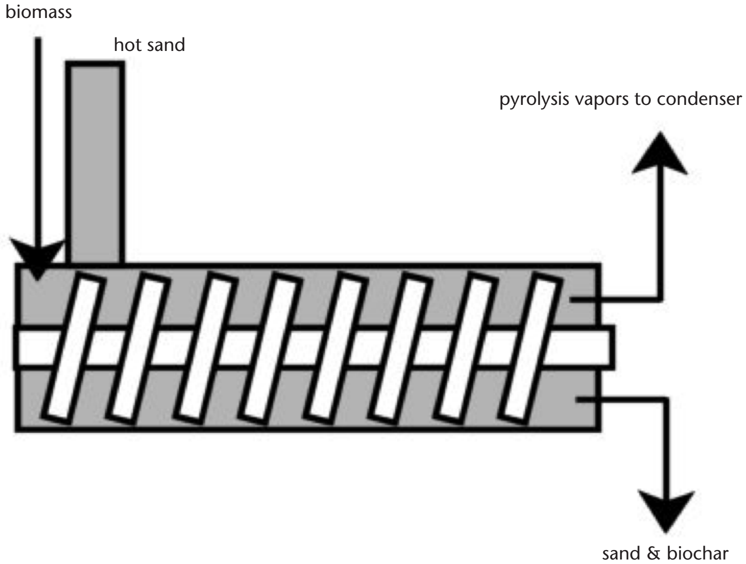


***Figure 1c. An auger reactor uses a heated tube where biomass and sand enter and move through the tube via the auger rotation. The biomass is continually fed into the cylinder with no oxygen, and is heated to temperatures high enough for pyrolysis to occur. Volatiles are collected and condensed to oils. Char and sand are collected at the end of the auger. Auger reactors are relatively simple designs and can be scaled up to larger reactor sizes.***

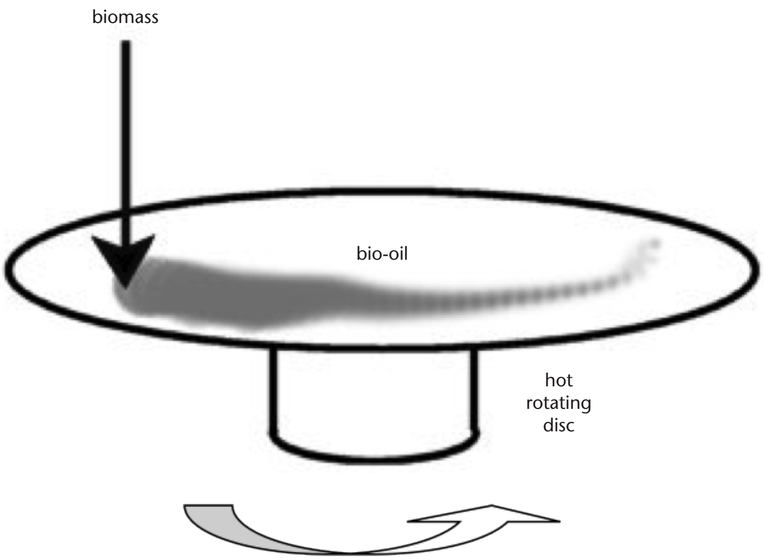


***Figure 1d. Ablative pyrolysis reactors are different from the other reactors, as it does not require the biomass particles to be of small size. Biomass is pushed into a spinning hot surface. The oils are released from the biomass feedstock and collected directly from the solid, hot source. The process has been described comparable to melting butter in a skillet, where the butter liquefies as pressure is applied and it moves over the hot surface of the skillet. The reactor can take large wood chips and even intact logs. This reactor, like the rotating cone reactor, tends to be small and will not scale up to larger reactor sizes. Ablative reactors have a significant level of complexity due to the moving parts. While scaling this reactor design is unpractical, this design does offer the potential of small niche mobile reactors to take on site where biomass can be harvested. Source: Adapted from D. Mohen et al. (2006)***

## Bio-oil Utilization

Bio-oil produced from fast pyrolysis has a wide range of applications. The major applications include heat and power generation, liquid fuels, and raw chemical products. The oils produced can be used directly in energy production by combustion, although the heating value of bio-oil is lower than that of fossil fuels (about 40% less than diesel fuel). Basic modifications on boilers to handle the viscosity of the bio-oil are needed to accommodate the material as a burning fuel. Bio-oil produces lower emissions of nitrogen oxide and sulfur gases when burned, especially when compared to fossil fuel emissions (Czernik et al. 2004). While emissions of greenhouse gases are lower in bio-oils than in fossil fuels, particulates are higher. Overall, bio-oil used for heat generation through combustion is considered carbon-neutral because all the carbon dioxide released in combustion is captured by the plants and trees during the photosynthesis process.

Chemicals extracted from bio-oil are used as food flavorings, resins, adhesives, agrichemicals, and fertilizers (Czernik et al. 2004). Table 1 (adapted from Garcia-Perez et al. 2011b) lists the potential uses of the chemical compounds from the pyrolysis of biomass.

While bio-oil has many applications, it is not suitable as a transportation fuel because of its problematic and unfavorable properties: corrosiveness, high viscosity, low energy density, and low thermal stability (Meier and O. Faix 1999). Given these challenges, bio-oil from fast pyrolysis needs to be upgraded in a secondary reactor in order to be used as a transportation fuel and realize the market value of the oil. The primary goal in the upgrading process is to remove oxygenated chemical groups from the bio-oil, making it compatible with the current infrastructure designed for hydrocarbon fuels. Additional complexities are added to the process when the need for flexibility is present to create a product that meets the needs of the different end users, such as jet fuel markets and diesel markets.

*Table 1. Uses of chemical products from pyrolysis of biomass. (Adapted from Garcia-Perez et al. 2011b).*

| Industrial raw chemicals | Products |
|---|---|
| Acetic Acid<br>Aldehydes and ketones<br>Alkylaromatics<br>5-hydroxymethyl furfural (HMF)<br>Levoglucosan<br>Methanol<br>Glucose | Adhesives<br>Asphalt paving substitution<br>Bio-carbon electrodes<br>Coal dust suppression<br>Fertilizer<br>Antioxidants<br>Food additives<br>Pesticides<br>Impermiabilizer<br>Road de-icer<br>Surfactants<br>Wood preservatives |

While transportation fuel upgrades and hydrogen upgrades are possible, economics and industrial constraints have historically limited the advancement. The recent increase in attention to the conversion of bio-fuels has caused rapid development of technologies to upgrade bio-oil (Qiang et al. 2009), in order to accommodate it into existing fuel production facilities (Bridgewater 2012). Matching the production method and biomass sources to the appropriate or logical use will further overcome many of the obstacles present today (Badger and Fransham 2006).

## Bio-oil Economics

Costs for production of bio-oil depend widely on key factors, beginning in the field and ending at the product user. Biomass types, properties, and localities can quickly damper the feasibility of collecting biomass for bio-oil production. Transportation alone, from the field or forest to a processing facility, often makes bio-oil production appear economically unsound. Multiple models outline potential supply-chain routes that make most sense for the different biomass types in Washington State, whether they originate from municipalities, agricultural operations, or forests (Garcia-Perez et al. 2009).

For example, the possibility of converting forest wood to biofuels has been questioned because a significant portion of the cost of producing bio-oil from forest residues is associated with harvesting and transportation of the solid biomass (Mahmoudi et al. 2009; Kumar et al. 2009). The wood needs to be transported from the point of collection to the point of conversion or end-use. Biomass in woody form has low energy content and low value making it difficult economically to move long distances.

The solid harvest byproduct handling process includes several operations such as harvesting, chipping, loading onto trucks, and transportation to the end-use point. In addition, handling includes the operations at the end-use point, such as weighing, dumping, screening, grinding, and storage. Handling solid forms of biomass is expensive for a number of reasons, including the distance to conversion facilities, the number of operations required and the low bulk density of the feedstocks (Kumar et al. 2009).

Freshly harvested woody biomass has a significant amount of weight in water. Wood chips need to be ground and dried to reduce the amount of water entering pyrolysis. The larger the wood chip, the more energy needed to dry it. Reducing water in pyrolysis products increases the quality and energy value of the bio-oil. Additional costs compound when storing large quantities of biomass and preprocessing the material to prepare it for refinement into a product of value, such as a bio-fuel used in transportation. As with many alternative fuel types produced by forest biomass, reducing harvest, transportation, and processing costs are paramount for producing an economically viable energy product (Badger and Fransham 2006).

Each biomass source, whether it be urban, forest or agricultural wastes, has collection, transportation, conversion, and refinement costs. There are several reactor configurations to produce bio-oil, and each reactor type has its advantages. However, no single fast-pyrolysis method wins as the most economical or efficient for every application. As the technology advances and methods are refined to take opportunities on readily available biomass feedstocks, reactor types will match the feedstock sources and scales.

With new energy and natural resource policies in place, markets and technologies are supporting biomass energy conversion and fast pyrolysis products are a logical product to incorporate into biomass conversion centers and manufacturers. Washington State forest managers, farmers and other biomass managers will soon have options to add value to otherwise lost waste streams (Garcia-Perez et al. 2011a). Key areas of research include matching appropriate biomass feedstocks to supply chains, and appropriate conversion technologies with high value refinements for the end use.

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## Matching Biomass Feedstocks with Best Conversion Technology: Beetle-killed Trees and Mobile Fast Pyrolysis

Millions of acres of Rocky Mountain forest have been killed by the mountain pine bark beetle, *Dendroctonus ponderosa*. An equal amount of pine forests have been impacted in British Columbia, Canada. Large, dead stands of beetle-killed trees pose many problems in the forest, from the loss of harvestable timber to creating dangerous stands of fire fuel. As the dead timber dries and insects colonize the wood, it becomes worthless for harvest, and there is little economic incentive to remove the trees.

Having such a wide availability of dry, woody biomass presents an opportunity for conversion of beetle-killed trees into economically valuable products like bio-oil (Kumar 2009). In turn, bio-oil production provides an economic path to remove the excessive dead wood in the forests and avoid high-heat forest fires. The dry, affected wood is an excellent feedstock for fast pyrolysis, since drying costs are minimized or even eliminated. The wood quality of the infested trees is slow to degrade and the infestation of beetles poses no quality ramifications to produce bio-oil. The chemical properties of bio-oil do not change, even when produced from trees that were standing dead from beetle-kill for up to four years (authors' unpublished data). Figure 2 shows four stages of degradation identified for lodgepole pine.

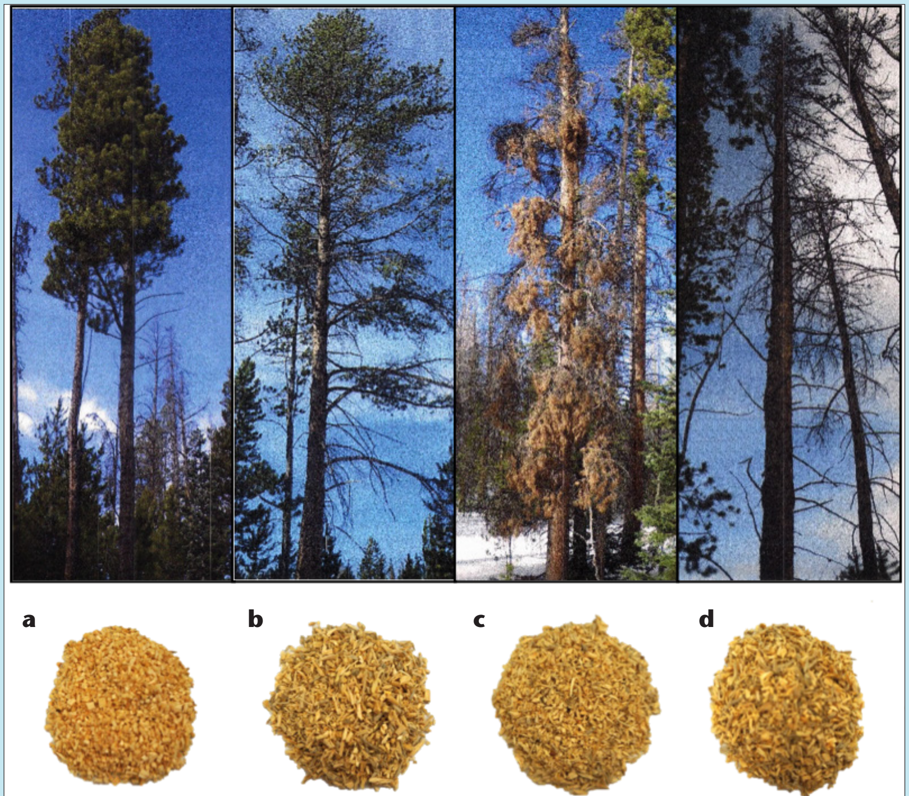


*Figure 2. Four levels of wood degradation due to beetle attack. A) Biomass from green, living wood material free of bark beetles. B) Partially green wood, infested with bark beetles. C) Standing dead wood, killed by bark beetles that season. D) Biomass from trees that have been dead from two to four years. Photo: M. Perry.*

Small scale, fast ablative pyrolysis reactors are being developed to experiment and demonstrate the effectiveness of mobile reactors to process dead beetle-killed trees. Ablative reactors do not need finely ground chips to process wood pieces, and are the most logical reactors to be scaled for mobile units. Alternative energy researchers and practitioners recognize that transportation costs greatly limit the feasibility for many forest biomass energy products. Scaling small, mobile fast pyrolysis units that process woody biomass in the forest allows for the transportation of high-energy, high-value bio-oil to end users (such as boilers for heat or conversion centers where the bio-oil is refined into higher valued products). At the University of Washington, Dr. Fernando Resende, and his research team are developing a small ablative reactor to demonstrate the potential of this technology in regions where beetle-killed trees can be harvested commercially for bio-oil (Figure 3).

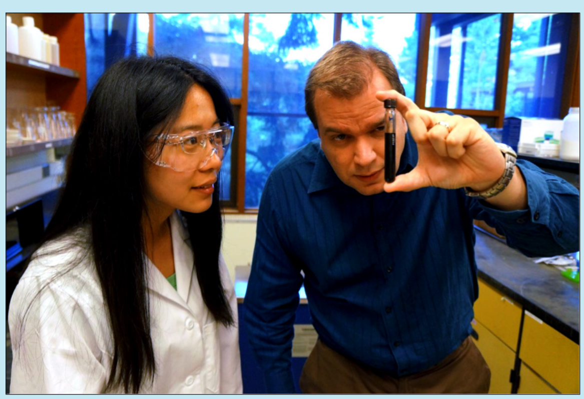

*Figure 3. Dr. Fernando Resende, and doctoral candidate, Guanqun Luo, are developing an ablative fast pyrolysis unit to experimentally process beetle-killed logdepole pines. Here, Dr. Resende holds a vial of bio-oil. Photo: F. Resende.*

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