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Pyrolysis and Bio-Oil

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Abstract

The proposed U.S. renewable fuels standards require increasing the domestic supply of alternative fuels to 36 billion gallons by 2022. Out of this, 21 billion gallons must come from advanced bio-fuels, i.e., ethanol and/or hydrocarbon fuels from lignocellulosic biomass (conversion of non-grain resources such as agricultural residues, energy crops, etc.). One conversion technology with the right footprint that fits the farm setting and that can have an immediate impact on the farmers' bottom line is "pyrolysis." It is the heating of biomass in the absence of oxygen to produce bio-oil and charcoal (biochar) that can be returned to the soil to build it up so food, fiber and bioenergy can be sustainably and simultaneously produced. Herein, we provide some basic facts about pyrolysis and bio-oil production technologies to the non-engineer.

What Is Pyrolysis?

The process of combustion, the burning of fuel in air to generate heat, is well known. There are three pieces of the puzzle in making fire by combustion, the so-called fire triangle – fuel, heat and an oxygen source (normally air). In combustion, the fuel first heats up to generate the carbon and volatile matter which find the oxygen in the air to burn and generate heat. The first step, prior to the exposure of combustible gases to air, is actually the pyrolysis process.

Pyrolysis is the initial process that takes place when organic matter is first heated in the absence of oxygen to produce combustible gases. Pyrolysis by itself does not normally release excessive heat, rather it requires heat to sustain it. Pyrolysis of organic materials such as biomass at high temperatures (greater than 428°F) decomposes the fuel source into charcoal (carbon and ash) and volatile matter. The latter comprises condensable vapors called pyrolysis oil (also known as bio-oil, biocrude, etc.) at room temperatures and non-condensable (permanent) gases such as carbon monoxide, carbon dioxide, hydrogen and light molecular weight hydrocarbon gases such as methane, collectively called synthesis gas (syngas or producer gas).

What Is Bio-Oil?

Bio-oil (Figure 1) is the liquid condensate of the vapors of a pyrolysis reaction. It is a dark brownish viscous liquid that bears some resemblance to fossil crude oil. It is at times marketed as "liquid smoke." However, bio-oil is

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a complex oxygenated compound comprised of water, water soluble compounds, such as acids, esters, etc., and water-insoluble compounds, usually called pyrolytic lignin because it comes from the lignin fraction of the biomass. The elemental composition of bio-oil is similar to that of the parent biomass, and as such, it is sometimes called "liquid plant matter." Because of its high oxygen content, the heating value (Btu per gallon) of bio-oil is lower than fossil fuel, typically only about half the heating value of fossil crude such as heavy fuel oil. However, it contains less nitrogen and only traces of metals or sulfur.



Figure 1. Bio-oil sample

Bio-oil is acidic with a pH in the 2 to 4 range, making it highly unstable and corrosive. It, therefore, presents transportation/piping and storage challenges, including the tendency to corrode most metals. Hence, it is usually transported and stored in stainless steel containers. Although freshly made bio-oil can be pumped and transported through pipelines, its viscosity increases with time. Unprocessed bio-oil cannot be readily mixed with petroleum-derived fuels. Despite the above-mentioned shortcomings, bio-oil has great potential. It can be used as heating oil if proper furnaces can be designed to do so, and nitrogen oxide emissions are low when combusted. Additionally, it can be potentially upgraded (or refined) to produce liquid transportation fuels and organic chemicals.

What Are Bio-Oil Properties?

Table 1 summarizes select properties of pyrolysis oil. It is typically a liquid, almost black through dark brown (or amber). The specific gravity of the liquid is about 1.10 to 1.25, which means it is slightly heavier than water, heavier than fuel oil and significantly heavier than the bulk density of the original biomass. The viscosity of the oil varies from as low as 25 cP up to 1,000 cP, depending on the water content and the original feedstock.

Due to large amounts of oxygenated components present in bio-oil, the oil tends to be polar (like water) and, therefore, does not mix readily with hydrocarbons. The degradation products from the biomass constituents include organic acids (like formic and acetic acid), giving the oil its low pH, typically between 2 and 4. Water is also an integral part of the single-phase chemical solution (water soluble fraction). Water content is typically 15 to 35 percent. Bio-oil has the tendency to phase-separate when the water content reaches the 30 to 45 percent range. The heating value (i.e., the higher heating value, HHV) is below 11,175 Btu/lb (26 MJ/kg) compared to 18,052 to 18,911 Btu/lb (42-44 MJ/kg) for conventional fuel oils. Some of the most recent research found that the high heating values of bio-oil (dry-ash free) of switchgrass (cave-in-rock), corn cob, corn stover (no cobs) and alfalfa stems at early bud are 10,164, 11,249, 10,448 and 14,249 Btu/lb, respectively.

Table 1. Properties of Pyrolysis Oil

Physical Property	Typical Value
Moisture content	15%-30%
pH	2.8-4.0
Specific gravity	1.1-1.2
Elemental analysis	
C	55%-64%
H	5%-8%
O	27%-40%
N	0.05%-1.0%
Ash	0.03%-0.30%
High heat value	6,878-11,175 Btu/lb (16-26 MJ/kg)
Viscosity (104°F and 25% water)	25-100 cP

What Types of Waste Can Be Processed?

Virtually all organic matter can be pyrolyzed. A wide range of materials can be handled by pyrolysis technologies; however, the yields of bio-oil are biomass-dependent. For example, waste materials such as chicken litter (containing high ash content) will yield lower volumes of bio-oil. Specific processes have been optimized to handle agricultural and forestry residues, tires and municipal solid waste.

What Are the Types of Pyrolysis?

Pyrolysis can be classified under slow, intermediate or fast pyrolysis. Slow pyrolysis is an old art whose origins can be traced to when man made fire. It maximizes charcoal yield and has been used to produce charcoal for use as fuel in developing countries. Although we said pyrolysis does not release heat, the slow pyrolysis reaction for converting biomass mainly to charcoal can be slightly exothermic (it releases heat), so large quantities of charcoal can be produced by burying the biomass underground and initiating the reaction.

Currently, most of the interest in pyrolysis focuses on fast pyrolysis, which maximizes liquid production rather than charcoal. It involves rapid heating rates and higher temperatures than slow pyrolysis and is endothermic (it does not release heat). The ideal conditions for fast pyrolysis involve rapid heating rates (> 400ºF per second) and temperatures usually in excess of 1,000ºF. Due to its short residence time, the main products from biomass fast pyrolysis are ethylene-rich gases that can be condensed to produce bio-oil and alcohols rather than char and tar. (Char or charcoal is produced from biomass that can store carbon. It is of increasing interest because of concerns about global warming caused by emissions of CO_2 and other greenhouse gases. In some cases, the term is used specifically to mean biomass charcoal produced via pyrolysis.) The approximate proportions of the pyrolysis reaction are as follows:

100 lb of biomass —(Heat (840°-930°F), No oxygen)→ 60 lb of bio-oil + 20 lb char + 20 lb of gas

These products can shift depending on the biomass composition – such as ash content – and operating conditions.

What Reactors Are Used to Carry Out Pyrolysis?

There are a number of different pyrolysis reactors (physical containers where the reaction is performed). As mentioned earlier, pyrolysis is a precursor to combustion and also gasification (partial combustion); therefore, the same reactors used for gasification can often be used for pyrolysis.

Bubbling fluidized bed pyrolyzers (Figure 2) have been popular because they are simpler to design and construct compared with other reactor designs. They also have good gas-to-solids contact, good heat transfer, good temperature control and a large heat storage capacity.

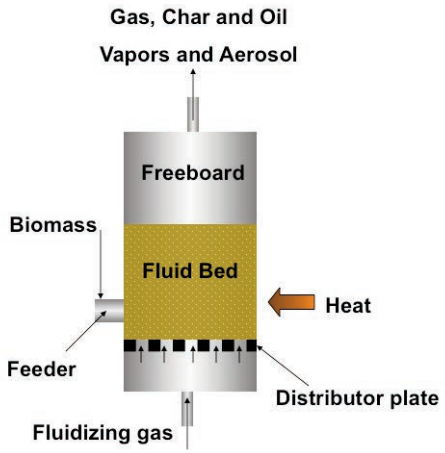


Figure 2. Bubbling fluidized bed pyrolyzer

In a fluidized bed pyrolyzer, a heated sand medium in a zero-oxygen environment quickly heats the feedstock (biomass) to 850ºF, where it is decomposed into solid char, gas, vapors and aerosols which exit the reactor by the conveying fluidizing gas stream. After exiting the reactor zone, the charcoal can be removed by a cyclone separator and stored. The scrubbed gases, vapors and aerosols enter a direct quenching system where they are rapidly cooled (< 125ºF) directly with a liquid immiscible (two liquids that don't mix) in bio-oil or indirectly using chillers (heat exchanger). The condensed bio-oil is collected and stored, and the non-condensable gas (syngas) may be recycled or used as a fuel to heat the reactor.

High liquid yields (about 60 percent weight of biomass on a dry basis) can be typically recovered. Small feedstock particle sizes are needed (< 2-3 mm) to ensure that the high heat rate requirement is fulfilled. The particle heating rate is the major factor limiting the rate of the pyrolysis reaction. Prior to recycling the syngas and residual bio-oil, aerosol droplets may be further scrubbed in an electrostatic precipitator to remove finer particulates and aerosols. The syngas (a medium Btu gas) may be burned to provide necessary heat to the reactor.

Circulating fluidized bed pyrolyzers (Figure 3) are similar to bubbling fluidized bed reactors but have shorter residence times for chars and vapors. The short residence times encountered in the reactor result in higher gas velocities, faster vapor and char escape and higher char content in the bio-oil than bubbling fluidized beds. However, they have higher processing capacity, better gas-solid contact and improved ability to handle solids that are more difficult to fluidize but are less commonly used. The heat supply typically comes from a secondary char combustor.

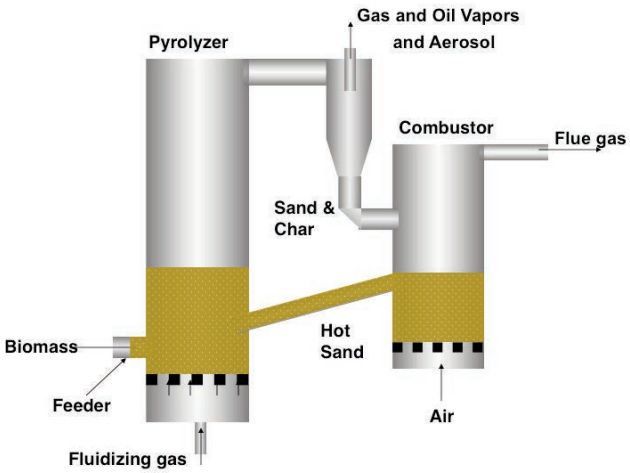


Figure 3. Circulating fluidized bed pyrolyzer

The **rotating plate pyrolysis reactors** (Figure 4) function on the premise that, while under pressure, heat transferred from a hot surface can soften and vaporize the feedstock in contact with it – allowing the pyrolysis reaction to move through the biomass in one direction. With this arrangement, larger particles, including logs, can be pyrolyzed without pulverizing them. The most important feature is that there is no requirement for an inert gas medium, thereby resulting in smaller processing equipment and more intense reactions. However, the process is dependent on surface area, so scaling can be an issue for the larger facilities.

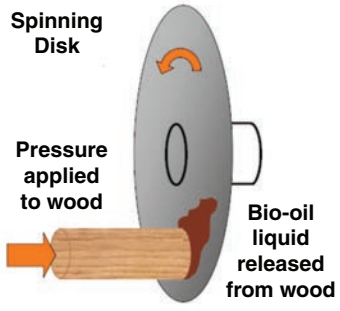


Figure 4. Rotary pyrolysis reactor

In a **rotating cone pyrolysis reactor** (Figure 5), biomass particles at room temperature and hot sand are introduced near the bottom of a cone at the same time. They are mixed and transported upwards by the rotation of the cone. The pressures of outgoing materials are slightly above atmospheric levels. Rapid heating and short gas phase residence times can be easily achieved in this reactor.

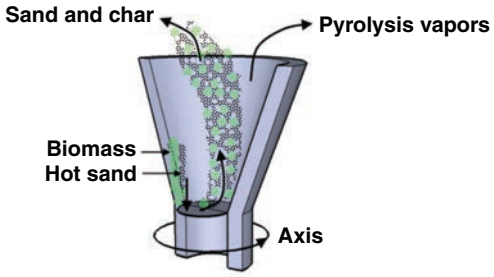


Figure 5. Rotating cone pyrolysis reactor

How Much Bio-Oil Can Be Produced From Wheat Straw From a One-Acre Field?

- 1 acre of wheat land produces about 3,000 pounds of wheat straw.
- Assume that 1 pound of wheat straw produces about 0.6 pound of bio-oil, 0.2 pound of char and 0.2 pound of gas when pyrolyzed.
- 1 acre of wheat land produces about 1,800 pounds of bio-oil.
- 1 acre of wheat land can produce about 12.3 MMBtu (from wheat straw).
- 1 acre of wheat straw could replace about 566 pounds of propane if converted to bio-oil.
- Some of the charcoal (char), about 600 pounds, can be applied to the soil to enrich it and/or sequester carbon.

What Are the Pyrolysis Oil Applications?

Bio-oil can be a substitute for fossil fuels to generate heat, power and/or chemicals. Boilers and furnaces (including power stations) can be fueled with bio-oil in the short term; whereas, turbines and diesel engines may become available on the somewhat longer term. Upgrading of the bio-oil to a transportation fuel is technically feasible but needs further development. Transportation fuels such as methanol and Fischer-Tropsch liquids (the so-called synthetic

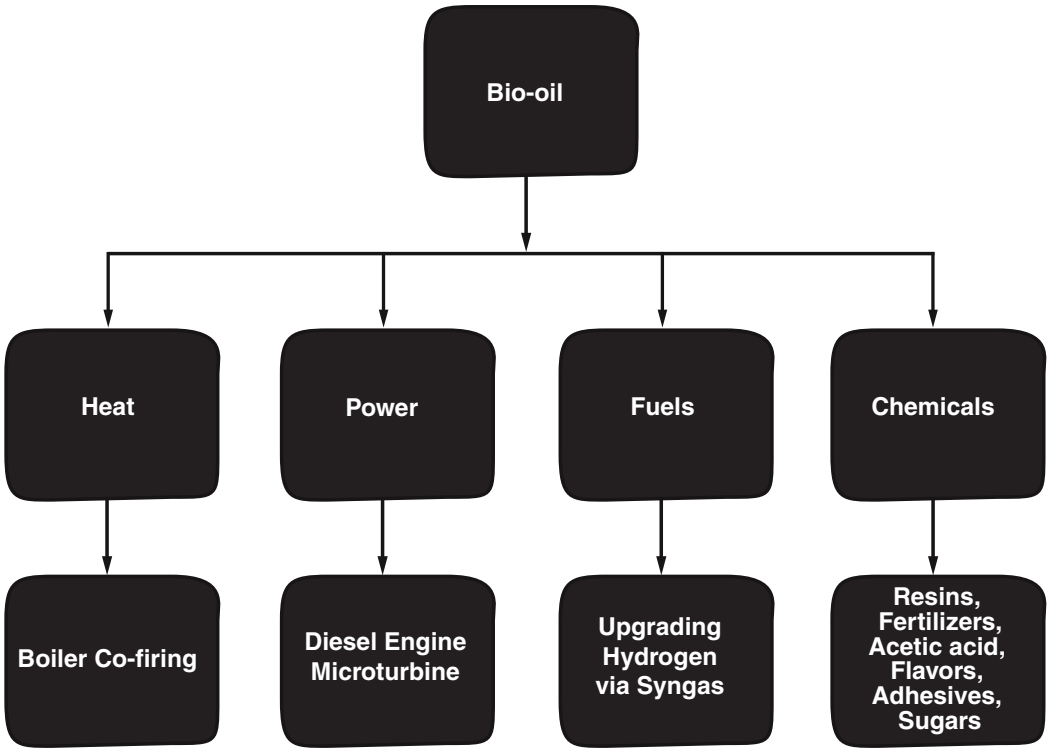


Figure 6. General overview of pyrolysis oil applications

diesel) can be derived from bio-oil, using the bio-oil as a gasifier feedstock instead of the bulky biomass, and can save some transportation costs. Furthermore, there is a wide range of chemicals that can be extracted or derived from bio-oil. A general overview of pyrolysis oil applications is depicted in Figure 6.

What Are the Benefits of Pyrolysis?

Pyrolysis of agricultural residues can help meet renewable energy targets by displacing fossil fuels and, thereby, deal with concerns about global warming. Pyrolysis offers more scope for recovering products from agricultural waste than simply burning it. When agricultural residues are burnt directly in a furnace/boiler, the only practical product is heat; however, when they are pyrolyzed first, bio-oil, gases and biochar can not only be used as a fuel but can also be purified and used as a feedstock for petrochemicals and other applications. The use of the biochar for soil amendment and as a carbon-sequestering, climate-mitigating agent is gaining worldwide attention. (For example, see the UN Convention for Combating Desertification, UNCCD website).

Sources for More Information

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