



Full Length Article

Characterization of pyrolysis products from fast pyrolysis of live and dead vegetation native to the Southern United States



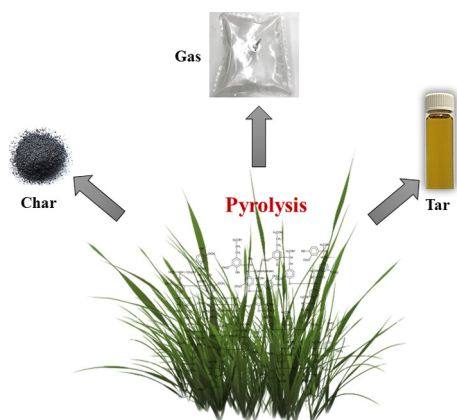
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GRAPHICAL ABSTRACT



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ABSTRACT

Prescribed burning (controlled burning) is used to decrease accumulation of combustible materials and reduce impact of uncontrolled wildland fires. Prescribed fires are often used to burn undergrowth in Southern forests of the United States. In order to improve prescribed fire application, accomplish desired fire effects, and limit potential runaway fires, an improved understanding of the fundamental processes related to combustion of heterogeneous fuel beds of live and dead fuels is needed. The initial processes of combustion involve pyrolysis and ignition. During this research, fast pyrolysis of 14 live and dead (biomass) plant species which are native to the Southern United States have been studied using a flat-flame burner (FFB) apparatus. The FFB apparatus enables experiments at a high heating rate ($\sim 100\text{ }^{\circ}\text{C s}^{-1}$, or $\sim 100\text{ kW m}^{-2}$) and moderate temperature ($\sim 765\text{ }^{\circ}\text{C}$) to imitate pyrolysis during typical fire spread conditions. Pyrolysis products have been analyzed in detail using a gas chromatograph equipped with a mass spectrometer (GC-MS) for analysis of tars, and a gas chromatograph equipped with a thermal conductivity detector (GC-TCD) for analysis of permanent (light or non-condensable) gases. Differences between yields of light gas species were small between plant species. Composition of tars included aromatic compounds with 1–5 rings with very few attachments. The pyrolysis products observed at this temperature and heating rate appear to have experienced secondary pyrolysis. The tar composition showed some large changes with plant species. Comparison of products from pyrolysis of live

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vegetation and dead vegetation of the same plant species showed differences in tar, gas, and char yields, but no major changes in the types of chemical compounds observed.

1. Introduction

Wildland fire is an important component of many ecosystems. Wildland fires often occur in highly dense live fuel forests, burn live and dead vegetation, and have significant ecological and economic impacts [1]. In 2000, an estimated 3.5 million km² were burned by wildland fire world-wide [2]. Prescribed burning (controlled burning) is one way to remove smaller plants in order to decrease accumulation of combustible materials and avoid occurrence of uncontrolled wildland fires [3]. The land managers use prescribed fire to manage a variety of ecosystems in the United States to reduce accumulation of hazardous fuels, manage wildlife habitat, and protect ecological forests and infrastructures [4]. In 2014, in the United States, an estimated 47,372 km² were treated with prescribed fire; in the southern U.S., 25,051 km² of forest land was treated [5]. Prescribed fires (as shown in Fig. 1) are often used to burn undergrowth in Southern forests of the United States.

During wildland fires, solid fuel samples undergo irreversible thermal degradation when exposed to high temperatures. The thermal degradation process consists of two sequential steps: pyrolysis and combustion [6]. In order to improve prescribed fire application, accomplish desired fire effects, and limit potential runaway fires, an improved understanding of the fundamental processes related to pyrolysis and ignition in heterogeneous fuel beds of live and dead fuels is needed.

The focus of this research is on pyrolysis, which is the first thermochemical reaction that occurs following the evaporation of moisture in the burning of some fuels like coal, wood, paper, polymers, plants, etc. As volatiles leave the surface, the mass transfer pushes the surrounding gas (presumably air) out of the way, creating a fuel-rich zone near the surface or in the interior of a flame. The results from this research can help to determine the heat release and investigate reactions that occur during the fast pyrolysis of live and dead vegetation. Finding mechanisms of formation of pyrolysis products helps to prepare more accurate combustion and fire spread models to predict the best conditions to properly perform prescribed burning, predict fire propagation, and limit fire runaway.

Pyrolysis is the thermal decomposition process of organic material without requiring oxygen. Flames occur when pyrolysis products and oxygen mix in the presence of an ignition source at high temperatures within the flammability limits. For example, by increasing temperature, lignocellulosic materials start to pyrolyze, releasing gaseous products which react with oxygen and may result in a flame. Pyrolysis can be classified into three groups: (1) conventional or slow pyrolysis which is performed with a slow heating rate (0.1–1 °C s⁻¹), low temperature (300–400 °C), and long gas and solid residence time (more than 30 min); (2) fast pyrolysis which is operated with a fast heating rate (1–100 °C s⁻¹), high temperature (500–900 °C), and short gas and solid residence time (10–20 s); and (3) flash pyrolysis which is operated under a very high heating rate (more than 1000 °C s⁻¹) and very short residence time (1 s) [7,8].

Pyrolysis of solid fuels includes two main steps: primary and secondary pyrolysis. In primary pyrolysis, the solid fuel degrades into volatile gases and char. The primary pyrolysis products of solid fuels are non-condensable (light) gases (e.g., CO, CO₂, H₂O, and H₂), light hydrocarbons (e.g., CH₄, C₂H₄), condensable gases (tars), solid residue (char), and mineral ash. If the products of primary pyrolysis undergo further reactions at higher temperatures and longer residence times, it is known as secondary pyrolysis. Secondary pyrolysis includes processes such as cracking, polymerization, condensation, and carbon deposition, which can occur either homogeneously (when reactants are in the gas phase), or heterogeneously (when the reactions occur at the surface of a

solid fuel or char particle). Secondary pyrolysis is not as widely studied as primary pyrolysis, but some secondary reactions, such as tar cracking, can have significant effects on the distribution of products [9]. During secondary pyrolysis, the tars heat up in the flame and either decompose to lighter gases or polymerize to form soot. The orange color of flames is due to the radiation from the tiny soot particles in the fuel-rich part of the flame [10]. Yields of tar and total volatiles, as well as distribution of volatile species, depend on heating rate, temperature, fuel type, etc. [11].

Pyrolysis of biomass (dead and dried vegetation) and wood have been explored in detail [10,12–14]. However, there are insufficient research studies in the field of pyrolysis of live plants. Live and dead plants burn differently [15]. A plant is considered dead when the dry-basis moisture content is less than 30 wt%, but may be as low as 4%. Dead fuels may have a moisture content higher than 35 wt% only when water from the surface of the leaf is absorbed into the cell cavities [16]. Dry-basis moisture content of live fuels may exceed 250 wt% which causes significant amounts of water to remain in the fuel during ignition. Wet dead fuels absorb water in their cell walls, and by heating the fuels, this vapor diffuses out. However, in live fuels, some of the un-evaporated water expands rapidly causing the cell walls to burst [1,17]. Moisture content in live fuels converts to water vapor, dilutes the gaseous pyrolyzates and has noticeable effects on flame behavior by slowing down the burning rate [3]. In addition, it has been suggested that components such as non-structural carbohydrates, fats, and other components may impact combustion behavior of live fuels, but are not usually found in dead fuels [18–20].

Biomass pyrolysis consists of 4 main steps; moisture evolution, hemicellulose, cellulose, and then lignin decomposition [21]. Hemicellulose, cellulose, and lignin are biopolymers that form plant cell walls. The temperature range of pyrolysis for hemicellulose, cellulose, and lignin is 180–240, 230–310, and 300–400 °C, respectively, depending on heating rate [8]. At temperatures lower than 180 °C, biomass is primarily stable and pyrolysis does not occur [22]. In addition to lignocellulosic materials, live plants contain significant fractions of proteins, starches, sugars, and lipids [23].

During this research, fast pyrolysis of 14 live and dead plant species which are native to the Southern United States have been studied using a flat-flame burner (FFB) apparatus. The FFB apparatus enables experiments at high heating rates and high temperatures to imitate prescribed fire conditions under a convective heating mode only. Distribution of pyrolysis products was studied at high heating rates using a gas chromatograph equipped with a mass spectrometer



Fig. 1. Prescribed burning of the southern forests of the U.S.

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