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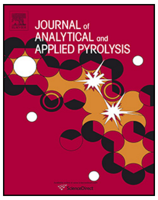

Insecticidal properties of pyrolysis bio-oil from greenhouse tomato residue biomass

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ABSTRACT

Fast pyrolysis is a recognized technology for the thermochemical conversion of biomasses into bio-oils that may contain valuable chemicals, including solvents, pharmaceuticals and biopesticides. The composition of the bio-oils is partly determined by the biomass feedstock. Bio-oil produced from the residues of greenhouse tomato plants has been investigated as a potential source of bioactive and pesticidal compounds. Fast pyrolysis of dried tomato residue biomass was performed in a bubbling bed reactor at 300 and 500 °C. The condensable vapors were collected using a condenser followed by an electrostatic precipitator (ESP). Bio-oil collected from the ESP exhibited a much greater insecticidal activity based on tests carried out using the Colorado potato beetle (CPB) *Leptinotarsa decemlineata* leaf disc bioassay. After an extraction with 1:1 water/dichloromethane, most of the activity remained in the organic phase. To further fractionate the components, amino solid phase extractions (SPE) followed by reversed phase LC separation were performed. Six LC fractions were collected and analyzed by GC–MS. Neophytadiene, phytol and a number of fatty acids were identified in the most active fraction, but only with combinations of these compounds was the greatest insecticidal activity obtained. Pyrolysis of tomato plant biomass affords a cost-effective source of bioactive compounds that can be further developed for biopesticide application.

1. Introduction

The pyrolytic conversion of agricultural residual biomass into bio-oil represents a potentially attractive technology for the removal and processing of agricultural waste from farms and greenhouses and its conversion into an alternative source of green energy and value-added chemicals [1]. Researchers at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at the University of Western Ontario designed a highly automated fast pyrolysis fluidized bed pilot plant to convert solid biomass into bio-oils, gases and bio-char at temperatures from 250 to 800 °C under near-atmospheric pressure [2]. Biomass previously dried and ground to <1 mm particle size is delivered to a bed of hot sand fluidized with inert gas (typically nitrogen) operating at temperatures between 300 and 550 °C and with gas residence times of the order of seconds. Through thermal cracking, the biomass is transformed first into solid bio-char residues, gases and vapors. They exit the reactor through a hot filter which retains the bio-char within the sand bed. This bio-char is valuable for use as a fertilizer [1]. The gases and vapors are directed to a condenser followed by an electrostatic precipitator (ESP) where the condensables are collected as bio-oil while the permanent gases are vented (Fig. 1). Such gases, including carbon monoxide, methane, hydrogen, carbon dioxide and inert nitrogen, have energy value that can be utilized for industrial processes [1]. The bio-oil accumulated in the ESP is soluble in acetone and has a higher density and viscosity than the aqueous fraction collected in the condenser. The difference in viscosity and density values can be attributed to the water content in the bio-oils [3].

Our group has been characterizing the biopesticide properties of bio-oils by testing the entire content and its fractions against selected insects, bacteria and fungi [4–8]. In the last few years, we attempted to isolate and identify the active chemicals responsible for the activities in bio-oils obtained from various biomasses. Bio-oils are complex in chemical composition, but in general, are mainly composed of water, organic compounds and a small amount of ash. According to Bridgwater, bio-oil is a miscible mixture of

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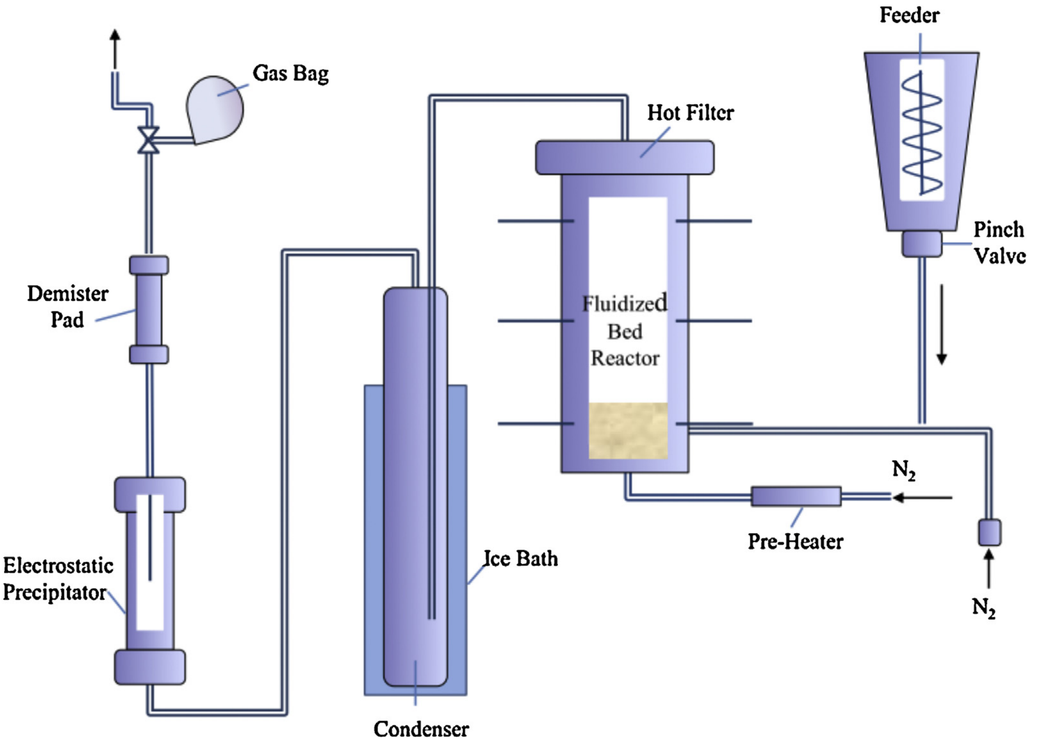

Fig. 1. Schematic process flow diagram of the ICFAR fluidized bed reactor used to convert tomato plant residue biomass into bio-oil.

polar organics (about 75–80 wt. %) and water (about 20–25 wt. %). It is obtained in yields of up to 80 wt. % in total (wet basis) of dry feed [1]. Our general analytical approach begins with the fractionation of bio-oils with solvent extractions followed by liquid chromatographic separations. Bioassays against an organism of interest are used to select the most active fraction for GC–MS identification. Our earlier work examined bio-oils from tobacco, coffee grounds, and grape seeds and skins. Briefly, nicotine, a chemical present in tobacco and a known pesticide, was found to remain intact during the pyrolysis process. While bio-oil from tobacco leaves has been examined for its pesticide properties against a variety of species of fungi and bacteria, and an insect, the Colorado potato beetle (*Leptinotarsa decemlineata*), it was found that the nicotine in tobacco bio-oil was not solely responsible for the observed pesticide activity and that nicotine-free fractions of the bio-oil demonstrated pesticide activity. According to the GC–MS data, this fraction was found to be rich in phenolic compounds [6]. Coffee ground bio-oils produced at 500 and 550 °C were the most active against two species of bacteria, whereas the 400 and 450 °C bio-oil samples were the most active against the CPB. After fractionation of the active fractions, it was found that both phenolic and non-phenolic containing fractions were active, likely due to the collective presence of various molecules [4]. Even though no pesticide bio-assays were performed with bio-oils from grape skins and grape seeds, the organic compounds octadecanoic acid, reported to have insecticidal effects against the fall armyworm (*Spodoptera frugiperda*) [9], and ethyl ester acids, reported to have strong bactericidal effects [10], were present in the aqueous phase [2].

Bio-oils obtained from the basic plant biomass components of lignin, cellulose, hemicellulose were analysed by our group as well [7]. The lignin bio-oil, collected in the ESP, was found to be the most insecticidal when tested individually. Collectively, the cellulose and hemicellulose components of the biomass were found to enhance the insecticidal activity of the lignin fraction when pyrolyzed altogether. Most recently, we expanded our studies to the bio-oils from canola and mustard straws [8]. These *Brassicacae* crops were chosen for their content of glucosinolates and isocyanates, compounds with recognized anti-herbivore activity. These two groups of compounds did not survive the pyrolysis process, but it was reported that the main compounds identified within the most active fractions were hexadecanoic and octadecanoic fatty acids.

In this work, the biomass of particular interest is greenhouse tomato plant waste. In 2011, Canada produced 540 ha of greenhouse tomato [11], and a typical vegetable greenhouse operation in Canada produces 40–60 tons of organic residues per hectare per year [12]. Similar to canola and mustard straws, tomato plants contain a variety of phytochemicals that provide natural defenses against pathogens and pests including fungi, viruses, bacteria, insects, and nematodes [13–16]. Specifically, tomatoes accumulate phenolic compounds, phytoalexins, protease inhibitors, carotenoids, lycopenes, and glycoalkaloids. For example, the glycoalkaloid tomatine is present in all parts of the tomato plant and have antibiotic properties against a variety of fungi and bacteria [17]. To date, however, there have been no reported studies of insecticidal activity of greenhouse tomato waste bio-oil. A positive use of the tomato plant residue though pyrolysis technology is therefore worthwhile. The objective of the research was therefore to assess the insecticidal activity of the bio-oils obtained from tomato plant waste, and isolate and identify the main active compounds. As in previous studies, our approach focuses on the bio-oil fractions that exhibit significant levels of pesticidal activity. Many separation techniques suitable for bio-oils have been reported in the literature [18–21]. For this study, liquid–liquid extraction with dichloromethane (DCM) and water was used to separate the bio-oil components based on polarity. Next, fractionation by amino solid phase extraction and reversed phase LC were performed. Fractions with significant insecticidal activities were characterized using GC–MS to identify the responsible compounds.