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On-line monitoring of pine needles combustion emissions in the presence of fire retardant using a "thermogravimetry (TG)-bridge/mass spectrometry method"

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Abstract

In this work a new method called TG-bridge/mass spectrometry is presented, for the on-line monitoring of the pine needles combustion emissions in a common lab furnace. The TG-bridge (thermogravimetry-bridge) system has been developed in-house as a TG–MS (thermogravimetry–mass spectrometry) interface, for TG–MS analysis. In this work, TG-bridge was used for directly sampling of the combustion emissions from the inside of the furnace and transferring them into the mass spectrometer (MS), without disturbing the sub-pressure conditions inside the MS ion source.

The effect of Fire-Trol 931 (a long-term fire retardant) on the emissions, produced during the combustion of pine needles, is tested in the lab for future application in the field. It was shown that in treated samples, increased evolution of ammonia and aromatic compounds took place, compared to untreated samples. Maximum concentrations of specific compounds, such as benzene and toluene, evolved during the combustion experiments in the furnace, were determined.

Keywords: Thermogravimetry (TG)-bridge; Mass spectrometry; Fire emissions; Combustion; Pine needles; Fire retardant; On-line monitoring

1. Introduction

Large-scale forest fires are a major environmental danger. The resultant smoke usually contributes a significant percentage of global air pollution with devastating environmental impacts, threatening not only the populations in the vicinity of the fire spot but the populations on a global basis. This is because forest fire smoke plumes can travel long distances and cross borders [1,2].

Forest fire smoke is a complex mixture of solids, liquids and gases and due to its composition can have short and long-term health impacts on the exposed population and the fire-fighters [3–6]. It consists of water vapour, permanent gases, such as CO_2, CO, NO_x, volatile organic compounds (VOCs), such as hydrocarbons (alkenes, alkynes), aldehydes (acetaldehyde, formaldehyde, furfural, acrolein), substituted furans, phenol, carboxylic acids, BTX (benzene, toluene, xylene), alkylbenzenes, semi volatile organic compounds (SVOCs), such as polyaromatic hydrocarbons (PAHs) and particulate matter (PM_{10}, $PM_{2.5}$); particulate matter usually consist of absorbed or condensed organic and inorganic compounds [7–9].

The chemical methods for fighting forest fires involve mainly the use of chemicals, either as suppressants, applied directly to the fire front to suppress the flame, or as retardants, applied ahead of a fire to reduce the rate of spread or intensity of the fire. Mixtures of ammonium sulphates and phosphates are the active ingredients of the most used fire retardants. The environmental impacts of these chemicals were considered so far to be small, in comparison with the huge benefits, which are obtained from the protection of forests. However, studies concerning the environmental impact of these chemicals have been reported in the literature [10]. In addition, retardants alter the pyrolysis process of forest fuel [11–13] and for that reason it is worth to study their impact on the emissions of specific compounds, such as aromatics.

It is in the purpose of this work to study possible changes in evolution profiles of forest fuel combustion emissions in the presence of fire retardants, using a new analytical method

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called *TG-bridge/mass spectrometry method*. The TG-bridge (thermogravimetry-bridge) system has been developed in-house as a TG–MS (thermogravimetry–mass spectrometry) interface, and has been successfully used for TG–MS analysis. Its performance evaluation (tests for monitoring the mass-flow stability, the gas transfer delay, the evolved-gas condensation effect and the interferences of the coupling system on TG and MS specifications), is presented in detail elsewhere [14]. In this work, TG-bridge was used for directly sampling of the combustion emissions from the inside of the furnace and transferring them into the mass spectrometer (MS), without disturbing the sub-pressure conditions inside the MS ion source. This method has already been used successfully in a previous work to monitor on-line the combustion emissions of untreated pine needles in a laboratory oven [15]. TG-bridge can also be used in combination with a portable mass spectrometer, for on-line monitoring in the field.

More specifically, the resulting changes in the evolution profiles of specific compounds (CO_2, NH_3, benzene, toluene and phenol), produced during pine needles combustion due to the presence of Fire-Trol 931, were monitored. The maximum concentrations of benzene and toluene were determined inside the furnace.

2. Experimental part

Combustion experiments of untreated and treated with retardant Fire-Trol 931 pine needles took place in a lab furnace in the temperature range of 125–650 °C. During the combustion experiments, dynamic phenomena and rapid changes of smoke concentration profiles take place. As a result, the evolution of smoke components is so turbulent and also their concentrations are so high that can displace oxygen. Hence, combustion under limited oxygen is favoured. In this case, a variety of products are evolved, and not mainly CO_2 and H_2O, as occurs in rich oxygen atmosphere. The sampling of combustion emissions, during the heating of the furnace was done very close to the burnt pine needle bed. The TG-bridge/mass spectrometry method was used for the on-line monitoring of selective combustion emissions. Evolution profiles of gases (CO_2, NH_3) and VOCs (benzene, toluene, phenol) during combustion experiments, with and without retardant, were monitored.

2.1. Sample pre-treatment

Untreated samples were prepared using green *Pinus halepensis* needles, collected from a forest nearby the National Technical University of Athens. The needles were dried for 5 days at 40–50 °C and the moisture loss was approximately 40–50% (w/w). Then, 50 g of dried pine needles were used to construct an untreated dried pine needle bed with approximate dimensions of 23 cm × 12 cm × 7.5 cm (length × width × height). Treated samples were prepared by spraying the untreated dried pine needle bed with a solution of a commercial fire retardant (Fire-Trol 931) 20% (v/v), in order to give a mean retardant application rate of $1.6\,\mathrm{L\,m^{-2}}$. The treated samples were similarly dried before the combustion procedure.

2.2. Instruments and apparatus

In Fig. 1, a schematic diagram of the apparatus used is shown. The combustion experiments took place in a Thermawatt furnace, with inner dimensions 24 cm × 17.5 cm × 10 cm (length × width × height) and temperature range of 0–1200 °C.

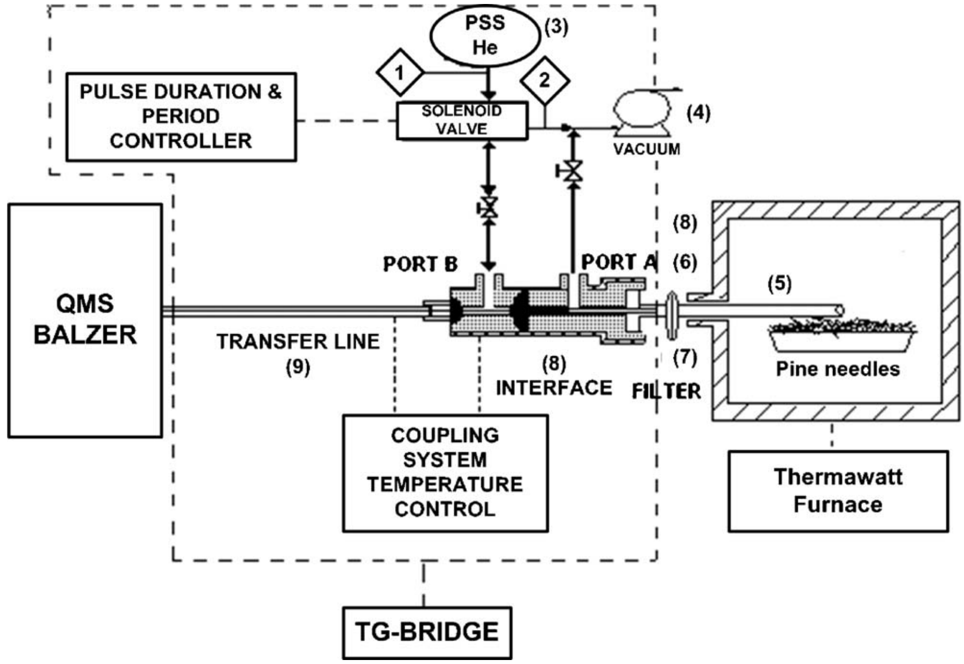

Fig. 1. Schematic diagram of the in-house made TG-bridge in conjuction with the mass spectrometer (MS Balzer), used in the furnace experiments: (1) *idle mode, (2) *sampling mode, (3) *pulsed sampling switch (PSS) He inlet, (4) *vacuum pump, (5) glass sampling tube, (6) vent hole, (7) fiber glass filter (8) *interface, (9) *transfer line. *These compartments are explained elsewhere [17].