

The U. S. EPA Biomass Fuel Analytical Laboratory

Evelyn Baskin and Chun Wai Lee
U. S. Environmental Protection Agency, NRMRL, MD-63, RTP, NC 27711
(919) 541-2429; Fax: (919) 541-7885

David F. Natschke
Acurex Environmental Corporation, 4915 Prospectus Drive, Durham, NC 27713

ABSTRACT

This paper describes the U.S. EPA's biomass fuel analytical laboratory at the EPA's Environmental Research Center in Research Triangle Park, NC. There is increasing interest in utilizing biomass based fuels in thermal energy systems as an effective means for global warming remediation. However, information on biomass combustion emissions, which is needed in order to assess the potential environmental impacts of biomass fuel combustion, is insufficient. To fill this need the laboratory is examining biomass fuels and their potential of forming in products of incomplete combustion (PICs) under different thermal conditions. The objectives are to evaluate the kinetics of combustion and emission characteristics (e.g., structure and composition) of representative samples of relevant types of biomass fuels through studying 1) the local pyrolysis and combustion processes and products, and 2) the overall degradation rate as influenced by heat transmission.

Biomass fuel samples will be examined by thermogravimetric analysis with an on-line Fourier transform infrared spectrometer (TGA-FTIR). EPA built a prototype TGA which is capable of handling a 100 g sample with 1 µg resolution for this laboratory. This instrument is capable of heating the sample to 1200°C. Samples can be pyrolyzed and combusted sequentially by automated gas switching. The effluent gases are passed to the heated gas cell of a Mattson FTIR for on-line identification and quantification of hydrocarbons, carbon monoxide, carbon dioxide, sulfur dioxide, and water. Summa canister samples are collected for analysis by gas chromatography/mass spectroscopy (GC/MS). Hydrogen is determined by gas chromatography/thermoconductivity detector (GC/TCD). Particulates are determined from the residue on the TGA sample pan and a filter sample collected between the TGA and FTIR and analysis gravimetrically by atomic absorption spectroscopy (AAS or inductively coupled argon plasm).

KEYWORDS

Biomass, TGA/FTIR, GC/MS, combustion, pyrolysis

BACKGROUND

Steam turbine power plants fired with fossil fuels are utilized to generate approximately 80 % of the electrical power worldwide. In an effort to reduce

greenhouse gas emissions in accordance with the Federal Climate Change Action Plan, other fuel sources are being investigated. Data on the emissions generated by the pyrolysis or combustion of non-woody feedstocks (e.g., herbaceous, agricultural waste) are not well documented or have not been demonstrated. Emissions data from woody feedstocks are more prevalent, but trace organic compounds emissions data are deficient. Characterization of a comprehensive range of biomass fuels can assist in designing feed and combustion systems, determining plant and component efficiency, determining life cycle costs, and determining environmental impacts. Biomass fuels can be utilized to produce various end products including those generated from: microbial and enzymatic processes to produce methane and ethanol; thermochemical processes (pyrolysis, gasification, direct liquefaction) to produce methanol, synthesis gas, or pyrolysis oils; and direct combustion for steam and electricity generation (Sanderson et al., 1996). The EPA's (Environmental Protection Agency's) APPCD (Air Pollution Prevention and Control Division) of the NRMRL (National Risk Management Research Laboratory) has undertaken the task to characterize representative samples of various types of biomass fuels which are carbon dioxide (CO₂) neutral. This evaluation couples environmental concerns and equipment performance utilizing biomass fuels.

The characterization will be done using thermogravimetric analysis (TGA) coupled with Fourier transform infrared (FTIR) spectroscopy for detection of evolved gases. Coupling these devices elucidates extensive information concerning the structure, composition, and combustion and pyrolysis kinetics of fuels. The FTIR provides constant monitoring (during pyrolysis and other reactions) of the IR spectra of evolving gases, as well as a quantitative analysis of gases. Utilizing the TGA/FTIR enables identification of the evolved gases that correlate to the specific TGA weight loss. The literature has shown that the TGA/FTIR combination provides more detailed and accurate data than using a TGA alone. Laboratory capabilities have been designed and planned to encompass a TGA/FTIR, gas chromatograph/thermal conductivity detector (GC/TCD), adiabatic bomb calorimeter, and access to a GC/mass spectrometer (MS) and open burning facility. All gases will be analyzed using the TGA-FTIR, GC/TCD, and GC-MS. Figure 2 illustrates the laboratory layout.

BIOMASS MATERIAL AND FUEL COMBUSTION EMISSIONS

Biomass and biomass fuels are from a variety of sources and fuel types, as seen in Fig. 1. Fuels are selected based on their availability for use as a sustainable feedstock for biomass power generation. Fuel viability will be region specific, since the abundance of a fuel source in one area of the country does not guarantee its availability in another (e.g., various agricultural wastes, different tree species). Biomass tested for non-power generation fuel applications is selected based on its environmental impact when burned (e.g., forest management, waste disposal).

Recent data reveal that gaseous methyl bromide (CH₃Br) is produced by biomass open burning and may account for 30% of the CH₃Br in the atmosphere (Cicerone 1994). CH₃Br has been shown to be released during the flaming and the smoldering phases of burning. Mano and Andreae (1994) measured CH₃Br emission from wildfires in the savannas, chaparrals, boreal forests, and laboratory biomass combustion experiments.

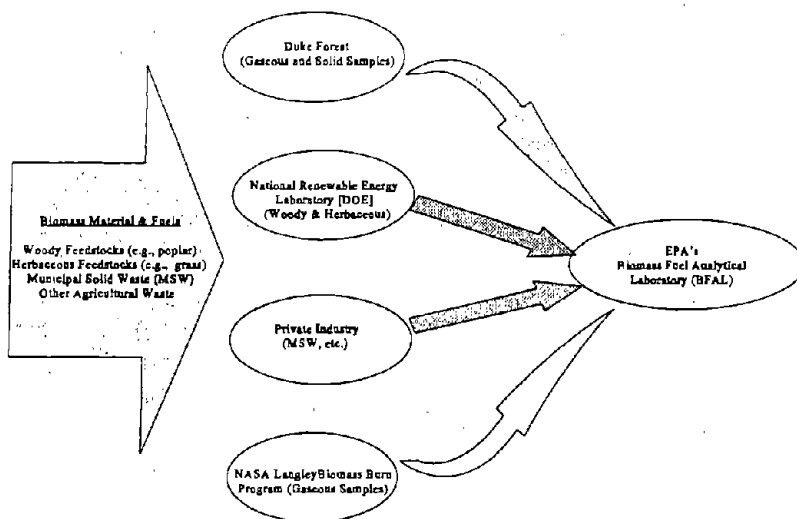


Fig. 1. Biomass material and fuel sources and variety.

From their work they estimated the global emission of CH_3Br to range from 10 to 50 Gg per year. The CH_3Br ozone depletion potential (ODP) is 1.9 for a time horizon of 30 yrs (UNEP 1992). CH_3Br is listed in the Clean Air Act as a Class I ozone-depleting substance, and its industrial production is scheduled to be phased out by the year 2001. CH_3Br is more reactive than the perhalogenated halon compounds; therefore, only a few percent of it emitted at the Earth's surface reaches the stratosphere.

The combustion of biomass material releases significant quantities of nitrous oxide (N_2O), nitric oxide (NO), and ammonia (NH_3) to the atmosphere. Experimental quantification of the type and amount of nitrogen gases returned to the atmosphere during burning estimates 20 to 36 Tg N per year. N_2O and NO are fundamental gases involved in global climate change. NO contributes to the production of ozone (O_3) in the troposphere; production of nitric acid (HNO_3), a component in acidic precipitation; and the chemistry of hydroxyl radical (OH), a chemical agent in the troposphere. N_2O is a greenhouse gas with a global warming potential 200 times that of CO_2 . Major sources of N_2O are uncertain, and recent discoveries indicate that at least 30% of its global production is not known (Levine *et al.*, 1997).

Studies of biomass burning from a global warming perspective recently have been published more frequently (Crutzen *et al.* 1985, Crutzen and Andreae 1990, Houghton 1990); however, most of these studies are narrowly focused on estimating global total emissions or emissions ratios relative to CO_2 ; emissions of other volatile organic species such as methyl bromide have not been investigated. The EPA has compiled emission factors for forest fires for total particulate, carbon monoxide (CO), total hydrocarbons, and nitrogen oxides (NO_x) (USEPA, 1985). A detailed study on measuring emission factors for CO_2 , CO, total hydrocarbons, formaldehyde, total organic acids, NO_x , total particulate, and nine polycyclic aromatic hydrocarbons (PAHs) from the open burning of "landscape refuse such as lawn clippings, leaves and

tree branches" found that total particulate and total hydrocarbons are the major emissions (Gerstle and Kemnitz 1967). Another study based on airborne measurements of open burning of logging debris also found that total particulate is the major emission from biomass open burning (Radke et al., 1978).

As emissions from open burning of a wide variety of combustible materials became increasingly a major air quality problem, the EPA conducted a series of emission tests at its Open Burning Simulation Facility also at Research Triangle Park. The facility was designed to provide open burning conditions similar to those in the field and is equipped with sampling equipment for detailed emission characterization from the simulated open burning tests. Tests have been performed to characterize emissions from combustion of agricultural plastic (Linak and Ryan 1989), used tires (Ryan 1989), automobile recycling fluff (Ryan and Lutes 1993), and fiberglass (Lutes and Ryan 1993) under simulated open burning conditions. It was found that the emission data generated from the simulated open burning experiments conducted at the facility correlated remarkably well with those collected from real fires. The facility has been found to be a valuable tool for systematic study of open burning on a wide variety of combustible materials.

TEST METHODS AND FACILITIES

Biomass Fuel Analytical Laboratory Test Methods

Biomass fuels used in previously published literature will be tested to validate the testing method and results using a thermogravimetric analysis/ Fourier transform infrared spectroscope (TGA/FTIR) and gas chromatography/mass spectroscope (GC/MS) that will be located in the biomass fuel analytical and combustion laboratories. Following substantiation of the method, gas plume and solid biomass fuel samples collected from prescribed fires at experimental forest sites will be tested. A testing protocol will be developed for each type of biomass fuel tested, and several tests of each fuel type will be performed. Chemical libraries containing suspected gas emissions from thermal degradation will be used in gas identification. Various biomass samples up to 100 g will be burned under various controlled temperatures and specified air supply conditions to establish an extensive characterization of the fuels in the laboratory. Thermal degradation will be evaluated using oxygen and nitrogen as combustion gases. Utilizing nitrogen will assist in studying pyrolysis, while use of oxygen will aid in studying material combustion. Argon will be used as a purge gas for evaluation of NO_x emissions from thermal degradation of the material. The TGA will provide kinetic data of the fuel. The kinetic properties will be evaluated under various temperature heating rates and temperature-hold settings. Allowing the evolving gases to flow into the FTIR from the TGA will link the kinetics and emissions properties of the biomass materials. Materials found to emit CH₃Br and methyl chloride (CH₃Cl) will be further tested in an open burning facility which can better simulate actual conditions to validate laboratory testing and determine how near-actual conditions affect emissions.

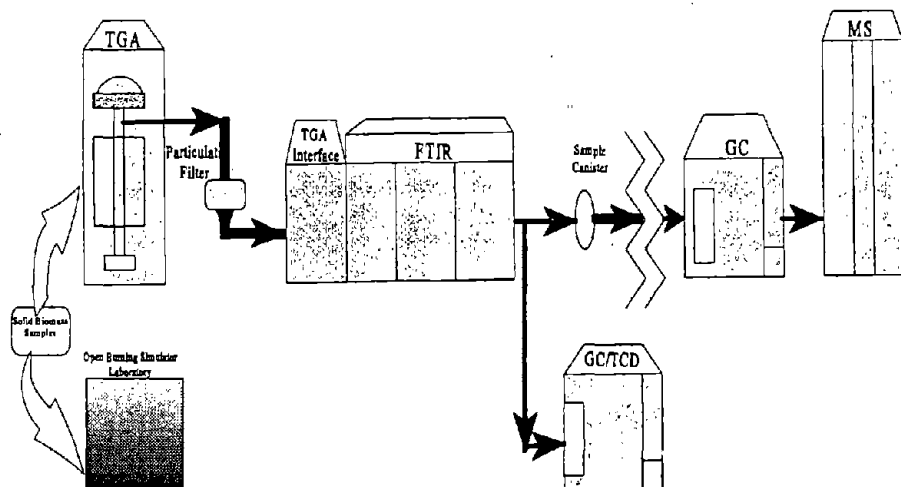


Fig. 2. Biomass facilities (zigzag lines indicate that equipment is located in separate laboratories, GC/MS is not realtime analysis)

Open Burning Test Methods

Experiments will be performed to measure CH_3Br and CH_3Cl from burning biomass fuels in the open burning facility which simulates the actual conditions of open field burning. Emphasis will be placed on identifying the air supply and temperature conditions under which CH_3Br and CH_3Cl emissions will likely occur during open burning. The open burning tests of this project are designed to collect and qualitatively and quantitatively characterize CH_3Br and other volatile organic emissions resulting from the simulated open combustion of biomass materials. Small quantities (9 to 21 lb, 4 to 10 kg) of biomass materials are combusted in several charges within a test facility specifically designed to simulate open-combustion conditions. A portion of the combustion effluent is diverted to an adjacent sampling facility through an induced draft duct. Samples are collected from this stream using the volatile organic sampling train (VOST). A portion of the sample from the induced draft duct is also analyzed by a series of continuous emission monitors (CEMs) for CO_2 , CO, NO, oxygen (O_2), and total hydrocarbons (THCs). Data provided by the CEM measurements can indicate combustion conditions. The organic constituents of the VOST samples are analyzed both qualitatively and quantitatively using gas GC/MS. Measured organic species concentrations are related to dilution air volumes and the measured net mass of biomass combusted to derive emission rates.

Biomass Fuel Analytical Laboratory Facility

The biomass fuel analytical laboratory is a 440 ft² (40.9 m²) space located at EPA's Environmental Research Center in Research Triangle Park, NC. The laboratory is

equipped with a TGA/FTIR system. The Galaxy 3020 FTIR and TGA interface are made by Mattson Instruments, Inc., and the TGA is made by Abess Instruments, Inc. The Galaxy 3020 is a single-beam spectrometer. The spectral range of the FTIR is 4000 - 400 wavenumbers (cm^{-1}) with a maximum resolution of 2 cm^{-1} . The system has nine scan velocities and a KBr beamsplitter. The system uses a dry air or nitrogen purge gas. The MCT (mercury cadmium telluride) detectors are cooled by liquid nitrogen. The TGA interface/heated transfer line is maintained at 300°C . The TGA accepts solid biomass fuel samples up to 100 g. The furnace achieves a maximum of 1200°C and is able to increase the gas temperature near the sample from 100°C to 1200°C at a rate of $1000^\circ\text{C}/\text{min}$. The TGA utilizes inert gas or combustion air as its purge gas. The TGA's computer controls the its temperature and collects mass data. The TGA and FTIR share a printer and plotter which generate data tables and plots from physical and chemical results. Each system has a 486 CPU data acquisition system. Additional gas analyses can be performed by extracting a sample from gases exiting the FTIR. This gas will be injected into a Hewlett Packard 6890E GC or a GC/MS for further analyses. See Fig. 2 for laboratory layout and Fig. 3 for the data collection and analysis process.

Open Burning Facility

The Open Burning Simulation Facility, located on the grounds of EPA's Environmental Research Center, in Research Triangle Park, NC, is used to simulate the open burning processes of a variety of combustible materials and study the resulting emissions. Examples of these materials have included tires, non-metallic automobile shredder residue, Chinese coals, fiberglass materials, household waste, and land clearing debris. Open combustion is simulated by burning the test material in a burn hut over a period of hours while maintaining a high dilution rate, thus allowing approximately two complete air exchanges per minute. The burn hut is an 8- by 8- by 8-ft (2.4- by 2.4- by 2.4- m) outbuilding modified for open-combustion experiments. The building has been fitted with a conditioned, dilution air handling system capable of delivering nominally $1,200 \text{ ft}^3/\text{min}$ ($34.0 \text{ m}^3/\text{min}$). This flow rate is sufficient to maintain a positive pressure within the facility. Thus, it could be assumed that the outflow rate from this facility is roughly equal to this inflow rate. The biomass material is combusted in a 16- by 16- by 16-in (0.4- by 0.4- by 0.4-m) stainless steel burn pit insulated with a fire brick enclosure and mounted on a platform scale to continuously monitor weight loss due to combustion. A deflector shield is located 4 ft (1.2 m) over the pit to deflect flames, protect the ceiling, and enhance ambient mixing. The sample transport duct, an 8-in (203-mm) O.D. stainless steel pipe, is located directly over the rear corner of the burn pit. This duct transports a representative portion of the gaseous sample to the sampling shed located adjacent to the burn hut. Temperatures are monitored in a variety of locations within the burn pit, sample duct, and air input ducts by means of thermocouples.

The sample shed contains the associated sampling equipment including the VOST system and the particulate removal system for the CEMs. The digital readout for the platform scale is monitored remotely in the sample shed. All gaseous samples are extracted from a sampling manifold within the duct located in the sample shed. The sample stream is pulled from the burn hut into the sample shed under vacuum by an

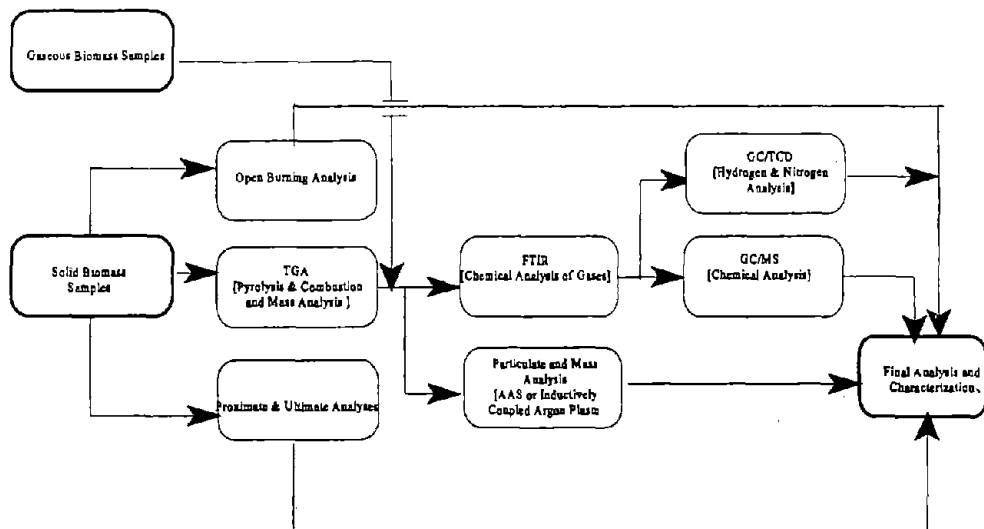


Fig. 3. Flow process of biomass fuel data collection and analysis.

induced draft (ID) fan downstream of the sample manifold. Methyl bromide and other volatile organics are collected through the VOST sampling train connected to the sample manifold. A heated, particulate-free sample is also obtained from the sample manifold and routed through a filter to individual CEMs for continuous measurement.

Quality Assurance


These studies will be performed in accordance with the approved laboratory and field testing quality assurance management plan. An EPA quality assurance project plan (QAPP) will be submitted prior to data collection. The QAPP will address, for instance, GC and FTIR response which will be calibrated to National Institute of Standards and Technology (NIST) reference gases. Replication and measurement variability will also be discussed in the QAPP.

EXPECTED RESULTS AND CONCLUSIONS

The EPA's state-of-the-art biomass fuel analytical laboratory will provide high quality fundamental combustion and pyrolysis analyses on a wide variety of biomass materials. The laboratory will also provide data from the thermal degradation of these materials that will reveal the environmental impact of utilizing them in various applications. Experimental results anticipated include detailed characterization of the pyrolysis and combustion of a wide variety of biomass materials at various TGA temperature ramp rates and hold settings. Coupled with these data will be the identification and quantification of gas emissions including trace organic compounds (e. g., methyl bromide and methyl chloride). Also, this research will supply data that will facilitate quantification of NO_x emissions from biomass burning. Results from this laboratory will be useful for the scientific community, the government, and industry.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
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Biomass		Thermogravimetry		Stationary Sources	
Combustion		Fourier Transformation		Global Warming	
Pyrolysis		Spectrometry		Thermoconductivity	
Fuels		Gas Chromatography		Atomic Absorption	
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