Primary Study of Woody Biomass and Coal for Energy Production Investigated by TGA-FTIR Analysis

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The purpose of this study was to determine the pyrolysis characteristics and gas properties of woody biomass and coal. The main gases from the pyrolysis of biomass, coal, and mixtures of different ratios of the two were identified using TGA-FTIR. The evolution of gases and their characteristics were investigated in real time. Thermal analysis demonstrated that the biomass sources decomposed easily and that most of their weight was lost under lower temperatures than those of coal. TGA-FTIR analysis indicated that H_2, CO_2, CH_4, and CO were the dominant gases released during the pyrolysis of biomass and mixtures. The results indicated that woody biomass could enhance coal pyrolysis or gasification and different types of biomass could have different influences on the thermal behavior of coal.

Keywords: Biomass; Coal; Energy; Pyrolysis; TGA-FTIR

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INTRODUCTION

Biomass is a renewable resource whose use for energy is more environmentally friendly than the use of coal or other fossil fuel. The U.S. has abundant woody biomass and coal resources available for conversion into bio-fuels and other bio-products. Fuel production from biomass and coal could be an alternative, economical way to more efficiently use coal and biomass, furthering economic development in the United States. In the U.S. there are 1.3 billion dry tons of biomass, 368 million of which is from forest land alone, available annually for conversion to fuels or other energies (Van Heiningen 2006). If biomass is grown and used sustainably, it is CO_2-neutral, and because it is a domestic resource, it is not subject to fluctuations in global price. This means it has the potential to be a cost effective and sustainable supply of energy (Demirbas 2001). Biomass is the only renewable source of fixed carbon and is considered the renewable energy source with the greatest potential to contribute to the energy needs of modern society. The most important environmental reason to consider a shift toward bioenergy is concerns about global warming, since fossil fuel use contributes to atmospheric carbon, and certain fossil fuel inventories are on the verge of becoming depleted (Sedjo 1997). If biomass is used in conjunction with coal to produce liquid fuels, the environmental impact of fossil fuel use could be diminished and the carbon footprint reduced.

Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) systems have been used in coal science for a number of characterizations and kinetics, to understand functional group compositions, and for temperature-programmed desorption. Research has previously been performed on the pyrolysis characteristics and

gases of coal, and the methods used to evaluate coal can be applied to biomass resources as well. TGA-FTIR methods were created to investigate the pyrolysis of Argonne premium coals (Solomon *et al.* 1990), and some functional group descriptions of oxygen-containing gases, in terms of their kinetics and maximum evolution temperatures, were determined. These methods have also been used in biomass research (Bassilakis *et al.* 2001; Liu *et al.* 2013; Ren *et al.* 2013), tobacco and glycerol-tobacco mixtures (Gómez-Siurana *et al.* 2013), commercial ethylene-vinyl acetate copolymers (Marcilla *et al.* 2005), waste materials including biomass wood waste, waste tyre, refuse derived fuel and waste plastic (Singh *et al.* 2012), and lignin extracted from prairie cordgrass, aspen, and kraft lignin (Zhang *et al.* 2012). The TGA-FTIR system was also used to study the possible synergetic effect between woody biomass and activated carbon during pyrolysis (Salema *et al.* 2014). All these studies were only related to biomass or polymers and no coal was added using a TGA-FTIR system. A few studies have focused on the analysis of biomass and coal, such as bio-chars from oil-palm empty fruit bunch co-combusted coals, which indicated that co-combustion of hydrothermally upgraded biochars with coals led to environmental benefits such as reduced toxic emissions of (CO), acidic gases (NO and SO_2), and greenhouse (CH_4 and CO_2) gases (Parshetti *et al.* 2014). This research used oil-palm fruit bunch and coal. There has been a lack of work related to coal and hardwood biomass co-combustion using the TGA-FTIR system.

The objective was to use a TGA/FTIR system to conduct pyrolysis of woody biomass, coal, and mixtures and analyze the resulting gaseous components. Two common types of woody biomass (yellow poplar and red oak) in the US, especially in the Appalachia region, were used because they have different types and/or percentages of chemical components compared with waste materials, tobacco, polymer, and lignin (Gómez-Siurana *et al.* 2013, Marcilla *et al.* 2005, Salema *et al.* 2014, Singh *et al.* 2012, Zhang *et al.* 2012). Understanding such pyrolysis characteristics will facilitate the co-combustion of these two natural materials, extend the life of the dwindling coal supply, and provide an alternative source of energy.

EXPERIMENTAL

Two common types of woody biomass (yellow poplar and red oak) and one type of coal (Kingwood) were used in this study. All materials were ground, and the resulting powders were sieved through a 40-mesh screen. The thermal degradation behavior and pyrolysis processes of the selected samples were investigated using a thermogravimetric analyzer (TGA Q50, TA Instruments, New Castle, DE).

The temperature ranged from ambient temperature (22 °C) to 950 °C with a heating rate of 10 °C/min. Nitrogen gas, at a flow rate of 50 mL/min, was used to prevent oxidation. The sample weights were approximately 10 mg.

The evolution of gases and volatile organic compounds were measured using a NicoletiS10 (Thermo-Scientific, Waltham, MA) FTIR connected *via* heated transfer line to the TGA analyzer.

The system is shown in Fig. 1. The infrared spectra of the gas mixture were generated every 30 sec at 4-cm^{-1} resolution. A one-minute delay between the TGA and FTIR gas cell was taken into account in the data analysis. The various ratios of coal and wood tested are shown in Table 1.

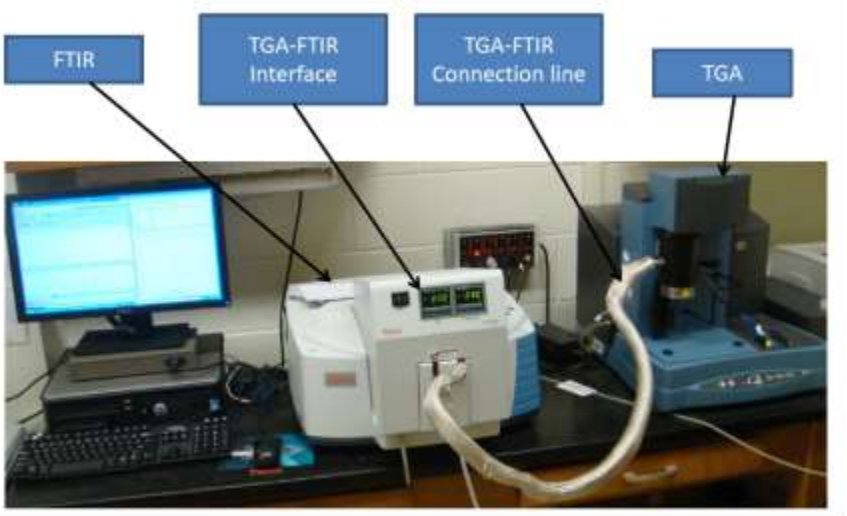

Fig. 1. TGA-FTIR system

Table 1. Coal and Wood Ratios (w/w %) Used in This Study

Material	Wt. %	Wt. %	Wt. %	Wt. %
Kingwood coal	90	80	70	50
Yellow poplar (Red oak)	10	20 (20)	30	50

RESULTS AND DISCUSSION

Neat Wood and Coal

The thermal behavior properties of yellow poplar, red oak, and Kingwood coal examined with TGA at various pyrolysis temperatures (22 to 900 ºC) are shown in Fig. 2. Poplar and oak samples showed similar degradation patterns, and two main phases in the decomposition of wood were observed. During phase 1, moisture content loss occurred at low temperature. During phase 2, cellulose, hemicellulose, and lignin degraded into volatiles at higher temperatures (200 to 400 ºC; Fig. 2).

Thermogravimetric derivative curve (TGD) peaks indicated that there was no appreciable difference in the peak rates of weight loss of poplar and oak woods (360 and 359 ºC, respectively). The peak at about 293 ºC was related to the decomposition of hemicellulose and cellulose because they have lower decomposing temperatures than those of lignin (Yang *et al.* 2007). However, TGD curves showed a slight difference in the degradation behaviors of poplar and oak, which could be due to their different chemical contents.

The pyrolysis behaviors of hemicellulose, cellulose, and lignin are significantly different (Yang *et al.* 2007). Poplar had lower residue content (9.85%) than that of oak (11.40%) due to its lower lignin content. This is because lignin, unlike cellulose, degrades slowly, with many nonvolatile segments (Adebayo *et al.* 2009). The maximum degradation of kingwood coal was at 469 ºC, a temperature much higher than those of the woody biomass, indicating it was much harder to degrade. The coal had much higher ash residue (around 69%).

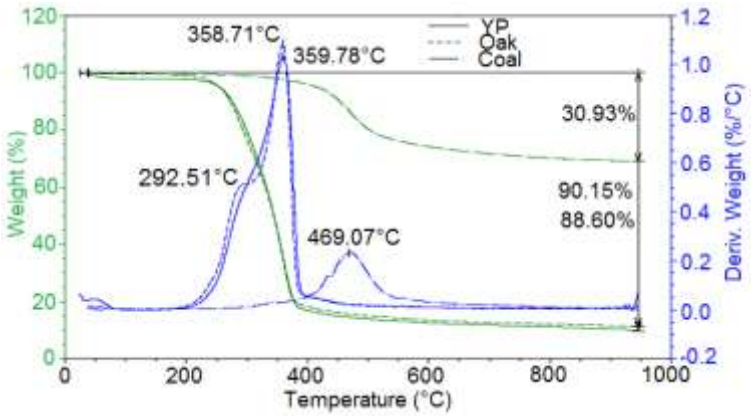

Fig. 2. TGA and DTG thermograms of yellow poplar, red oak, and Kingwood coal

Typical TGA-FTIR spectra of poplar and oak are plotted in Fig. 3, in three dimensions. The FTIR spectra indicate the gases generated during the pyrolysis of wood samples as a function of both wave number and temperature. Temperatures at which gases were released were used to observe sample weight loss (Fig. 2). The main volatile components identified by FTIR were H_2O, CH_4, CO_2, CO, and some organics (a mixture of acids, aldehydes (C=O), alkanes (C–C), and ethers (C–O–C)). Spectra for the two wood samples indicated similar release times and temperatures for most gases, but the release conditions of some gases differed due to differences in wood composition. Lignin consists mainly of aromatic groups, which have higher chemical bond energies than the polysaccharide structures of cellulose (Ren *et al.* 2013; Yang *et al.* 2007), and are therefore more difficult to break down. The 3D spectra of Kingwood coal from TGA-FTIR analysis (Fig. 4) were much different than those of the wood samples. More CH_4 was released from the coal than other gases at temperatures around 400 to 600 ºC (Fig. 2). Some organic oxygen, in the form of H_2O, CO_2, CO, and various oxygen functional groups in aliphatic and aromatic molecules, were detected by TG-FTIR in the gases of different coals (Giroux *et al.* 2006). The increased distribution of and presence of multiple functional groups in woody biomass during heating, as compared to coal, was expected because coal has a higher energy density. This could be resolved with light torrefaction (Via *et al.* 2013). However, the objective of this study was to pursue using wood in its native form, which is not as well-understood and would be more cost-effective than using modified wood.

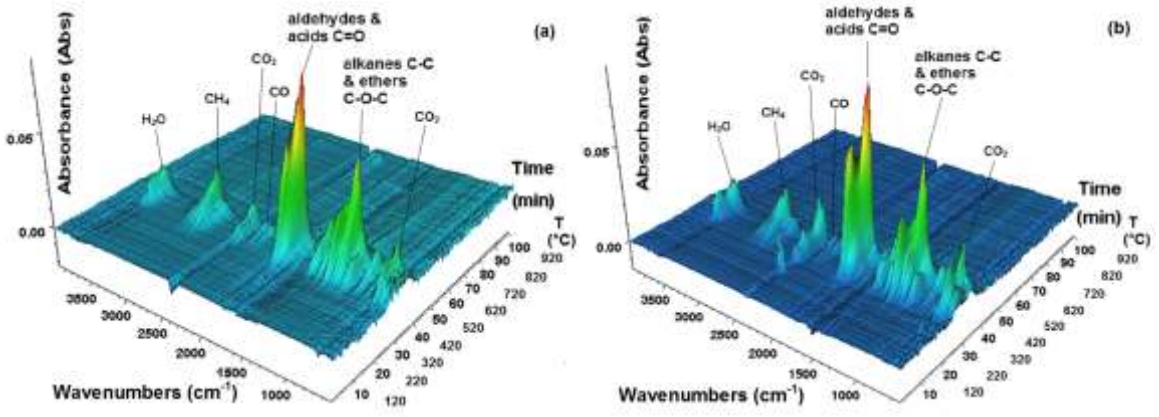

Fig. 3. Gases released from yellow poplar (a) and red oak (b), as detected by TGA-FTIR

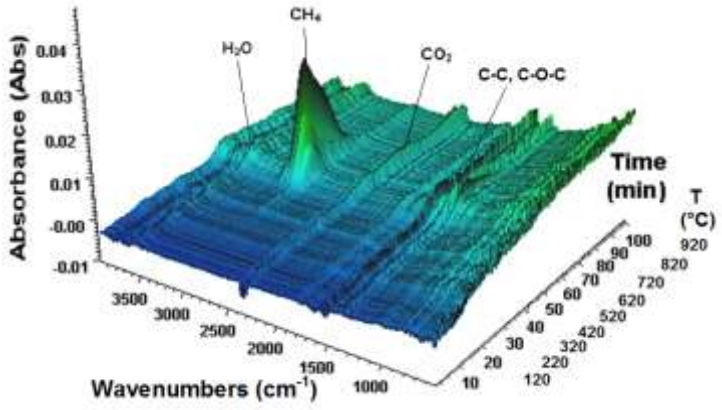

Fig. 4. Gases released from Kingwood coal, as detected by TGA-FTIR

Mixture of Wood and Coal

Table 2 shows the temperatures of the maximum pyrolysis rates (decomposing) for different starting coal and yellow poplar wood ratios (including pure wood and coal) and the peaks of DTG thermograms. It appeared that the wood and coal decomposed separately. This is evident from the fact that two DTG clear peaks were obtained for the coal and wood mixtures, and the wood peaks had the same temperature as that of pure wood samples. The results indicated that all mixtures had peaks at a temperature of around 360 ºC, the same as woody biomass, and peaks at a temperature of around 437 ºC, from the coal. The more coal in the mixtures, the higher the residue content obtained.

It was also noticed that the peak decomposition temperature of coal in the mixtures was much lower than that of the neat coal (437 °C *vs.* 469 °C). This indicates that woody biomass can enhance or stimulate the coal pyrolysis and gasification process. Adding biomass can decrease the coal decomposition temperature and be helpful to the coal pyrolysis and gasification process for gas or liquid fuels, reducing energy consumption. Similar results have been reported, of synergistic interactions taking place between the fuels during co-combustion of oil-palm empty fruit bunch hydrochars and coals and the co-combustion of hydrochars with coals leading to environmental benefits (Parshetti *et al.* 2014).

Table 2. Temperatures of Maximum Pyrolysis Rates (Decomposing) for Different Starting Coal and Yellow Poplar Wood Ratios

Coal/wood ratio	100/0	90/10	80/20	70/30	50/50	0/100
Wood max decomposing temp (°C)	-	360	360	360	360	360
Coal max decomposing temp (°C)	469	437	437	437	437	-

Different types of woody biomass may have different effects on the thermal behavior of the wood and coal mixtures (Fig. 5). The peak decomposition temperature of the coal in the mixture of red oak and coal was much higher than that of the yellow poplar and coal mixture (468 *vs.* 436 °C), which was likely due to the greater lignin content of the red oak (Adebayo *et al.* 2009).

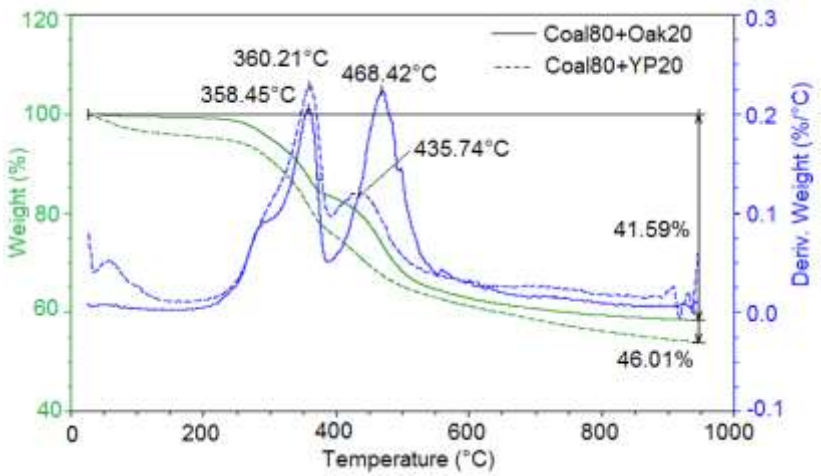

Fig. 5. TGA and DTG thermograms of 20% yellow poplar and red oak with 80% coal

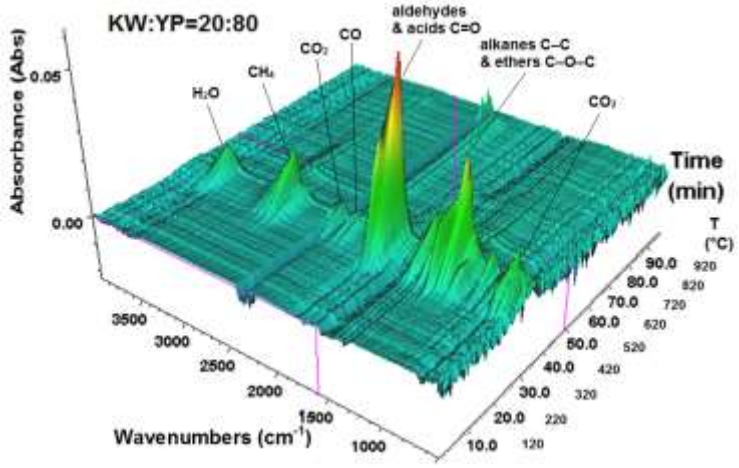

Fig. 6. Gases released from 20% yellow poplar and 80% coal, as detected by TGA-FTIR

Figure 6 shows the 3D spectra of the gases released from the wood and coal mixture (coal-to-yellow poplar ratio of 20:80) as determined by TGA-FTIR analysis. The volatile components generated from the mixture of wood and coal were a combination of the gases generated from wood and coal individually. The 3D spectra were similar to those of the spectra of the wood samples due to the high wood content in the mixture.

This primary study focused on determining the thermal behavior of wood, coal, and mixtures thereof. Further studies are necessary to understand how mixing biomass with coal could enhance or stimulate the pyrolysis or gasification processes of coal and to quantitatively analyze the resulting gaseous components because some study concluded that the coal/oil palm biomass blends appear to undergo an independent thermal degradation without any synergistic interaction as such its behaviour during co-pyrolysis can be estimated from those of parent fuels by TGA (Idris *et al.* 2010), while some study found that synergistic interactions taking place between the fuels during co-combustion of oil-palm empty fruit bunch hydrochars and coals (Parshetti *et al.* 2014).

CONCLUSIONS

1. The thermogravimetric analysis/Fourier transform infrared (TGA/FTIR) system is a powerful tool to conduct pyrolysis of woody biomass, coal, and mixtures and analyze the resulting gaseous components.
2. Woody biomass was found to be more easily decomposed, with most of its weight lost at lower temperatures than in coal.
3. Woody biomass, when blended with coal, could enhance coal pyrolysis or gasification. Different types of biomass could have different influences on the thermal behavior of coal.
4. The main gaseous products from the pyrolysis of biomass, coal, and their mixtures include CO_2, CH_4, CO, H_2O, and some acids, aldehydes, alkanes, and ethers organic compounds.

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