

## 스위치그라스 열분해에 대한 TGA-FTIR 분석

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### Thermogravimetric and Fourier Transform Infrared Analysis of Switchgrass Pyrolysis

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#### Abstract

This study was conducted to investigate the pyrolysis characteristics of switchgrass using TGA-FTIR instrument. Switchgrass is a high yielding perennial grass that has been designated as a potential energy crop, because of its high energy value. Ground switchgrass were pyrolysed at different heating rates of 10, 20, 30, and 40°C/min in a TGA-FTIR instrument. The thermal decomposition characteristics of switchgrass were analyzed, and the gases volatilized during the experiment were identified.

The thermal decomposition of switchgrass started at approximately 220°C, followed by a major loss of weight, where the main volatilization occurred, and the thermal decomposition was essentially completed by 430°C. The pyrolysis process was found to compose of four stages; moisture evaporation, hemicellulose decomposition, cellulose decomposition, and lignin degradation. The peak temperatures for hemicellulose decomposition (306°C to 327°C) and cellulose decomposition (351°C to 369°C) were increased with greater heating rates.

FTIR analysis showed that the following gases were released during the pyrolysis of switchgrass; CO<sub>2</sub>, CO, CH<sub>4</sub>, NH<sub>3</sub>, COS, C<sub>2</sub>H<sub>4</sub>, and some acetic acid. The most gas species were released at low temperature from 310 to 380°C, which was corresponding well with the observation of thermal decomposition.

**Keywords** : Pyrolysis, Switchgrass, TGA-FTIR, Thermal decomposition, Peak temperature

## 1. INTRODUCTION

The world economy is presently dominated by technologies that rely on energy from fossil fuels (petroleum, coal, and natural gas) to produce power, chemicals, and materials. However, fossil fuels are a limited and non-renewable energy source. In addition, there are environmental problems associated with extracting, transporting, and using fossil fuels. And, nowadays there is an increasing concern with environmental problems associated with the rising emissions of

CO<sub>2</sub>, NO<sub>x</sub>, and SO<sub>x</sub>, resulting from the use of fossil fuels.

For these reasons, more attentions are paid to renewable energy, especially biomass energy that can contribute to reduce the consumption of fossil fuels and relieve the environmental and energy problems. Biomass is a renewable resource. Compared with other renewable energy resources, biomass is abundant in annual production, with a geographically widespread in the world. There is a large amount of biomass in the form of agricultural or agroindustrial residues.

Among various biomass, switchgrass is a high yielding

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perennial grass species native to North America. And, switchgrass has been designated as a potential bio-energy crop by the U.S. Department of Energy, because of its high energy value (McLaughlin and Kszos, 2005). It also has excellent conservation attributes and is compatible with conventional farming practices (McLaughlin et al., 1999).

Conversion of these biomass materials by thermochemical processes, such as pyrolysis, combustion, and gasification, can significantly and immediately allow energy recovery from reducing the mass and volume of waste. Among these thermochemical processes, pyrolysis is considered to be one of the promising thermal approaches in converting biomass to energy. Studies on pyrolysis have been widely conducted for converting waste organic materials such as waste biomass materials and waste plastics into liquid and gaseous hydrocarbons (Marcilla et al., 2005; Fang et al., 2006; Kim and Agblevor, 2007). However, pyrolysis is an extremely complex process that goes through a series of reactions and can be influenced by many factors. It is thus essential to study the fundamentals of biomass pyrolysis.

Previous investigations of biomass pyrolysis were mostly focused on yields of solid, liquid, and gas products, as a function of various parameters, including heating rate, sample size, final temperature, and volatiles residence time (Yang et al., 2004; Sabio et al., 2006). However, the real-time gas release in the course of pyrolysis closely related to the mechanism of biomass decomposition is rarely studied. A better understanding of the fundamentals and mechanism in pyrolysis is essential to achieve high yields of the targeted products.

In this study, the pyrolysis technique, which is one of the promising thermal approaches in converting biomass to energy, was used in order to investigate the basic thermal decomposition characteristics of switchgrass. For converting switchgrass to energy by pyrolysis, the thermal decomposition characteristics of switchgrass and the rate of production of components of the syngas should be qualified. The experimental instrument used in this study was the TGA-FTIR (Thermogravimetric Analyzer coupled with Fourier Transform Infrared) spectrometer system, which is one of the most common techniques used to study the primary reactions of thermal decomposition of solids (Basilakis et al., 2001; Yang et al., 2004; Marcilla et al., 2005).

Therefore, the primary objectives of this study were : 1) to determine the thermal decomposition characteristics of

switchgrass that has been subjected to pyrolysis under different operating conditions (heating rates) in TGA, 2) to investigate the real-time evolution of gases during the switchgrass pyrolysis using an integrated system of TGA- FTIR spectrometer.

## 2. MATERIALS AND METHODS

### A. Materials and Equipments

The switchgrass used in this study was collected from the E. V. Smith Experiment Station (Auburn University), Tallassee, Alabama. The switchgrass samples were ground in a hammer mill (New Holland grinder model 358, New Holland, Pa) using a 0.8 mm screen.

The TGA-FTIR instrument used in this experiment, as shown in Figure 1, consisted of a thermogravimetric analyzer (TGA: Pyris 1 TGA, PerkinElmer, USA) coupled with a fourier transform infrared (FTIR: 100 FT-IR, PerkinElmer, USA) spectrometer for the analysis of evolved gases. The TGA-FTIR method has been developed for the study of low heating rate pyrolysis of coal, but has also been found useful in other applications.

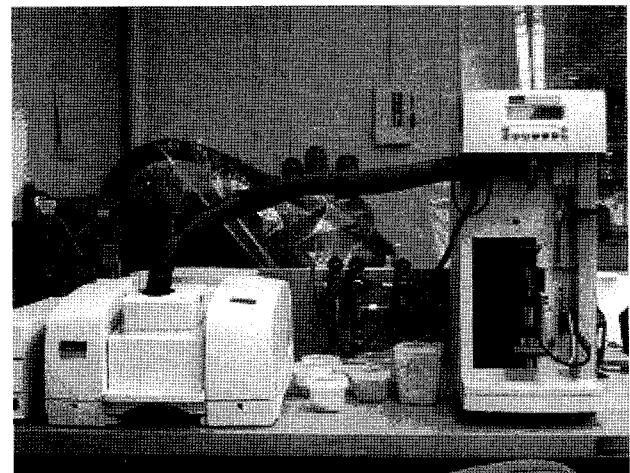


Fig. 1 Photo for TGA-FTIR instrument used in the experiment.

The TGA apparatus consists of a sample tray suspended from a balance and placed in a stream of nitrogen flowing within a furnace. As the sample is heated, the evolving volatile products are carried out of the furnace directly into a gas cell (heated to an internal temperature of 220°C) where the volatiles are analyzed by FTIR spectrometer. The maxi-

imum temperature of the furnace of TGA was 1000°C and the precision of the temperature measurement was 2°C.

Purified nitrogen gas at a constant flow rate of 20 mL/min was used as the carrier gas to provide an inert atmosphere for pyrolysis and remove the gaseous and condensable products, minimizing any secondary vapor-phase interactions.

Although the thermogravimetric analysis using TGA supplies important information in regard to the thermal decomposition characteristics of switchgrass, including the rate of pyrolysis, temperature range for degradation, etc., understanding of the gas species evolved during the pyrolysis is still limited. The gases evolved during the pyrolysis of switchgrass were investigated using the FTIR spectrometer. The system continuously monitors thermal decomposition (weight loss), temperature-dependent evolution of the gases, and weight of the non-volatile material (residue).

Table 1 indicated specifications of the TGA and the FTIR spectrometer used in this experiment.

**Table 1** Specifications for TGA and FTIR spectrometer

Item	Remarks
TGA (Thermogravimetric Analyzer)	Model : Pyris 1 (PerkinElmer, USA) Design : A vertical design with a high sensitivity balance and a quick response furnace Furnace : Temp. range; ambient to 1000°C Scanning rate; 0.1 to 200°C/min Temp. precision; ±2°C Balance : Sensitivity; 0.1 µg Accuracy; better than 0.02% Capacity; 1300 mg
FTIR spectrometer	Model : Spectrum 100 FTIR (PerkinElmer, USA) General : Sealed and desiccated optical unit Vibration isolated baseplate Wavelength range: 7800~350 cm <sup>-1</sup> Wavelength accuracy: Better than 0.1 cm <sup>-1</sup> at 1600 cm <sup>-1</sup>

## B. Experimental Methods

The pyrolysis of switchgrass was first conducted in a Pyris 1 TGA. To mitigate the difference of heat and mass transfer, the sample weight was kept at 5~6 mg from the results of pre-experiment. The sample was heated up to 900°C with constant heating rates of 10, 20, 30, and 40°C/min to identify the thermal decomposition characteristics of switchgrass by the different heating rates.

The gases released in the TGA were swept immediately to a gas cell, followed by the FTIR spectrometer analysis. The transfer line and gas cell were heated to an internal temperature of 220°C to avoid condensation or adsorption of semi-volatile products. Each IR spectrum was obtained in every 15 s to determine the evolution rate and composition of several gases, and the infrared scanning range was from 4000 to 700 cm<sup>-1</sup> of wavenumber. The distribution of gaseous products from pyrolysis was analyzed with respect to the changing of reaction temperatures, from 150°C to 900°C from the IR spectrum using Pyris software and reference spectra supplied by the FTIR instrument company.

The TGA curves (weight loss of the samples) were directly obtained from the instrument, while the DTG curves (derivative weight loss of the samples) were obtained by electronic differentiation of the weight signal, using Pyris software.

In order to analyze the thermal decomposition characteristics of switchgrass pyrolysis, the results of thermogravimetric experiments were expressed as a function of conversion of weight loss  $X$ , which was defined as following;

$$X = \frac{W_0 - W}{W_0 - W_\infty}$$

where  $W_0$  : initial weight of sample

$W$  : weight of the pyrolyzed sample

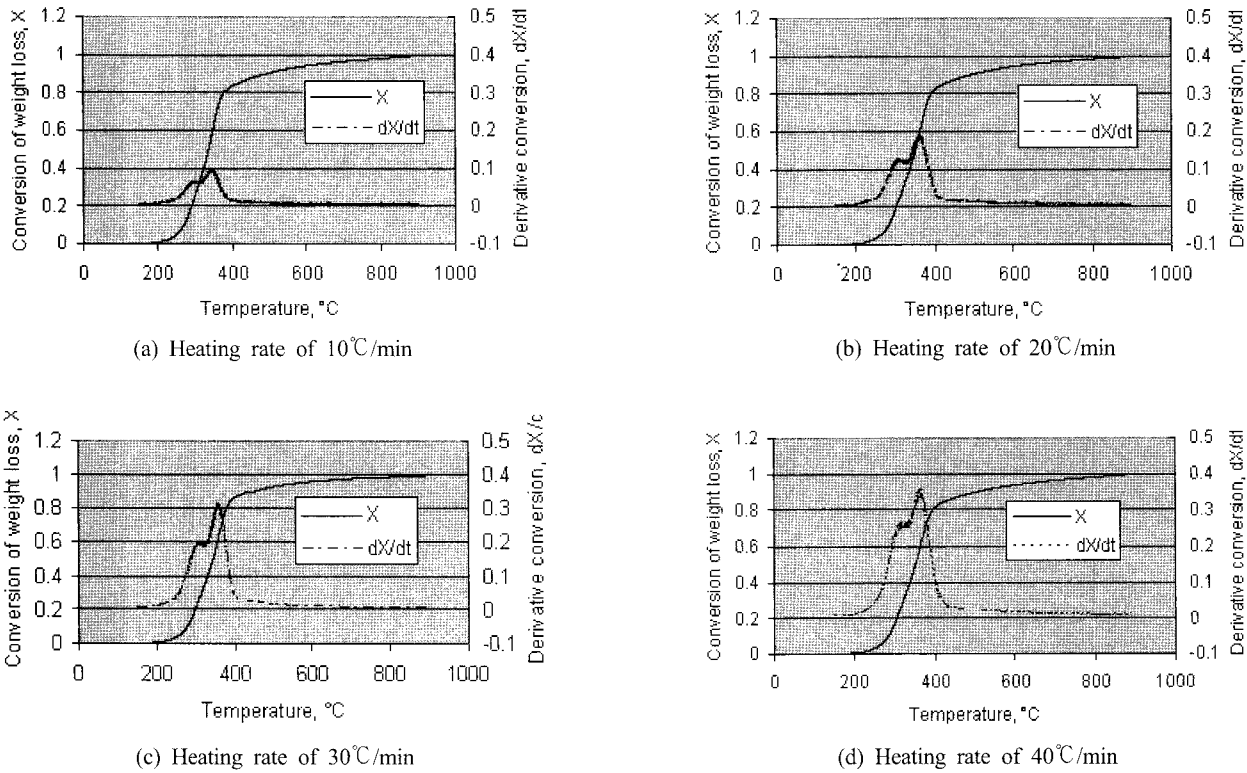
$W_\infty$  : final residual weight

And, the derivative conversion of weight loss,  $dX/dt$ , was obtained from differential thermogravimetric analysis (DTG).

## 3. RESULTS AND DISCUSSION

### A. Thermal Decomposition Characteristics for Switchgrass Pyrolysis

The conversion of weight loss ( $X$ ) and the derivative conversion ( $dX/dt$ ; DTG) profiles of switchgrass pyrolysis as a function of temperature were shown in Figure 2. Similar trends were represented with respect to the different heating rates. From the Figure 2, it could be observed that the thermal decomposition of switchgrass started at approximately 220°C, followed by a major loss of weight, where the main volatilization occurred, and the thermal decomposition was essentially completed at 430°C. The early minor



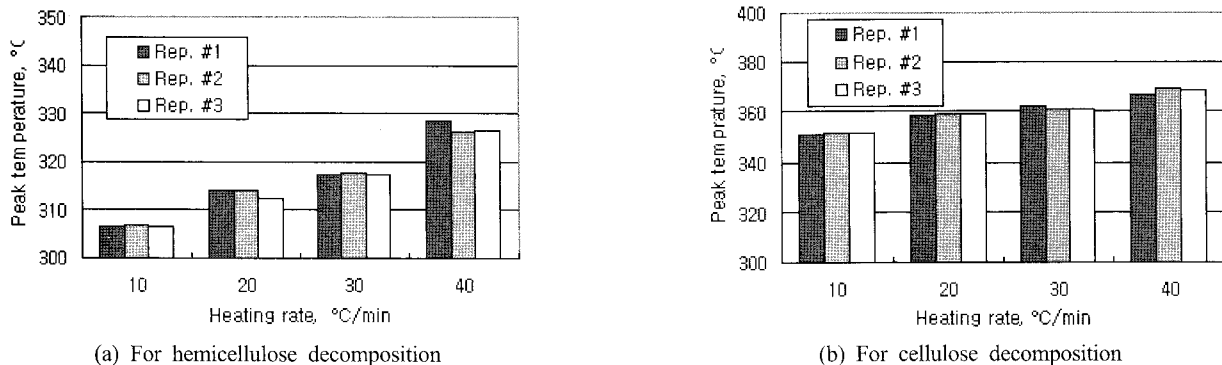
**Fig. 2** Weight loss and derivative conversion (DTG) by heating rates.

weight loss in the sample at temperatures lower than 220°C was attributed to evaporation of moisture.

In the faster step of conversion process, the DTG curves presented two overlapping peaks, producing a single peak with a shoulder located on the left as shown in Figure 2. Cellulose, hemicellulose, and lignin are the main components of lignocellulosic biomass including switchgrass. Usually, biomass materials contain 40-60% cellulose, 20-40% hemicellulose, and 10-25% lignin on a dry basis. According to research of Yang et al. (2007), hemicellulose decomposes in the range between 220 and 315°C, and cellulose decomposes in the range between 315 and 400°C. Thus, it could

be considered that the lower temperature shoulder represented the decomposition of hemicellulose and the higher temperature peak represented the decomposition of cellulose. The flat tailing section of the DTG curves at higher temperature corresponded to the decomposition of lignin. Therefore, the pyrolysis process was found to be composed of four stages; moisture evaporation, hemicellulose decomposition, cellulose decomposition, and lignin degradation.

For the thermal decomposition characteristics of switchgrass according to the different heating rates, as shown in Figure 2 and Figure 3, the peak temperatures for hemicellulose decomposition and cellulose decomposition were



**Fig. 3** Peak temperatures for hemicellulose and cellulose decomposition at different heating rates.

increased with greater heating rates as from 306 to 327°C, and from 351 to 369°C, respectively. As shown in Figure 3, the peak temperatures for hemicellulose decomposition were 306, 313, 317, and 327°C with heating rates of 10, 20, 30, and 40°C/min, respectively. And, those for cellulose decomposition were 351, 358, 362, and 369°C with heating rates of 10, 20, 30, and 40°C/min, respectively.

The peak heights of DTG curve were increased with greater heating rates as shown in Figure 4. This DTG peak height is directly proportional to the reactivity during pyrolysis. So, the pyrolysis of switchgrass showed more reactivity with the increase in heating rates.

The experiments were replicated three times to determine their reproducibility, which was found to be very good as shown in Figure 3.

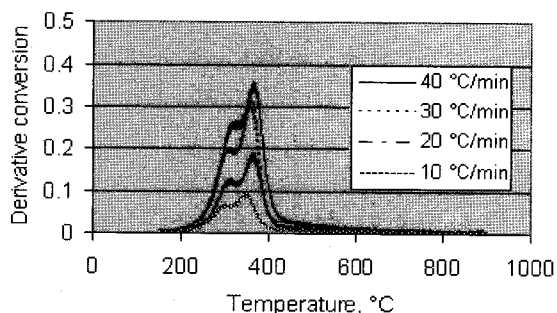


Fig. 4 Derivative conversion of weight loss (DTG) by heating rate.

## B. Fourier Transform Infrared Analysis for Gas Products

Generally, the following gas species evolve during the pyrolysis of most biomass: CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>O, NH<sub>3</sub>, HCN, SO<sub>2</sub>, and COS. The distribution of these gas products is dependent on the associated elements that are present in the sample (Yang et al., 2004).

According to the analysis of IR spectra for switchgrass pyrolysis obtained in every 15 s as a function of both wave-number and temperature, the main gas products of switchgrass were CO<sub>2</sub>, CO, CH<sub>4</sub>, NH<sub>3</sub>, COS, C<sub>2</sub>H<sub>4</sub>, and some acetic acid. The gas products began to release at approximately 220°C, and most gas species were released at low temperatures from 310 to 380°C, which was corresponding well with the observation of thermal decomposition in TGA, except for some CO<sub>2</sub> and CO evolving out at a higher temperature. According to the literature (Yang et al., 2007),

the releasing of CO<sub>2</sub> and CO from biomass pyrolysis was mostly contributed by hemicellulose at low temperature and by lignin at high temperature, while cellulose only contributed a small portion of it at low temperature.

The release of CO<sub>2</sub> and CH<sub>4</sub> first increased as the temperature increase and reached their maximum yields at around 330°C. However, as the temperature increased further, the evolution of methane is decreased sharply after its peak point. In regard to CO<sub>2</sub>, there was also a sharp decrease in its evolution to the temperature of about 390°C, but beyond that temperature, it started to increase slightly. CO has demonstrated performance similar to that of CO<sub>2</sub>, except its maximum evolution occurred at about 270°C. NH<sub>3</sub> has also demonstrated performance similar to that of CH<sub>4</sub>.

And the specific wave number of the IR absorbance peak of the main gas species evolved from switchgrass pyrolysis were observed as following; CO<sub>2</sub>: 2340 cm<sup>-1</sup>, CO: 2170 cm<sup>-1</sup>, CH<sub>4</sub>: 3020 cm<sup>-1</sup>, NH<sub>3</sub>: 1050 cm<sup>-1</sup>, COS: 2050 cm<sup>-1</sup>, C<sub>2</sub>H<sub>4</sub>: 950 cm<sup>-1</sup>.

This approach provides a rapid FTIR scan within seconds, which facilitates our research on the kinetics and gaseous species evolution. Determination of the evolution rate and modelling of the gas-product release process under various operating conditions will be studied in detail in our future study.

## 4. CONCLUSIONS

This study was conducted to investigate the pyrolysis characteristics of switchgrass using TGA-FIIR (Thermogravimetric analyzer coupled to a Fourier transform Infrared spectrometer). Switchgrass is a high yielding perennial grass that has been designated as a potential energy crop, because of its high energy value. Ground switchgrass were pyrolysed at different heating rates of 10, 20, 30, and 40°C/min in a TGA-FTIR instrument. The thermal decomposition characteristics of switchgrass were analyzed, and the gases that were volatilized during the duration of experiment were identified. The following conclusions could be summarized from this study.

- (1) The thermal decomposition of switchgrass started at approximately 220°C, followed by a major loss of weight, where the main volatilization occurred, and

the thermal decomposition was essentially completed at 430°C. The early minor weight loss in the sample at temperature lower than 220°C was attributed to evaporation of moisture.

- (2) The pyrolysis process for switchgrass was found to be composed of four stages; moisture evaporation, hemicellulose decomposition, cellulose decomposition, and lignin degradation.
- (3) The peak temperatures for hemicellulose decomposition (306 to 327°C) and for cellulose decomposition (351 to 369°C) increased with greater heating rates.
- (4) The main gas species released during the pyrolysis of switchgrass were CO<sub>2</sub>, CO, CH<sub>4</sub>, NH<sub>3</sub>, COS, C<sub>2</sub>H<sub>4</sub>, and some acetic acid.
- (5) The gas products began to release at approximately 220°C, and most gas species were released at low temperature from 310 to 380°C, which was corresponding well with the observation of thermal decomposition.

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