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TG-FTIR Analysis of Switchgrass Pyrolysis

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Abstract. *Switchgrass is a high yielding perennial grass that has been designated as a potential energy crop. One method of converting switchgrass to energy is by thermochemical conversion to syngas. This requires that the rate of thermal decomposition of switchgrass and the rate of production of components of the syngas be quantified. Ground switchgrass were pyrolysed at heating rates of 10C/min to 40C/min in a thermogravimetric analyzer coupled to a Fourier transform infrared spectrometer. The amount of gases (ppm) that were volatilized during the duration of experiment were quantified. The pyrolysis process was found to compose of four stages: moisture evaporation, hemicellulose decomposition, cellulose decomposition and lignin degradation. The peak temperature for hemicellulose (288C to 315C) and cellulose degradation (340C to 369C) increased with heating rate. FTIR analysis showed that the following gases were given off during the pyrolysis of switchgrass: carbon dioxide, carbon monoxide, acetic acid, ethanol, and methane.*

Keywords: thermochemical conversion, gasification, pyrolysis kinetics

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Introduction

Switchgrass (*Panicum virgatum*) is a high yielding perennial grass species that is native to North America. The crop has been designated as an energy crop by the US Department of Energy because of its high biomass production from which renewable sources of fuel and electricity can be generated (Missaoui et al., 2005; McLaughlin and Kszos, 2005), and because it has excellent conservation attributes and has good compatibility with conventional farming practices (McLaughlin et al., 1999).

Pyrolysis is one of the promising thermal approaches in converting biomass to energy (Yang et al., 2004). It is the first step in the thermochemical conversion of biomass materials to bioenergy. The pyrolysis process is highly complex and depends on several factors such as biomass composition and heating rate (Rao and Sharma, 1998). Thermogravimetric (TG) analysis is the preferred technique for obtaining thermal events and quantifying thermal decomposition kinetics during pyrolysis. This is because of the relative ease and straightforward manner for obtaining mass loss data (Vamvuka et al., 2003; Vuthaluru, 2003), that is needed for determination of pyrolysis kinetics. Knowledge of the pyrolysis kinetics during the thermal decomposition of biomass materials is needed for the design, operation and control of thermochemical conversion units such as gasifiers and pyrolysis reactors (Miranda et al., 2007).

Most of previous investigations on biomass pyrolysis have focused on mass loss rate as a function of various parameters such as heating rate and sample size. However, the real time analysis of gas release during course of pyrolysis is rarely studied. Information on the type, quantity and time of release of a gas product is essential to complete understanding of the fundamentals of and mechanism involved in pyrolysis of biomass. Gases that are generally evolved during pyrolysis of organics and bio-polymers such as biomass are methane (CH₄), ethane (C₂H₄), carbon dioxide (CO₂), carbon monoxide (CO), ammonia (NH₃), hydrocyanic acid (HCN), sulfur dioxide (SO₂) and carbonyl sulfide (COS) (Bassilakis et al., 2001). Fang et al (2006) found that the following gas products that were obtained from thermal decomposition of different species of wood (merbau, cotton straw, birch and red sandal) – CO₂, CO, H₂O, CH₄, acetic acid (CH₃COOH) and methanol (CH₃OH).

The objectives of this study were to (a) determine the rate and kinetics of thermal decomposition of switchgrass, and (b) quantify the composition of gas evolved during the thermal pyrolysis process.

Materials and Methods

The switchgrass used in this study was collected from the E.V. Smith Experiment Station (Auburn University), Tallassee, Alabama. Before use, switchgrass sample was ground to pass a 40 mesh screen using a Wiley mill. Pyrolysis of the ground sample was carried out in a Pyris 1 TGA - thermogravimetric analyzer (Perkin-Elmer, Shelton, CT). A sample mass of 5 mg was used for the thermogravimetric analysis at heating rates of 10, 20, 30 and 40 C/min. Nitrogen was used a carrier gas at a flow rate of 20 ml/min. The samples were heated from 25°C to 800°C.

A Fourier Transform infrared (FTIR) spectrometer (Model 100, Perkin-Elmer, To prevent condensation of the less volatile gases, the transfer line between the TGA and FTIR, and the gas measurement cell were maintained at 493 K (Marcilla et al., 2005). Shelton, CT) coupled to

the TGA was used to analyze the gases evolved from the TGA. The software provided by the FTIR spectrometer manufacturer was used to obtain spectra of the gas flowing through the measurement cell every 20 s. Quantitative analysis of the series of spectra was then carried out by (a) matching the spectra against those from the library search of a software (QASOFT, Infrared Analysis, Inc., Anaheim, CA) thereby identifying the constituent of the gas at each spectra, and (b) using the software to quantify the concentration of the identified gases.

Results and Discussion

Pyrolysis study

Observed thermal behavior (TG curve) of switchgrass during pyrolysis is shown in Fig. 1. For each heating rate, the percent mass loss rate initially decreased by about 5% between 30°C and 150°C due to the release of moisture in the samples. The thermal decomposition of the samples was therefore deemed to have started at 150°C. The figure also shows that a significant loss of sample mass (60% of original weight) occurred within the temperature range of 150°C and 350°C, and that thermal decomposition is essentially complete at 550°C with a residual content of 20% of original weight. In general, there was a slight increase in mass loss rate with increase in heating rate within the temperature range of 150C and 350C. Similar trends in mass loss rates with heating rates were reported by Hu et al. (2007) for cellulose and by Miranda et al (2007) for textile wastes. Possible cause of this response of biomass during pyrolysis to different heating rates has been attributed to increased thermal lag at higher heating rates (Yang et al., 2004; Gronli et al., 1999). However, there was not a substantial effect of heating rate on the values of the thermal kinetic parameters (see next section), thus indicating that thermal lag was not significant in this study.

Figure 2 shows the mass loss rate curves (derivative thermograms – DTG curves) for switchgrass within the temperature range (150 to 800C) at which thermal decomposition of the samples occurred. The mass loss rate (α) was obtained as follows:

$$\alpha = \frac{m - m_o}{m_f - m_o} \quad (1)$$

There was an obvious effect of heating rate on the thermograms of switchgrass. As typically found in biomass thermogravimetric studies, all the thermograms produced two overlapping peaks – a single peak and a shoulder peak on the left of the single peak (Tsamba et al., 2006; Sorum et al., 2001). Based on studies that have been carried on biomass feedstocks, the shoulder at the left side corresponds to hemicellulose decomposition while the higher temperature peak represents the degradation of cellulose (Tsamba et al., 2006; Vamvuka et al., 2003). The flat tailing section of the DTG curves at higher temperatures corresponds to the decomposition of lignin, the pyrolysis of which is known to occur in a wide temperature range (Vamvuka et al., 2003; Gronli et al., 1999).

The temperature at which highest mass loss rate increased from 350C at heating rate of 10C/min to 372C at heating rate of 40C/min. The values of the mass loss rates are within the range that have been obtained for other biomass wastes (olive kernel, forest residue, cotton

residue – Vamvuka et al., 2003; coconut and cashew nut shells – Tsamba et al., 2006; rice husk and cotton straw – Hu et al., 2007).

Pyrolysis kinetics

As described in the previous section, the DTG curves of biomass frequently contain shoulders and/or tailing. This is an indication that more than one reaction occur during biomass pyrolysis, thus resulting in partially overlapping peaks (Hu et al., 2007). Mathematical models are typically used for the deconvolution of these overlapping peaks in the DTG curves. Most authors that have studied the kinetics of biomass pyrolysis have assumed three parallel independent reactions, with each reaction corresponding to the decomposition of the constituent pseudo-components hemicellulose, cellulose and lignin (Varhegyi, 2007; Vamvuka et al., 2003). The pyrolysis rate for three independent reactions is described as follows:

$$\frac{d\alpha}{dt} = \sum_{i=1}^3 c_i \frac{d\alpha_i}{dt} \quad (2)$$

where c_i is the relative contribution of the partial processes to the overall mass loss.

The separate conversion α_i for each component is given by:

$$\alpha_i = \frac{m_i - m_{o,i}}{m_{f,i} - m_{o,i}} \quad (3)$$

where $m_{o,i}$, m_i and $m_{f,i}$ are the initial sample mass, the actual sample mass and the final yield of component i , respectively. The components are all assumed to decompose individually according to the n th order reaction equation:

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right) (1 - \alpha_i)^{n_i} \quad (4)$$

where A_i , E_i , R and n_i denote the frequency factor, activation energy, gas constant and reaction order respectively.

The ForK (Formal Kinetic Models) software, developed by ChemInform SaintPetersburg (CISP) Ltd, was used to estimate the kinetic parameters from the above set of equations. This involved the use of Runge-Kutta numerical integration scheme and non-linear optimization. The values of the estimated parameters for switchgrass at heating rates of 10C/min to 40C/min are given in Table 1. Figure 3 shows that the pyrolysis of switchgrass is well described by the three independent n th order parallel reactions model as seen by the good fit of predicted to experimental data for switchgrass pyrolyzed at heating rate of 20C/min. Similar fits were obtained for all the other samples. The first pseudo-component corresponded to hemicellulose, which was reactive at temperatures between 180C and 360C, the second component

corresponded to the cellulose fraction that decomposed between 250 and 440°C while the third component was for lignin that decomposed within a broad temperature range of 150 and 800°C. For all the heating rates, cellulose and lignin had the highest and lowest activation energies respectively (138 to 146 kJ/mol for cellulose, 38 to 43 kJ/mol for lignin). These values are within the range that has been reported for biomass samples (Vamuka et al., 2003b; Sorum et al., 2001, Hu et al., 2007). Increasing heating rate increased the values of the parameters for hemicellulose decomposition. There does not seem to be any effect of heating rate on the parameters for cellulose and lignin decomposition.

FTIR Analysis of Gas Products

Figure 4 shows a typical three-dimensional plot of the spectral obtained from the gas evolved during the pyrolysis of switchgrass. The main gases identified from the spectra were carbon dioxide, carbon monoxide, acetic acid and ethanol (Figure 5). Low concentrations of the following gases were also identified: methane, carbonyl sulfide and methyl isocyanate and isocyanic acid (Figure 6). These gases are typically obtained from the pyrolysis of biomass (Yang et al., 2004; Bassilakis et al., 2001; Baker, et al., 2005).

At any temperature, the concentration of the main gaseous products increased with increase in heating rate (Figure 5). In addition, the peak concentrations for ethanol, acetic acid and carbon dioxide were found to correspond to and confirm the mass loss rate peaks (during decomposition of hemicellulose and cellulose) that were obtained from the thermogravimetry aspect of this study. The shoulder peak for carbon monoxide was not evident.

Beyond the cellulose decomposition region (sometimes called the char combustion region, Baker et al, 2005), the concentration of CO and CO₂ increased with pyrolysis temperature. In addition, there was no significant production of other small molecular organic compounds. Similar trend was obtained by Baker et al. (2005). The rise in concentrations of CO and CO₂ was attributed to the oxidation of the carbonized substrate (char) and to the high-temperature reaction that is shown below:



The total volume (ml) of the major gaseous products produced over the duration of the experiment was obtained as follows:

$$V = \frac{10^{-6} IF}{60} \quad (5)$$

where I is the value obtained by integrating the concentration-time curve (using Simpson's rule) and F is the flow rate of nitrogen carrier gas through the infrared spectrometer (20 ml/min). Results obtained indicate that heating rate did not significantly affect the total amount of the major gaseous products and the total amount of gaseous products obtained (Table 2).

Conclusions

The following conclusions can be drawn from this study:

- Thermal decomposition of switchgrass occurred within temperatures of 150C and 550C. Beyond 550C, there was only a slight change in mass loss.
- Mass loss rate increased with increase in heating rate with the highest mass loss rate occurring at temperatures of 350C to 372C
- Pyrolysis kinetics indicate that decomposition of the three main components of switchgrass (cellulose, hemicelluloses and lignin) occur at different temperature ranges
- The major gases evolved during switchgrass pyrolysis were acetic acid, carbon monoxide, carbon dioxide and ethanol
- Heating rate did not affect the total amount of gases evolved

References

- Baker, R.R., Coburn, S., Liu, C. and Tetteh, J. 2005. Pyrolysis of saccharide tobacco ingredients: a TGA-FTIR investigation. *J. Anal. Appl. Pyrolysis* 74: 171-180.
- Bassilakis, R., Carangelo, R.M. and Wojtowicz, M.A. 2001. TG-FTIR analysis of biomass pyrolysis. *Fuel* 80: 1765-1786.
- Fang, M.X., Shen, D.K., Li, Y.X., Yu, C.J., Luo, Z.Y. and Cen, K.F. 2006. Kinetic study on pyrolysis and combustion of wood under different oxygen concentrations by using TG-FTIR analysis. *J. Anal. Appl. Pyrolysis* 77: 22-27.
- Gronli, M., Antal, M.J. and Varhegyi, G. 1999. A round-robin study of cellulose pyrolysis kinetics by thermogravimetry. *Ind. Eng. Chem. Res.* 38: 2238-2244.
- Hu, S., Jess, A. and Xu, M. 2007. Kinetic study of Chinese biomass slow pyrolysis: comparison of different kinetic models. *Fuel* 86: 2778-2788.
- Marcilla, A., Gomez, A. and Menargues, S. 2005. TG/FTIR study of the thermal pyrolysis of EVA copolymers. *J. Anal. Appl. Pyrolysis* 74: 224-230.
- McLaughlin, S.B. and L.A. Kszos. 2005. Development of switchgrass (*Panicum virgatum*) as a bioenergy feedstock in the United States. *Biomass and Bioenergy* 28: 515-535.
- McLaughlin, S.B., J. Bouton, D. Bransby, B. Conger, W. Ocumpaugh, D. Parrish, C. Taliaferro, K. Vogel, and S. Wullschleger. 1999. Developing switchgrass as a bioenergy crop. In: *Perspectives on New Crops and New Uses*. Janick J (ed.). Alexandria, VA: ASHS Press, p. 282–299.
- Miranda, R., Sosa_Blanco, C., Bustos-Martinez, D. and Vasile, C. 2007. Pyrolysis of textile wastes I. Kinetics and yields. *J. Anal. Appl. Pyrolysis* 80: 489-495.
- Missaoui, A.M., Fasoula, V.A. and Bouton, J.H. 2005. The effect of low plant density on response to selection for biomass production in switchgrass. *Euphytica* 142: 1-12.
- Rao, R.T. and Sharma, A. 1997. Pyrolysis rates of biomass materials. *Energy* 23: 973-978.
- Sorum, L., Gronli, M.G. and Hustad, J.E. 2001. Pyrolysis characteristics and kinetics of municipal solid wastes. *Fuel* 80: 1217-1227.
- Tsamba, A.J., Yang, W., Blasiak, W. 2006. Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. *Fuel Processing Technology* 87: 523-530.
- Vamvuka, D., Pasadakis, N., Kastanaki, E., Grammelis, P. and Kakaras, E. 2003b. Kinetic modeling of coal/agricultural by-product blends. *Energy and Fuels* 17: 549-558.
- Vamvuka, D., Kakaras, E., Kastanaki, E. and Grammelis, P. 2003a. Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. *Fuel* 82: 1949-1960.

- Varhegyi, G. 2007. Aims and methods in non-isothermal reaction kinetics. J. Anal. Appl. Pyrolysis 79: 278-288.
- Vuthaluru, H.B. 2003. Thermal behavior of coal/biomass blends during co-pyrolysis. Fuel Processing Technology 85: 141-155.
- Yang, H., Yan, R., Chin, T., Liang, D.L., Chen, H. and Zheng, C. 2004. Thermogravimetric analysis – fourier transform infrared analysis of palm oil waste pyrolysis. Energy and Fuels 18: 1814-1821.

Table 1: Estimate of parameters of the three independent nth order parallel reactions (Eqns. 2 to 4).

	10C/min	20C/min	30C/min	40C/min
Ln A ₁	22.059	23.598	25.117	24.854
E ₁ (kJ/mol)	126.467	133.120	137.688	137.231
n ₁	0.902	0.949	0.984	1.008
c ₁ (%)	18.187	19.518	19.940	20.504
Ln A ₂	21.795	22.304	23.974	22.953
E ₂ (kJ/mol)	138.576	140.528	145.982	141.546
n ₂	1.111	1.060	0.987	1.059
c ₂ (%)	49.730	49.168	49.525	49.717
Ln A ₃	1.944	2.058	2.298	2.279
E ₃ (kJ/mol)	42.616	40.796	39.084	38.795
n ₃	2.650	2.623	2.359	2.533
c ₃ (%)	33.083	32.844	31.731	31.312
R ²	0.999	0.999	0.999	0.999
s.e.*	0.00154	0.00612	0.0149	0.0228

*R² is the coefficient of determination. An R² of 1 indicate a perfect fit. s.e. is standard error of estimate – the average deviation between experimental and fitted data. The lower the s.e., the better the fit.

Table 2. Effect of heating rate on the concentration (mL) of gases produced during the pyrolysis of switchgrass.

Gas type	10C/min	20C/min	30C/min	40C/min
Carbon dioxide	0.0257	0.0213	0.0131	0.0056
Carbon monoxide	0.0478	0.0425	0.0498	0.0483
Isocyanic acid	0.0015	0.0005	0.0037	0.0019
Carbonyl sulfide	0.0028	0.0022	0.0021	0.0022
Acetic acid	0.0197	0.0227	0.0222	0.0203
Methane	0.0015	0.0022	0.0028	0.0024
Ethylene	0.0001	0.0007	0.0002	0.0004
Ammonia	0.0011	0.0007	0.0007	0.0004
Hydrogen cyanide	0.0002	0.0004	0.0005	0.0014
Methyl isocyanate	0.0008	0.0023	0.0021	0.0012
Ethanol	0.0219	0.0286	0.0250	0.0241
TOTAL	0.1239	0.1244	0.1224	0.1086

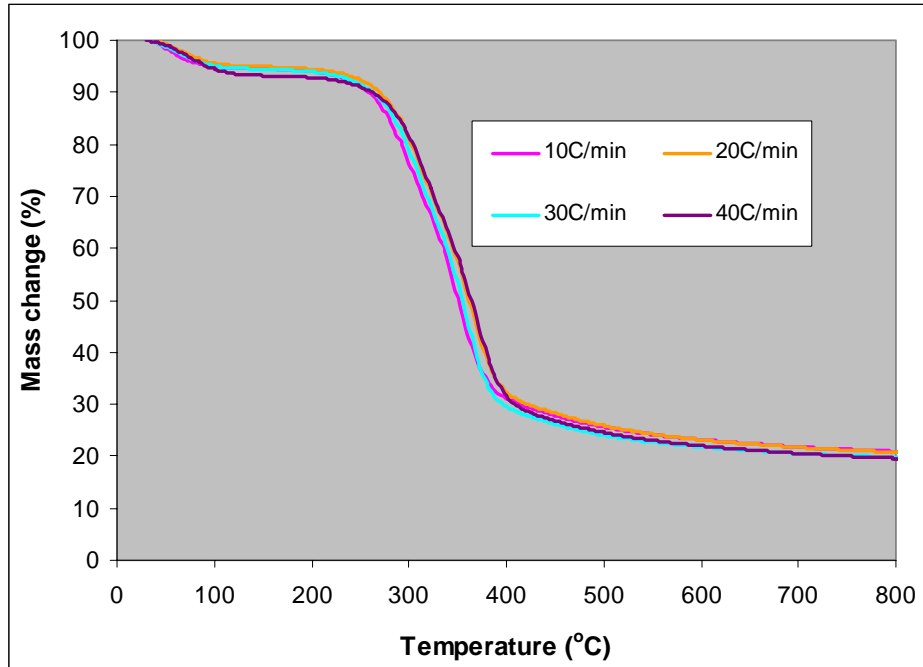


Figure 1. Mass loss from thermal decomposition of switchgrass at different heating rates.

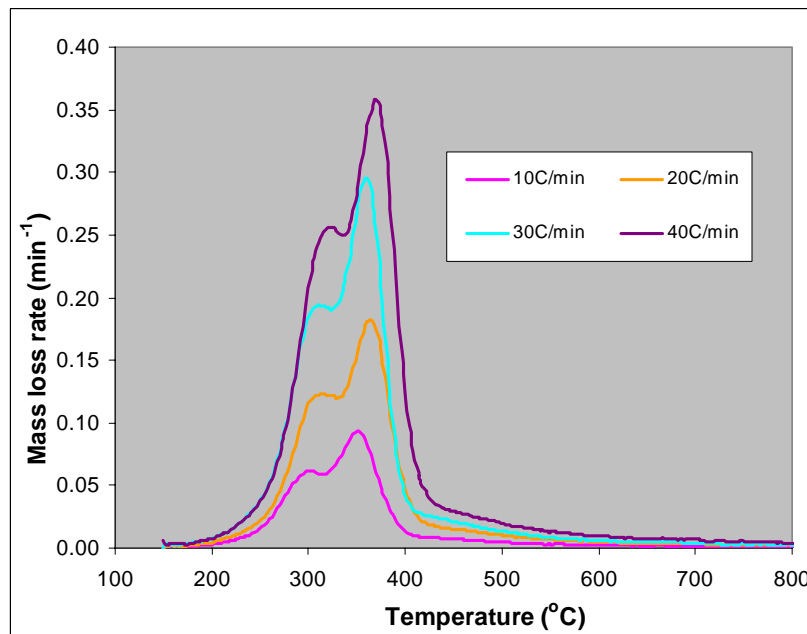


Figure 2. Mass loss rate from the thermal decomposition of switchgrass at different heating rates.

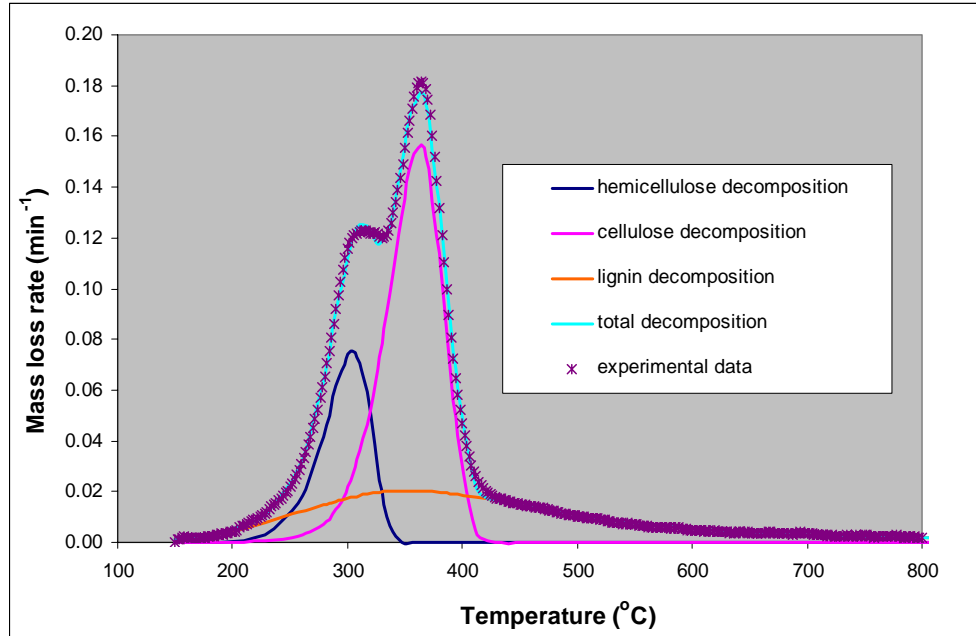


Figure 3. Prediction of the decomposition of hemicelluloses, cellulose and lignin components of switchgrass at heating rate of 20C/min.

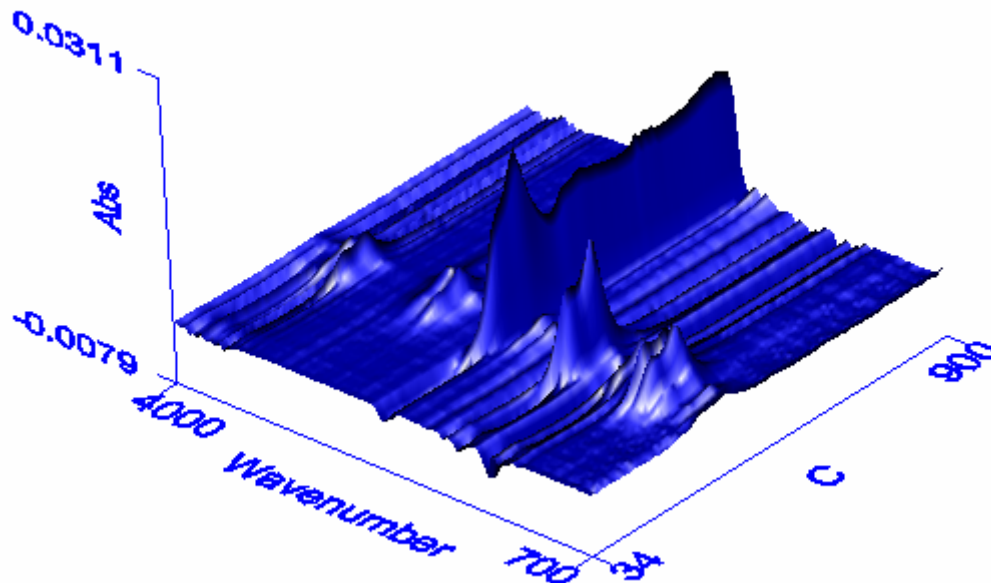


Figure 4. Three dimensional spectral plot of gases produced from pyrolysis of switchgrass at heating rate of 20 C/min.

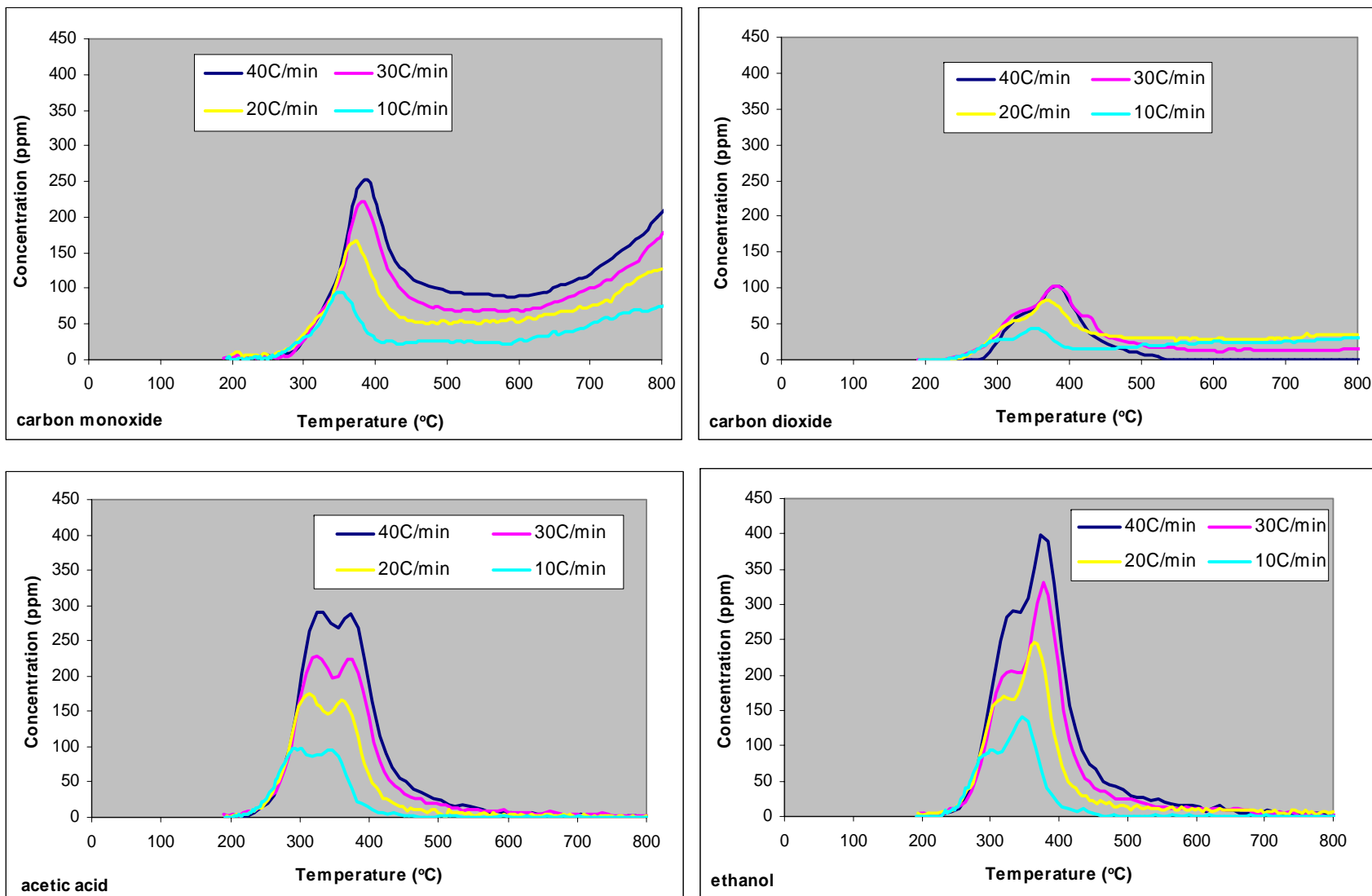


Figure 5: Concentration of the major gases evolved during pyrolysis of switchgrass at heating rates of 10C/min to 40C/min.

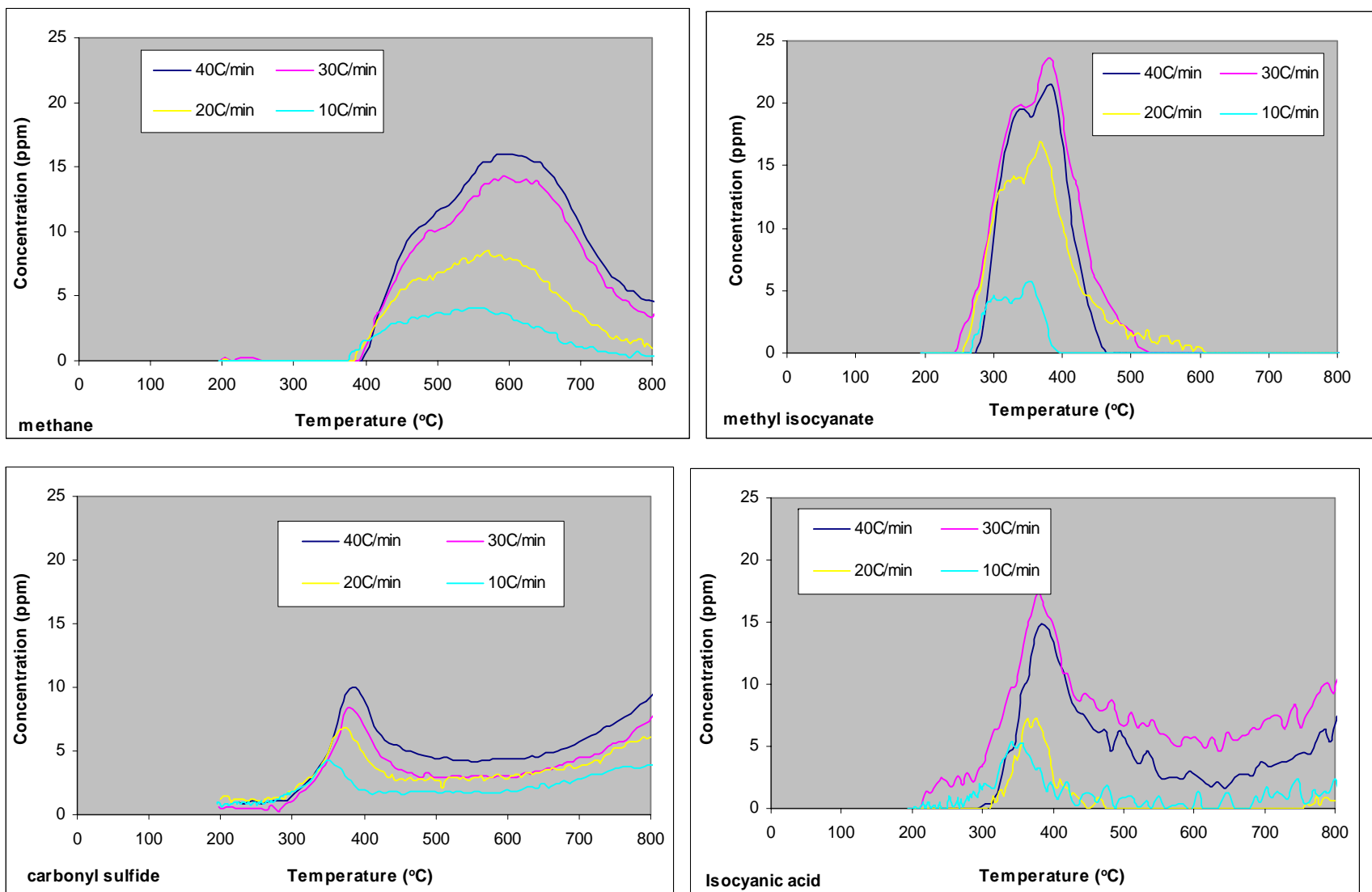


Figure 6. Concentration of minor gases evolved during pyrolysis of switchgrass at heating rates of 10C/min to 40 C/min.