

STUDY ON PYROLYSIS OF SAWDUST UNDER DIFFERENT HEATING RATES BY USING TG-FTIR ANALYSIS

XIAOLI GU, CHENG LIU, HENG YIN, XUEWEI MENG, KANGHUA CHENG, MING HE
ZHONGZHENG LI
NANJING FORESTRY UNIVERSITY, COLLEGE OF CHEMICAL ENGINEERING
MOBILE STATION FOR POST-DOCTORAL IN FORESTRY ENGINEERING
NANJING, CHINA

(RECEIVED OCTOBER 2011)

ABSTRACT

Pyrolysis of certain sawdust was studied using thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR). Different heating rates of 20°C.min⁻¹, 40°C.min⁻¹ and 80°C.min⁻¹ were applied with final temperature of 950°C. A total loss weight of 78 %, 79 % and 83 % was observed respectively, and the temperature trend of evolving gaseous products, such as CH₄, H₂O, CO and CO₂ was investigated. The pyrolysis of 20°C.min⁻¹ turned out to be the most concentrative, followed by 40°C.min⁻¹ and 80°C.min⁻¹. There are several differences in yield among different heating rates. However, the study in this paper is essential for sawdust pyrolysis model and the TG-FTIR approach is potential to provide valuable inputs for predictive modeling of sawdust pyrolysis. More studies are needed to get the kinetic parameters and pyrolysis models that can predict yields and evolution patterns of selected volatile products for Computational Fluid Dynamics (CFD) applications.

KEYWORDS: Sawdust, pyrolysis, TG-FTIR analysis.

INTRODUCTION

Pyrolysis is one of the promising thermal approaches that can be used to convert biomass into energy (Yang et al. 2004). It plays an important role 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). Few detailed pyrolysis information that can predict product specification and yields on sawdust pyrolysis was found in the available literature. The lack of data leads to difficulties in understanding emission behavior of sawdust during the thermal treatment process.

TG is used widely in thermal analysis and kinetics parameters under both nitrogen and air atmosphere (Osvalda 2007, Liou 2003, Bingham et al. 2005, Font et al. 2005). For pyrolysis,

different heating rates are carried out to obtain the kinetic model. But the composition of evolved gas in each weight loss steps cannot be observed only by using TG. On the other hand, Fourier transform infrared spectroscopy (FTIR) results can be used to evaluate the functional groups and provide plenty of information on mixed gases. This can be used for identification of mixture composition, as well as quantification of CO₂, CO, H₂O and CH₄, etc. (Becidan et al. 2007, Li et al. 2001).

TG combining with FTIR is a useful tool in dynamic analysis as it monitors continuously both the time dependent evolution of the gases and the weight of the non-volatile materials (residue). It has already been used widely to investigate biomass pyrolysis (Basilakis et al. 2001) and polymer thermal degradation (Herrera et al. 2001). But very limited kinetics studies were conducted with TG-FTIR on sawdust.

The aim of the present work is to make a systematic investigation of the sawdust pyrolysis using dynamic TG techniques. In this study, volatile products from TG during TG-FTIR experiment were swept into gas cell immediately by carrier-gas so that secondary reactions were minimized. At the same time, 3D spectrums that reflect the effect of time and wavenumber with different heating rates were generated by Nicolet spectrometer. The result of weight loss and composition of evolved gases obtained through the study, provide plentiful information to understand the pyrolysis characteristics of sawdust.

MATERIAL AND METHODS

Proximate analysis (moisture, ash, volatile content and fixed carbon of sawdust residue sample) and ultimate analysis of the combustible fraction (in weight-by-weight percentage) are shown in Tab. 1. After being dried in an oven at 105°C for 3 h, the original materials were crushed and pulverized to a size of <0.2 mm before they were analyzed.

Tab. 1: Proximate and ultimate analysis of material.

	Proximate analysis				Ultimate analysis			
	Moisture	Ash	Volatile	Fixed carbon	C	H	O	N
Concentration (wt %)	11.26	0.61	75.32	12.81	50.02	5.54	44.40	0.04

A Bruker Vector 22 spectrometer and a Setsys Eolution TG92 thermo analyzer are coupled by a Thermo-Nicolet TGA special connector; the stainless steel transfer pipe and gas cell (20 cm optical path length) are heated at 180°C to minimize secondary reactors. Nitrogen is used as carrier gas with a flow rate of 100 ml.min⁻¹ for both TGA and spectrometer. Resolution in FTIR was set as 1.cm⁻¹, number of scans per spectrum was set as 4 times.min⁻¹ and the spectral region was set as 400-600.cm⁻¹.

A certain heating rate (20-80°C.min⁻¹) was applied, with a final temperature of 900°C. To FTIR, a weight loss about 10 mg usually gives adequate signal, so approximately 15 mg of samples was used in this study. Medium-sized crucible of 70 µl made of Al₂O₃ was adopted as the sample container.

RESULTS AND DISCUSSION

TG and DTG analysis

TG and DTG curves with different heating rates were shown in Fig. 1a, b. For sawdust, the DTG curve exhibits a single peak at about 300-350°C. The weight loss start temperature (T_s , pyrolysis rate $>2\% \cdot \text{min}^{-1}$) is $T_{s,20^\circ\text{C}\cdot\text{min}^{-1}} > T_{s,40^\circ\text{C}\cdot\text{min}^{-1}} > T_{s,80^\circ\text{C}\cdot\text{min}^{-1}}$. The weight loss finish temperature (T_f , pyrolysis rate $<2\% \cdot \text{min}^{-1}$) is $T_{f,20^\circ\text{C}\cdot\text{min}^{-1}} < T_{f,40^\circ\text{C}\cdot\text{min}^{-1}} < T_{f,80^\circ\text{C}\cdot\text{min}^{-1}}$. So the temperature range ($\Delta T = T_f - T_s$) for thermal decomposition is: $\Delta T_{20^\circ\text{C}\cdot\text{min}^{-1}} < \Delta T_{40^\circ\text{C}\cdot\text{min}^{-1}} < \Delta T_{80^\circ\text{C}\cdot\text{min}^{-1}}$. It indicates that the pyrolysis of sawdust is more concentrative with slower heating rate. And a total loss weight of 78.2 %, 79.1 % and 82.5 % was observed respectively.

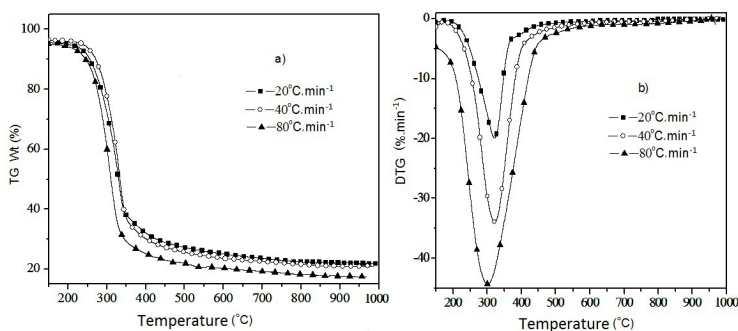


Fig. 1: Curve of TG a) and DT b) for sawdust at different heating rates.

It was shown that the intensity of pyrolysis (reaction) and the gas production rate are both reduced at lower heating rates and a slower sensitivity of the infrared detector will result from dilution effects by the carrier gas. On the other hand, a too high heating rate will cause heat transfer control and incomplete thermal degradation at the inner of the sample. Thus, $20^\circ\text{C}\cdot\text{min}^{-1}$ was chosen as optimal heating rate.

As seen from Fig. 1, the pyrolysis process can be subdivided into three stages. The first is a loss in weight upon drying the sample (below 200°C), and mainly moisture is released at this stage. The second stage is fast thermal decomposition between 200°C and 350°C ; weight loss occurs mainly in this temperature range. The maximum of the DTG curve (weight loss rate) is attained at about 320°C . The last stage is high temperature charring of the residue; the weight loss is much smaller. Still, there remains little residue at 950°C , i.e., about 20 wt % of original weight.

Tab. 2 summarizes the temperature of start pyrolysis (T_s), finish pyrolysis (T_f), maximum pyrolysis rate (T_{max}) and the char residual content at 900°C . From all tested samples, a lateral shift can be noticed in the thermograms towards higher temperatures. This is explained with the occurrence of an increased thermal lag as the heating rate increases (Raman et al. 1981). In general, heating rate does not have a significant influence on pyrolysis parameters and gas yields don't show major changes within the measured range.

FTIR analysis

Infrared spectrum is often used to distinguish various inorganic and organic compounds for pyrolysis. The 3D infrared spectrum of evolution gases includes information of infrared absorbance, wavenumber and temperature. Based on infrared spectrum, the change of spectral intensity along time direction is similar to TG results. But the temperature at the spectral intensity peak is decided by TG because there are several seconds delay from TG to FTIR.

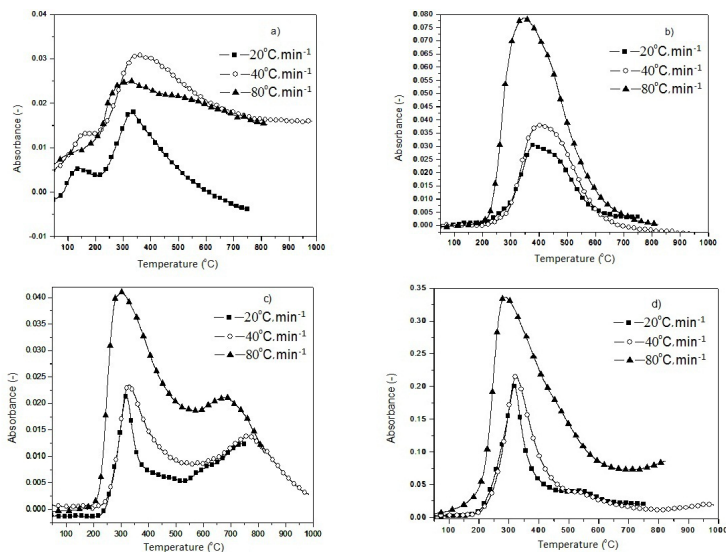
Tab. 2: Temperature of sawdust pyrolysis and residue as functions of different heating rates.

	Heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)		
	20	40	80
T_s ($^{\circ}\text{C}$)	226.0	209.0	198.7
T_f ($^{\circ}\text{C}$)	413.1	461.7	521.8
T_{\max} ($^{\circ}\text{C}$)	321.2	321.9	301.8
(dY/dT) ($\% \cdot ^{\circ}\text{C}^{-1}$)	-19.884	-33.860	-44.323
Residue at 900°C (wt %)	21.96	20.88	17.46
Loss weight at 900°C (wt %)	78.04	79.12	82.54

After evolved gases from TG were swept into the gas cell, absorbance information at different wavenumber and different time can be obtained by Fourier transform. When the time is fixed, absorbance information at different wavenumber can be obtained under this wavenumber to analyze the certain component as a function of time.

Some evolved volatile products of sawdust pyrolysis at first DTG peak with different heating rates are shown in Fig. 2. The typical spectra of evolved gases from the sawdust are given in Fig. 3 with some certain temperatures at the heating rate of $20^{\circ}\text{C}\cdot\text{min}^{-1}$.

Fig. 2 shows that the main gas products are identified as follows: CO_2 , CO , H_2O and CH_4 , combined with the 3D spectrum. Fig. 2 shows that H_2O (bands of $4000\text{--}3400\cdot\text{cm}^{-1}$ and $2000\text{--}1270\cdot\text{cm}^{-1}$) and a little of CO (band of $2250\text{--}2000\cdot\text{cm}^{-1}$) release at the DTG peak temperature, abundant CO_2 (band of $2400\text{--}2250\cdot\text{cm}^{-1}$ and $780\text{--}600\cdot\text{cm}^{-1}$) and small amounts of CH_4 (band of $3100\text{--}2800\cdot\text{cm}^{-1}$) evolve $20^{\circ}\text{C}\cdot\text{min}^{-1}$ and $40^{\circ}\text{C}\cdot\text{min}^{-1}$ are similar in gas products distribution. But for $80^{\circ}\text{C}\cdot\text{min}^{-1}$, the appreciate amount of CO_2 was found. Because the evolved gas could be swept into the gas cell immediately after it is formed, the slower the heating rate selected, the higher the sensitivity expected.

Fig. 2: TG-FTIR pyrolysis gas product evolution pattern a) H_2O , b) CH_4 , c) CO , d) CO_2 for sawdust.

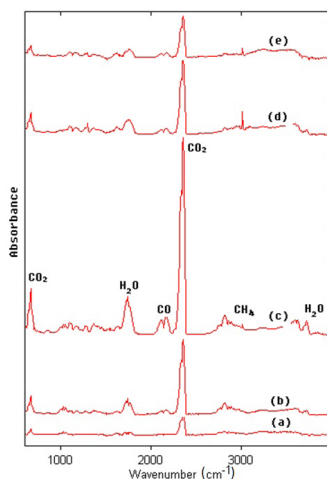


Fig. 3: FTIR spectrum for pyrolysis products evolving from the sawdust sample at different temperatures a)250°C, b)300°C, c)DTG peak $T_{max} = 321.2^{\circ}\text{C}$, d)500°C, e)700°C.

Fig. 3 presents the spectra of the sawdust with $20^{\circ}\text{C}\cdot\text{min}^{-1}$. When the temperature increases, CO_2 production is observed from the FTIR analysis. It was indicated that H_2O and CO_2 are released at the start of experiment up to 250°C , then a large amount of CO and CH_4 evolve at 320°C DTG peak temperature. At the same time, CO_2 decreases and CH_4 increases until 500°C . At 700°C , the dominate component is CO_2 . The gas products from pyrolysis of biomass materials were investigated (Fairbridge et al. 1978) and it was concluded that the products under helium atmosphere were mainly H_2O , CO_2 , CO , CH_4 and H_2 , but no CH_4 when temperature was below 300°C . The products under oxidative atmosphere were mainly H_2O , CO_2 and CO . Gas products from thermal decomposition of sawdust were affected by oxidization of samples, as concluded in this paper.

CONCLUSIONS

We successfully analyzed the sawdust pyrolysis process and evolved gases by using TG-FTIR. However the study here is only based on qualitative analysis. Our work in this paper is essential for sawdust pyrolysis models. In conclusion, TG-FTIR approach has a good potential to provide valuable parameters for predictive modelling of biomass pyrolysis. However, more work is needed to optimise the experimental technique, to better utilize the rich information obtained from this analysis and to quantitatively validate simple and useful correlations for practical applications.

ACKNOWLEDGMENT

A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions. The authors are grateful to the financial support from China Postdoctoral Science Foundation funded project (20110491435), Jiangsu Planned Projects for Postdoctoral

Research Funds (No. 1101028C), Forestry industry research special funds for public welfare project (201104032), National Natural Science Foundation of China (50903043) and '863' National High Technology Research and Development Key Program of China (2010AA101602).

REFERENCES

1. Bassilakis, R., Carangelo, R.M., Wojtowicz, M.A., 2001: TG-FTIR analysis of biomass pyrolysis. *Fuel* 80(12): 1765-1786.
2. Bingham, P.A., Hand, R.J., Forder, S.D., Lavaysierre, A., 2005: Vitrified metal finishing wastes: II. Thermal and structural characterisation. *Journal of Hazardous Materials* 122(1-2): 129-138.
3. Becidan, M., Skreiberg, Ø., Hustad, J.E., 2007: Products distribution and gas release in pyrolysis of thermally thick biomass residues samples. *Journal of Analytical and Applied Pyrolysis* 78(1): 207-213.
4. Fairbridge, C., Ross, R.A., Sood, S.P., 1978: A kinetic and surface study of the thermal decomposition of cellulose powder in inert and oxidizing atmospheres. *Journal of Applied Polymer Science* 22(2): 497-510.
5. Font, R., Fullana, A., Conesa, J., 2005: Kinetic models for the pyrolysis and combustion of two types of sewage sludge. *Journal of Analytical and Applied Pyrolysis* 74(1-2): 429-438.
6. Herrera, M., Wilhelm, M., Matuschek, G., Kettrup, A., 2001: Thermoanalytical and pyrolysis studies of nitrogen containing polymers. *Journal of Analytical and Applied Pyrolysis* 58-59(1): 173-188.
7. Li, S., Lyons-Hart, J., Banyasz, J., Shafer, K., 2001: Real-time evolved gas analysis by FTIR method: An experimental study of cellulose pyrolysis. *Fuel* 80(12): 1809-1817.
8. Liou, T.H., 2003: Pyrolysis kinetics of electronic packaging material in a nitrogen atmosphere. *Journal of Hazardous Materials* 103(1-2): 107-123.
9. Osvalda, S., 2007: Kinetics of pyrolysis, combustion and gasification of three biomass fuels. *Fuel Process Technology* 88(1): 87-97.
10. Rao, R.T., Sharma, A., 1998: Pyrolysis rates of biomass materials. *Energy* 23(11): 973-978.
11. Raman, K.P., Walawender, W.P., Fan, L.T., Howell, J.A., 1981: Thermogravimetric analysis of biomass. Devolatilization studies on feedlot manure. *Industrial & Engineering Chemistry Process Design and Development* 20(4): 630-636.
12. Yang, H., Yan, R., Chin, T., Liang, D.T., Chen, H., Zheng, C., 2004: Thermogravimetric analysis-Fourier transform infrared analysis of palm oil waste pyrolysis. *Energy Fuels* 18(6): 1814-1821.

XIAOLI GU, CHENG LIU, HENG YIN, XUEWEI MENG, KANGHUA CHENG, MING HE
ZHONGZHENG LI
NANJING FORESTRY UNIVERSITY
COLLEGE OF CHEMICAL ENGINEERING
MOBILE STATION FOR POST-DOCTORAL IN FORESTRY ENGINEERING
NANJING 210037
CHINA

Corresponding author: njfuchemistry@gmail.com