Research Article

Thermal with Mass Spectroscopic Analysis of Wood and Cereal Biomass Torrefaction

René Laryea-Goldsmith and Chris Woolard

Sasol Advanced Fuels Laboratory, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch, Cape Town 7701, Western Cape, South Africa

Correspondence should be addressed to René Laryea-Goldsmith; laryea@email.com

Torrefaction is a mild form of pyrolysis that, when applied to biomass, has the effect of improving the energy density of biomass-derived solid fuels. In this study, thermogravimetric analysis (coupled with mass spectrometry) was applied to two biomass fuels (pine wood and white maize ear) to investigate a potential representative torrefaction thermal treatment process. The mass loss from the torrefaction process was indicative of emission of aliphatic hydrocarbons, evidenced by mass spectroscopic data and it is evident that optimal torrefaction conditions are determined by the type of biomass to which torrefaction processing is applied.

1. Introduction

Torrefaction is a relatively benign thermolysis process, whereby a substance is subjected to a typical temperature range of 230–300°C in the absence of oxygen (i.e., a form of the ancient practice of *pyrolysis*). When applied to biomass, the primary purpose of torrefaction is to increase significantly the energy density of biomass, making transportation for subsequent thermal conversion (such as gasification) more cost effective. Other advantages of torrefaction of biomass are (a) improved friability (therefore facilitating comminution especially beneficial for cofiring with coal), (b) reduction of water content to negligible quantities (increasing calorific content), and (c) conversion of biomass to become hygroscopic [1].

2. Materials and Methods

This paper is a brief communication of ubiquitous thermal analysis, of two biomass types of significance to South Africa: loblolly pine (*Pinus taeda*) as an example wood resource and maize (*Zea mays*) as an example of agricultural crop waste (after cultivation for food supply). For this study, the maize ear (both the core and the residue remaining after removal of the maize grain) was chosen for analysis to represent a waste resource (i.e., not used directly for human consumption). Thermal analysis was performed using a TA Instruments model Q5000IR Thermogravimetric analyser (TGA) coupled with an MKS Instruments model Cirrus 2 mass spectrometer (MS). These instruments were supplied with high purity nitrogen gas to produce a nitrogen flow rate of 25 mL min^{-1} to the TGA. The Curie points of Ni (354°C) and Fe (770°C) were used for the temperature calibration of the TGA. The MS was calibrated using synthetic air and the thermogram test parameters are summarised as follows:

(i) gas supply to sample, nitrogen (99.999% purity) at 25 mL min^{-1};

(ii) initial temperature 29°C, maintained for 1 min;

(iii) temperature ramp rate 54°C min^{-1}, to 300°C (maximum maintained for 1 minute).

3. Results and Discussion

Thermogravimetric analyses were performed twice for each biomass type. Test sample sizes for pine were 2.742 mg and 0.87 mg and for maize were 1.396 mg and 1.311 mg; subsequent data presented in this paper corresponds to the *first* biomass
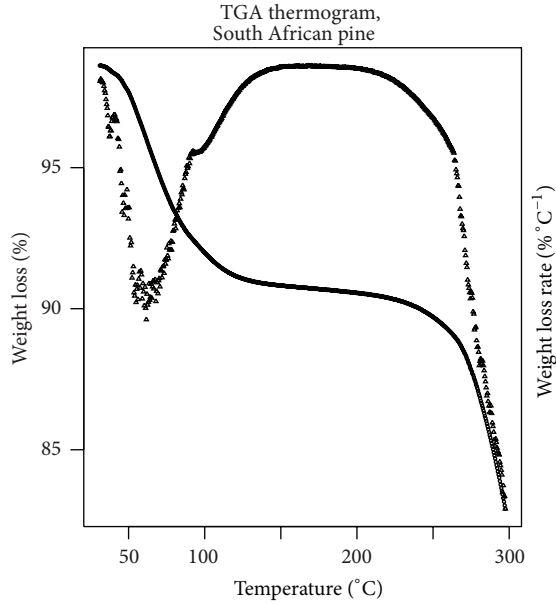
Figure 1: Thermogram of South African pine. Weight loss indicated by solid line.
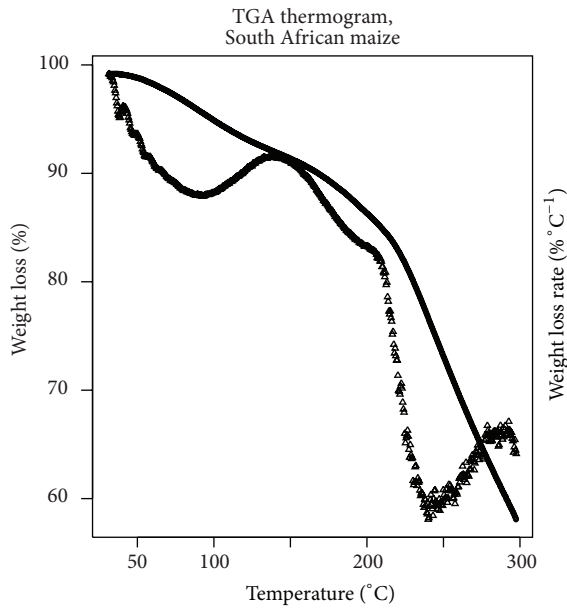

Figure 2: Thermogram of South African maize. Weight loss indicated by solid line.

samples stated. The following figures show how the mass of the biomass samples changes during the experimental tests.

The mass spectrometer was coupled directly to the TGA via a heated capillary (0.53 mm internal diameter) tube to enable evolved gas analysis in real time as the torrefaction process progressed.

Original experimental data are provided as supplementary data sets, freely available on the terms of "Open Data" [2]; it is envisaged that other researchers will make use of this
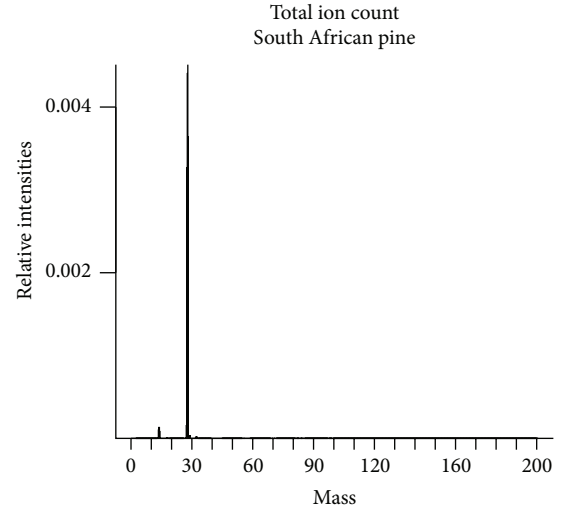

Figure 3: Mass spectrogram (total ion mode) of South African pine; full scan range amu 0–200.
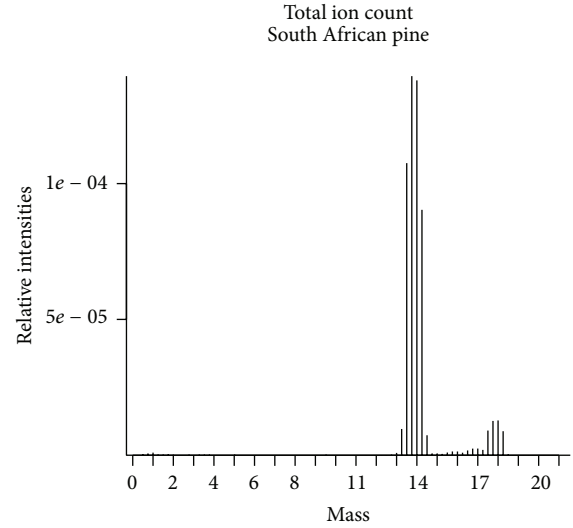

Figure 4: Mass spectrogram (total ion mode) of South African pine. Within the full scan range amu 0–200, graph shows only mass range 0–20.

data to conduct further research such as kinetic modelling study, outside the scope of this paper.

From a design perspective, a general torrefaction process is governed by the following factors [3], that is, temperature (1) and heating rate (2) as being the most important to consider:

$$200\,^{\circ}\mathrm{C} < \theta_{\mathrm{torr}} < 300\,^{\circ}\mathrm{C}, \tag{1}$$

$$\frac{\theta_{\mathrm{torr}} - 200}{t_{\mathrm{heating}}} < 1\,^{\circ}\mathrm{C}\ \mathrm{s}^{-1}, \tag{2}$$

where θ_{torr} = maximum torrefaction temperature and t_{heating} = duration of torrefaction > 200°C.
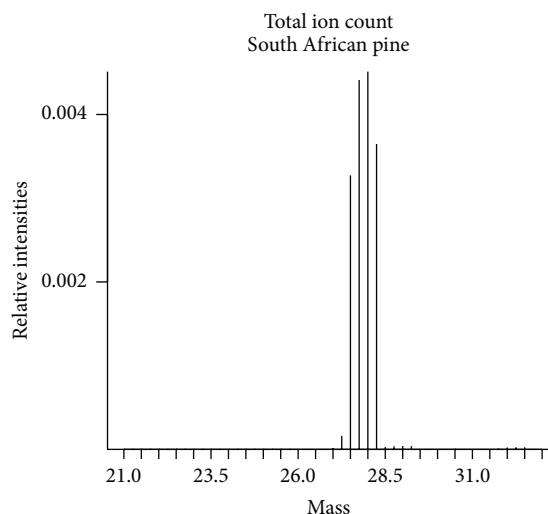
Total ion count
South African pine

FIGURE 5: Mass spectrogram (total ion mode) of South African pine. Within the full scan range amu 0–200, graph shows only mass range 21–32.

Total ion count
South African maize

FIGURE 7: Mass spectrogram (total ion mode) of South African maize; full scan range amu 0–200.

Total ion count
South African pine

FIGURE 6: Mass spectrogram (total ion mode) of South African pine. Within the full scan range amu 0–200, graph shows only mass range 33–105.

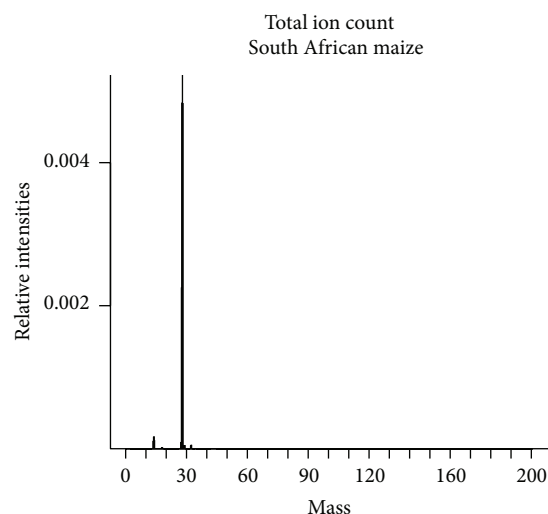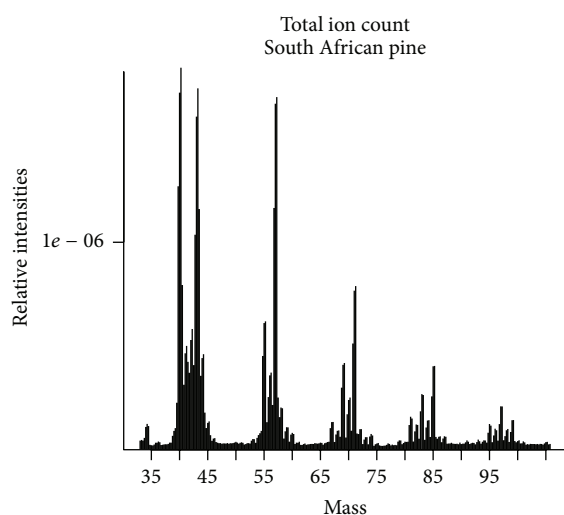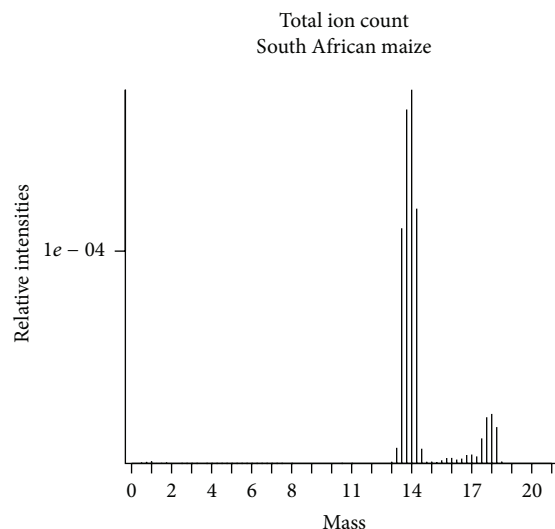Total ion count
South African maize

FIGURE 8: Mass spectrogram (total ion mode) of South African maize. Within the full scan range amu 0–200, graph shows only mass range 0–20.

Thus, for the experimental conditions employed in this study, the heating rate of $0.9°C\,s^{-1}$ is an appropriate representation of a potential commercial process of torrefaction of a biomass resource. Torrefaction of pine wood resulted in a mass yield of 75% (i.e., 25% of original mass was lost via thermolysis) and for maize ear a mass yield of 51% was found. The thermograms suggest that stability of the solid torrefied residue is not attained at the end of the thermogram test. As a consequence, commercial application of a torrefaction process similar to that conducted in this study may probably experience further mass loss (with concomitant emission of volatile compounds) during any subsequent packaging or further manual handling of the torrefied biomass solids.

Comparison of the experimental data in this study with previous work by others was surprisingly difficult due to lack of similar experimental tests conducted elsewhere. In general, thermogravimetric analysis of the pyrolysis and/or torrefaction of biomass has been performed over a temperature range of 0–900°C; for example, pyrolysis of pine over this range [4] showed a similar thermogram to that found in this study (Figure 1), although only for the corresponding temperature range, to 300°C. Thermogravimetric data for torrefaction of maize (Figure 2) could not be found in a review of the published academic literature. It should be noted that in a review of the state of commercial development of torrefaction technology, the temperature limits were less than 500°C and residence times ranged between 2 and 90 seconds [5]. Within
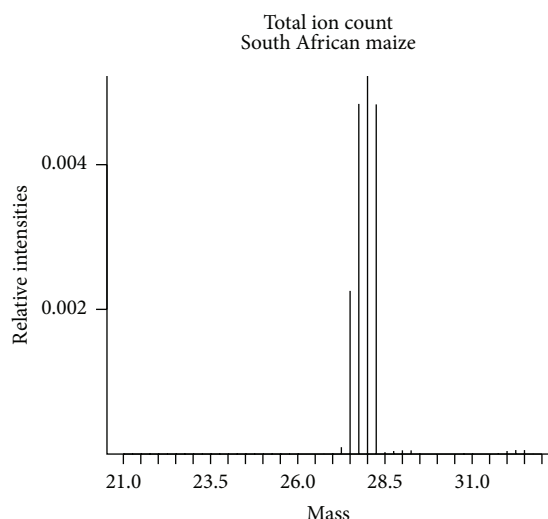
Figure 9: Mass spectrogram (total ion mode) of South African maize. Within the full scan range amu 0–200, graph shows only mass range 21–32.

Figure 11: Mass spectrogram (selected ion mode) of ion 44 amu (presumed to be CO_2).
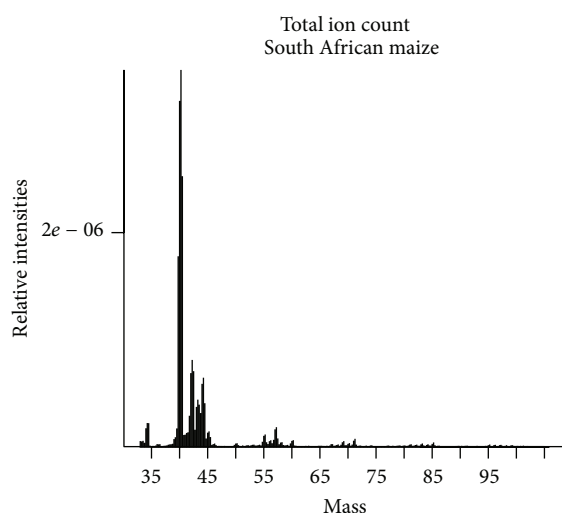

Figure 10: Mass spectrogram (total ion mode) of South African maize. Within the full scan range amu 0–200, graph shows only mass range 33–105.

the temperature range below the maximum 250°C, decomposition of both biomass samples types can be attributed to depolymerisation of two of the three major components of biomass in general, hemicellulose and cellulose [1] (with the third component being lignin). Previous studies have indicated that hemicellulose polymers are the most reactive component [6] and thus the most likely cause of thermal degradation observed in this study. Moreover, it has been found that two competitive pathway mechanisms have been proposed [7] for the decomposition of cellulose, which is of relevance to this study since cellulose is naturally prevalent in the biomass samples assessed. Such degradation is characterised as dehydration mostly (occurring below 280°C) and to a lesser extent, initial depolymerisation which is said to start
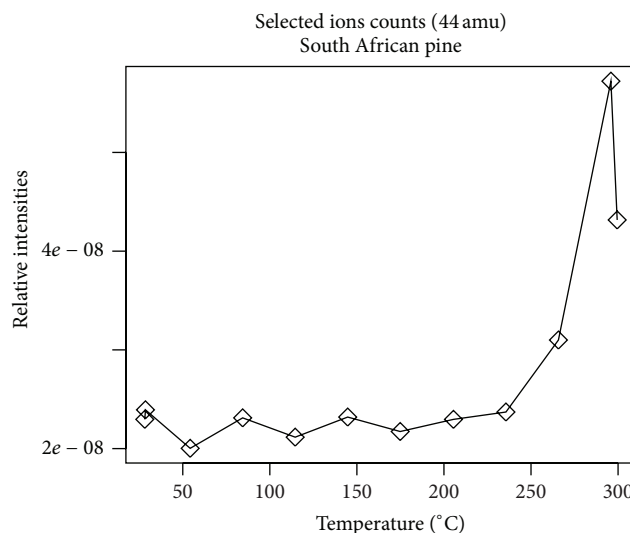
at temperatures above 280°C [8]. For clarification, water loss at low temperatures (<200°C) corresponds to evaporation of free water within the sample. Dehydration refers to chemical loss of water from the cellulose structural ring, resulting in formation of furanic moieties as water is released and eventual formation of solid char [9]. This is consistent with the detection of water as implied by the m/z 18 (e.g., Figure 4). In addition, the difference in thermolysis behaviour between pine wood and maize ear as indicated in the thermograms is most likely due to the different composition. In particular, lignin content in an analogous wood, willow, has been measured at 20% by mass (dry, ash free basis), while wheat straw (as a cereal grain crop analogous to maize) has a lignin content of approximately 8% [10].

A "broad scan" mass spectrum of the pine sample (Figure 3) revealed that the presence of nitrogen as the inert fluid indicated by the relative intensities for the peaks at m/z 28 and 14 is too dominant relative to other components (e.g., Figure 5). This was also observed with the corresponding maize ear samples (Figures 7, 8, and 9). As a consequence, total ion count scans were redrawn into group segments. The spectrum for the mass range 33–105 (Figure 6) is an example of such a partial spectrum. The shape is indicative of sequential fragmentation of a saturated hydrocarbon, whereby cleavage of C–C bonds after ionisation leads to the formation of CH_2 intermediates [11] and similar spectra obtained from GC-MS have also been observed elsewhere [12]. The suggestion that degradation of biomass occurs via methylidene free radicals could not be confirmed within this study; however, it has been proposed elsewhere that free radicals arise (at experimental temperature 375°C) in the ionisation region of the mass spectrometer detector. These are formed as a result of demethylation of biomass biopolymers *en route* to formation of polyaromatic hydrocarbons [13]. Furthermore, a study of the pyrolysis of birch [14] shows

similar degradation of cellulose to yield predominant formation of water, carbon monoxide, and carbon dioxide. In contrast, the corresponding spectrum from analysis of maize ear (Figure 10) implies similar structure, but the seemingly lower intensities of peaks for masses greater than 55 suggest fewer quantities of aliphatic hydrocarbons within the maize volatiles emitted during torrefaction. A measure of selected ions counts presumed to correspond to CO_2 (Figure 11) suggests that even under inert, nonoxidising conditions, atomic oxygen present within the molecular structure of biomass components (e.g., cellulose, starch) reacts during thermolysis to form CO_2. The prevalence of cellulose—a naturally ubiquitous polymer consisting of approximately 3000 oxygen-containing glucose units [15]—would seemingly provide the source of oxygen for oxidation in a paradoxically "pyrolytic" decomposition environment. The relative quantities of CO_2, however, are low, and therefore rapid torrefaction should remain to be considered a viable method of biomass pretreatment.

4. Conclusions

Due to the lower content of lignin in maize compared to pine, thermolysis of maize for a specific thermogravimetric test results in greater loss of volatile components compared to pine. This suggests that if various biomass types are to be torrefied on a commercial basis, such systems will require flexibility in design in order to adjust torrefaction conditions for optimal production of torrefied biomass fuels. Mass spectroscopic analysis indicates that decomposition of pine, representing a "woody" biomass type, under torrefaction conditions occurs via sequential, successive losses of methylene functional groups of alkane that are most likely formed as a result of rearrangement reactions that occur during the thermolysis process.

Thermogravimetric & Mass Spectroscopic Data. Spectroscopic data sets are provided as "Open Data" for subsequent use by other researchers [16].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

References

[1] P. C. A. Bergman, A. R. Boersma, J. H. A. Kiel, M. J. Prins, K. J. Ptasinski, and F. J. J. G. Janssen, "Torrefaction for entrained-flow gasification of biomass," in *Proceedings of the 2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection*, pp. 10–14, Rome, Italy, May 2004.

[2] P. Murray-Rust, "Open data in science," *Serials Review*, vol. 34, no. 1, pp. 52–64, 2008.

[3] P. Basu, *Biomass Gasification and Pyrolysis*, Academic Press, Burlington, Mass, USA, 2010.

[4] S. Singh, C. Wu, and P. T. Williams, "Pyrolysis of waste materials using TGA-MS and TGA-FTIR as complementary characterisation techniques," *Journal of Analytical and Applied Pyrolysis*, vol. 94, pp. 99–107, 2012.

[5] J. S. Tumuluru, S. Sokhansanj, C. T. Wright, and R. D. Boardman, "Biomass torrefaction process review and moving bed torrefaction system model development," Tech. Rep. INL/EXT-10-19569, Idaho National Laboratory, Idaho Falls, Idaho, USA, 2010.

[6] S. S. Abdullah, S. Yusup, M. M. Ahmad, A. Ramli, and L. Ismail, "Thermogravimetry study on pyrolysis of various lignocellulosic biomass for potential hydrogen production," *World Academy of Science, Engineering and Technology*, vol. 1, no. 48, pp. 129–134, 2010.

[7] S. Soares, G. Camino, and S. Levchik, "Comparative study of the thermal decomposition of pure cellulose and pulp paper," *Polymer Degradation and Stability*, vol. 49, no. 2, pp. 275–283, 1995.

[8] M. van de Velden, J. Baeyens, A. Brems, B. Janssens, and R. Dewil, "Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction," *Renewable Energy*, vol. 35, no. 1, pp. 232–242, 2010.

[9] J. Scheirs, G. Camino, and W. Tumiatti, "Overview of water evolution during the thermal degradation of cellulose," *European Polymer Journal*, vol. 37, no. 5, pp. 933–942, 2001.

[10] T. G. Bridgeman, J. M. Jones, I. Shield, and P. T. Williams, "Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties," *Fuel*, vol. 87, no. 6, pp. 844–856, 2008.

[11] J. Barker, "Mass spectrometry," in *Typical Fragmentation Patterns of Common Functional Groups*, D. J. Ando, Ed., Analytical Chemistry by Open Learning, John Wiley & Sons, Chichester, UK, 2nd edition, 1999.

[12] J. M. Jones, M. Kubacki, K. Kubica, A. B. Ross, and A. Williams, "Devolatilisation characteristics of coal and biomass blends," *Journal of Analytical and Applied Pyrolysis*, vol. 74, no. 1-2, pp. 502–511, 2005.

[13] A. M. Herring, J. T. McKinnon, K. W. Gneshin et al., "Detection of reactive intermediates from and characterization of biomass char by laser pyrolysis molecular beam mass spectroscopy," *Fuel*, vol. 83, no. 11-12, pp. 1483–1494, 2004.

[14] A. Khelfa, A. Bensakhria, and J. V. Weber, "Investigations into the pyrolytic behaviour of birch wood and its main components: primary degradation mechanisms, additivity and metallic salt effects," *Journal of Analytical and Applied Pyrolysis*, vol. 101, pp. 111–121, 2013.

[15] A. Streitwieser, C. Heathcock, and E. Kosower, *Introduction to Organic Chemistry*, Macmillan, New York, NY, USA, 4th edition, 1992.

[16] R. Laryea-Goldsmith, "Thermal analysis biomass thermogravimetric mass spectroscopic data," 2013, http://dx.doi.org/10.6084/m9.figshare.719280.