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TG, TG-MS and FTIR Characterization of High-Yield Biomass Charcoals.

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Abstract

The pyrolysis and combustion characteristics of various high-yield charcoals manufactured in a process development unit were studied by thermogravimetry, thermogravimetry – mass spectrometry, and Fourier transform infra-red spectrometry. Charcoals resulting from two runs with a macadamia nutshell feedstock, and one run with a Eucalyptus wood feedstock are compared. The peculiarities of devolatilization, oxygen gasification (temperature-programmed combustion), and the formation of nitrogen oxides are discussed. Small sample sizes (0.2 – 4 mg) were employed to minimize the effects of heat and mass transfer limitations; nevertheless the results offered a reliable characterization of kilograms of charcoal. Samples produced in different runs or taken from different parts of the reactor behaved similarly with only minor differences that we attribute to reactor inhomogeneities and variations in feedstock composition. In the presence of oxygen, two partial processes were detected. The lower temperature weight loss may be due to devolatilization of the char and oxidation of the volatile matter, that results in a carbonized residue. The residue burns off around 450 – 500°C. The rate of both processes evidenced strong dependence on oxygen concentration, indicating an unexpected influence of oxidation on the low temperature devolatilization processes. The intensity of the mass-spectrometric ion signal for NO^+, which represents the formation of nitrogen oxides, did not follow the overall mass loss rate curves (DTG). The peak temperatures of the NO^+ and DTG curves differed by 3 – 9 °C. These differences were influenced by the feedstock composition, but did not depend on such operating conditions as the heating rate and oxygen concentration. Elevated pressure thermogravimetry revealed that a very high partial pressure of CO_2 in the carrier gas (577 kPa) has only negligible influence on the rate of the temperature programmed combustion.

Introduction

Approximately four million tons of charcoal are produced yearly for various purposes.[1] The theoretical yield of charcoal from biomass lies in the range 50 - 80% on a dry weight basis. In spite of the fact that mankind has been manufacturing charcoal for about 6000 years, traditional methods for charcoal production in developing countries realize yields of 20% or less and modern industrial technology offers yields of only 25 - 37%. Recently a new method[1] was developed for producing charcoal from biomass with yields of 42 - 62 %, within a reaction time of 15 min to 2 h. The method is based on closed reactors employing elevated pressures. Under such conditions little carbon is lost as tar: the amount of volatiles yielding tar in the conventional reactors is also transformed into charcoal and light gases. Analyses of these high-yield (HY) charcoals revealed that the HY charcoals closely resemble commercial mesquite charcoal, which retails at \$2.20/kg or more. The chemical mechanism of the charcoal formation itself differs in the classical and the HY methods, as shown by recent studies[2-4]. The aim of the present study is to learn about the chemical properties, thermal behavior and reactivity of the HY biomass charcoals. Thermogravimetry has proved to be a useful tool for charcoal studies.[5-7] Simultaneous thermogravimetry – mass spectrometry helps to obtain a deeper knowledge about the gasification properties of chars[8-13] and the devolatilization of biomass materials.[14-15] Fourier transform infrared spectroscopy (FTIR) is frequently used to characterize biomass chars.[2, 16-18]

Experimental Section

Sample preparation. A reactor was designed and built to the requirements of the American Society of Mechanical Engineers (ASME).[1] It is capable for the elevated pressure devolatilization of 1 – 3 kg of lignocellulosic substances under conditions resulting in HY charcoal. The raw material may be chips of wood, nutshells and fruit seeds. The usual operation pressure and temperature are 1.0 MPa (130 psi) and 400°C. The inner part of the reactor consisted of a 760 mm high canister with an inner diameter of 114 mm. During unloading, the upper and lower third of the charcoals were separated and mixed separately. One of the goals of the present study was to learn about the differences in the samples caused by the different conditions in the upper and lower parts of the reactor. Two different runs with Macadamia nutshell feedstock (*Macadamia ternifolia)* and one run with Eucalyptus wood (*Eucalyptus Grandis)* were studied in the present work. The Macadamia nutshell, a common agricultural by-product in tropical countries, was received from a farm in the form of mostly hemispherical pieces with 25 mm diameter and 2-4 mm thickness. The Eucalyptus wood was cut to chips of about 60 mm x 25 mm x 25 mm. The charcoal retained its original shape with about 90% of its original (linear) dimension. Some of the particles broke during handling. For the present study, the samples were ground to <120µm in a centrifugal mill flushed with nitrogen continuously. The analytical data, presented in Table 1, were determined from the ground samples used for the TG, TG-MS and FTIR studies.

Table 1: Analytical data[a] on dry basis of the charcoals studied.

Name	C	H	N	Ash[b]	O by difference
Eucalyptus Top	72.7	4.0	0.7	0.7	21.9
Eucalyptus Bottom	75.9	3.2	0.3	1.4[c]	19.2
Macadamia 1 Top	72.8	4.5	0.6	0.8	21.3
Macadamia 1 Bottom	75.0	4.2	0.6	1.0	19.2
Macadamia 2 Top	72.4	4.4	0.7	0.9	21.6
Macadamia 2 Bottom	72.1	4.1	0.6	1.3	21.9

[a] The C, H and N data were obtained by a Fisons EA1108 Elemental Analyzer.
[b] The ash content was determined by prolonged combustion with a final temperature of 580ºC.
[c] The ash content of this sample was determined in thermobalance by heating to 720ºC.

TG-MS Apparatus. A computerized atmospheric pressure thermobalance - mass spectrometer (TG - MS) system was built earlier from a Perkin Elmer TGS - 2 thermobalance and a Balzers QMG - 511 mass spectrometer[14]. Recently the mass spectrometer was replaced by a Hiden HAL 3F/PIC model equipped with a fast ion counter. Selected peak intensities were recorded as functions of time. The formed gases were led from the TG furnace to the ion source through a heated capillary. The sensitivity of the equipment was checked in test experiments by using 0.05 mg calcium oxalate monohydrate samples[19]. The experimental data were processed by DOS/Windows programs developed by the authors. The intensity curves were corrected by their baseline shift during the experiments. Intensities m/z 16 and 28 were also corrected by taking into account the fragmentation of H_2O and CO_2. The amount of $^{13}CO^+$ and $C^{18}O^+$ isotope ions were subtracted from intensities m/z 29 and 30. The DTG curves (mass loss rate, -dm/dt) were determined by spline smoothing. The results of the constant heating rate experiments are drawn as the function of temperature. At stepwise heating, the data are plotted as a function of time, but the horizontal axes of these Figures indicate the temperature marks for better readability.

Experimental Conditions. 10 and 50ºC/min heating rates were employed. Parts of the temperature programs included a 60-minute isothermal section at 320 – 420ºC. The ambient atmosphere was argon and argon – oxygen mixtures with O_2 content of 21, 11 and 6%. The samples were evenly distributed on a sample pan of 6 mm diameter. The sample size varied between 0.2 and 4 mg. The reason for the low sample masses was to avoid self-heating effects in the oxidation (controlled temperature combustion) experiments. The lowest sample size (0.2 mg) was employed at the high heating rate study of the Eucalyptus charcoal samples in 21% O_2.

Elevated pressure thermogravimetry. A Hiden IGA high pressure microbalance system was equipped with an alumina furnace. The temperature of the furnace was programmed by a Eurotherm 906 EPC programmer. Elevated pressure gas (6 bar) was led to the furnace so that the pressure surrounding the furnace was identical with the pressure inside. The pressure was regulated with an Aalborg PSV-1 proportional solenoid valve and an Omega CN 76163-PV programmer unit. The gas flow rate was controlled at the outlet of the system. The sample mass was around 1.5 mg.

FTIR measurements. The FTIR spectra were measured by a Perkin Elmer 1710 instrument using a DTGS detector, a Perkin Elmer DRIFT accessory, and microsampling. The charcoals were measured in powder form, using KBr as reference material. The spectra were recorded from 4400 to 400 cm^{-1} by averaging 200 scans at 2 cm^{-1} resolution.

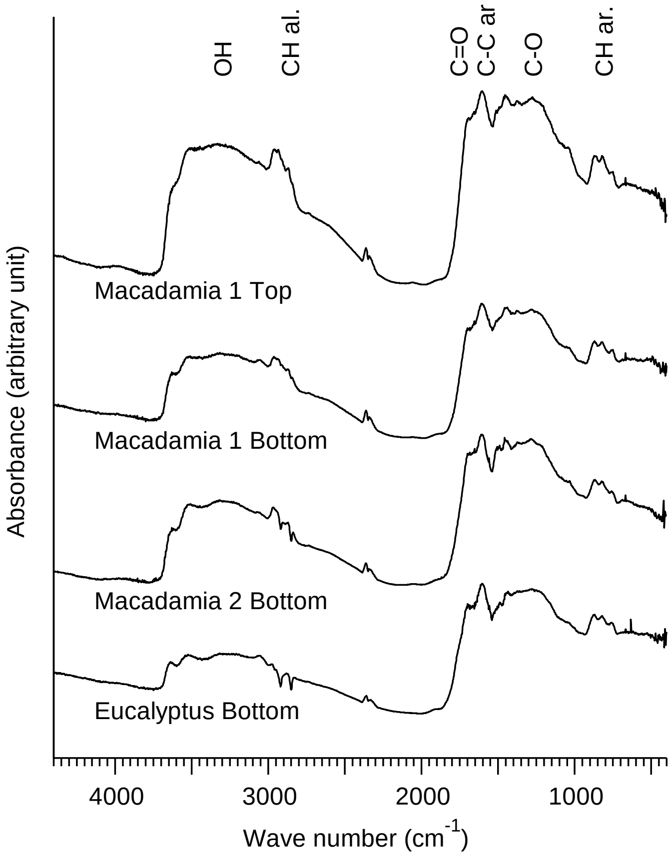

Figure 1. FTIR spectra of four charcoals.

Results and Discussion

FTIR analysis. The spectra of the HY samples were similar, as shown in Figure 1. The same main bands appeared with more or less different shapes and relative intensities. The main band features were identical with the ones obtained for cellulose charcoals prepared at elevated pressures, at similar experimental conditions.[2] The spectra indicate an alkyl aromatic charcoal structure (3000 – 2800 cm^{-1} and 900 – 700 cm^{-1}) with numerous oxygen-containing functional groups: OH (3700 – 2000 cm^{-1}), COOH (a shoulder around 2600 cm^{-1}), C=O (1700 cm^{-1}), C-O-(C) (1275 cm^{-1}) and C-O-(H) (~1050 cm^{-1}). The most intense band of the spectra (~1600 cm^{-1}) can be due to an aromatic skeletal mode, significantly intensified by the presence of oxygen containing polar substituents. The biomass charcoals of the present work reveal less amount of carbonyl groups (1700 cm^{-1}) than HY cellulose charcoals produced at conditions similar to the present work.[2] The Eucalyptus wood charcoal contained less residual OH (3700 – 2000 cm^{-1}) and aliphatic

CH (3000 – 2800 cm^{-1}) than the Macadamia nutshell charcoals (Figure 1.) The quantity of the aromatic CH groups (900 – 700 cm^{-1}) were approximately the same in all of the samples. The stronger carbonization in the bottom part of the reactor resulted in less oxygen containing functional groups, less aliphatic CH and more aromatic CH (Figure 1).

Effect of grain size on the devolatilization. Charcoal pieces of about 2 mg were taken randomly from the non-ground charcoal fractions and were measured by TG and TG-MS. The devolatilization of single charcoal pieces (○ ○ ○) was compared with that of the ground samples (—) in an inert gas flow. To check further the effect, the DTG curves of charcoal ground roughly to 0.5 mm pieces (**- - -**) were also involved into the comparison. As Figure 2 shows, volatile formation is hindered in large grains between 300 and 520ºC. The total mass losses belonging to curves **—**, **- - -** and ○ ○ ○ are 29, 24 and 20%, respectively. This may be due to the secondary cracking of the volatiles during the diffusion from the inner part of the particles. The drying section, around 100 – 200ºC in the plot, is also wider in large particles. Above 550ºC, however, the three DTG curves revealed a surprising similarity, indicating that the carbonization reactions are irreversible at higher temperatures and the volatiles evolving here do not form carbons by secondary cracking.

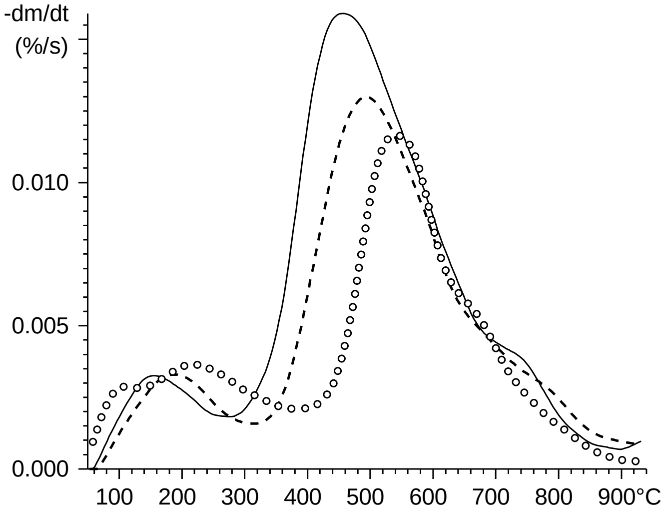

Figure 2. Effect of grain size on the devolatilization of sample *Macadamia 1 Bottom*. The DTG curves of finely ground charcoal (< 120 µm, **—**); roughly ground char (~ 0.5 mm, **- - -**); and a single piece of 2 mg (○ ○ ○) are shown. Heating rate: 10ºC/min.

Similarity of the samples taken from the top and the bottom part of the reactor. Panel (a) of Figure 3 compares the devolatilization of the top and bottom fractions of sample *Macadamia 1*. As the DTG curves indicate, a lower amount of volatiles forms from the bottom fraction between 300 and 550ºC, but the rest of the curves is almost the same. Further checks were made on this similarity by applying a stepwise heating program, shown in Panel (b). An isothermal section of 30 min at 130ºC separated the drying and devolatilization sections. A second isothermal section of 60 min at 380ºC was used to study the peculiarities of the low temperature devolatilization. The top and bottom fractions revealed an almost identical behavior. It is interesting to note that the amount of volatile matter capable of devolatilization at this temperature is almost completely exhausted within an hour. Upon further heating, the devolatilization restarted. The linear and stepwise heating programs did not affect the overall mass loss.

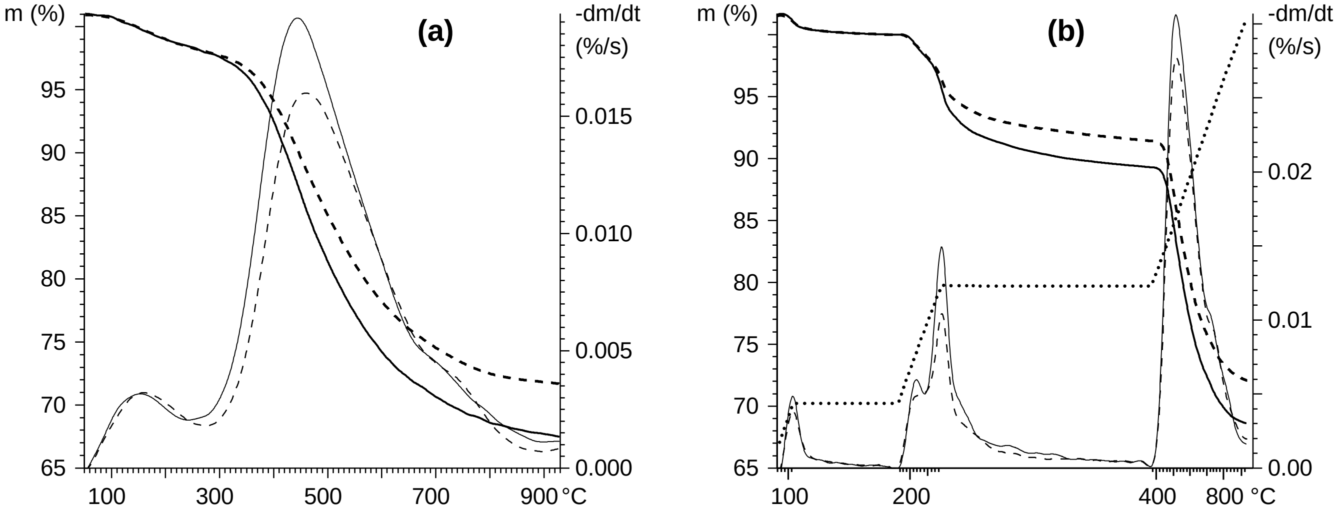

Figure 3. Effect of the feedstock position in the reactor on the properties of the charcoals. TG and DTG curves of samples *Macadamia 1 Top* (**—**) and *Macadamia 1 Bottom* (**- - -**) are shown. Panel (**a**): Constant heating rate experiments (10ºC/min). Panel (**b**): stepwise temperature program (•••) experiments with isothermal sections at 133 and 375ºC and ramps of 20ºC/min.

TG-MS characterization. In the experiments with linear heating at 10ºC/min the mass spectrometric intensities plotted as a function of temperature showed two, well separated regions of devolatilization. (See Figure 4.) Below 600ºC the decomposition of the non-aromatic structures and the splitting off of the aliphatic side groups and functional groups take place. At higher temperatures, the aromatic compounds merge into larger units, releasing the excess hydrogen and their oxygen heteroatoms in the form of H_2O, CO, CO_2 and H_2. About 7% mass loss (22% of the overall mass loss) occurs above 600°C. Panel (a) of Figure 4 reveals double peaks for the H_2O and CO_2 intensities and a multiple CO peak spanning the whole temperature domain. Methane also formed in both regions, but its intensity decreased to zero around 750 ºC. Panel (b) displays the mass spectrometric fragment intensities arising only in the first region, below 600ºC. The abundance of these intensities is lower, hence an eight-time magnification was applied in panel (b).

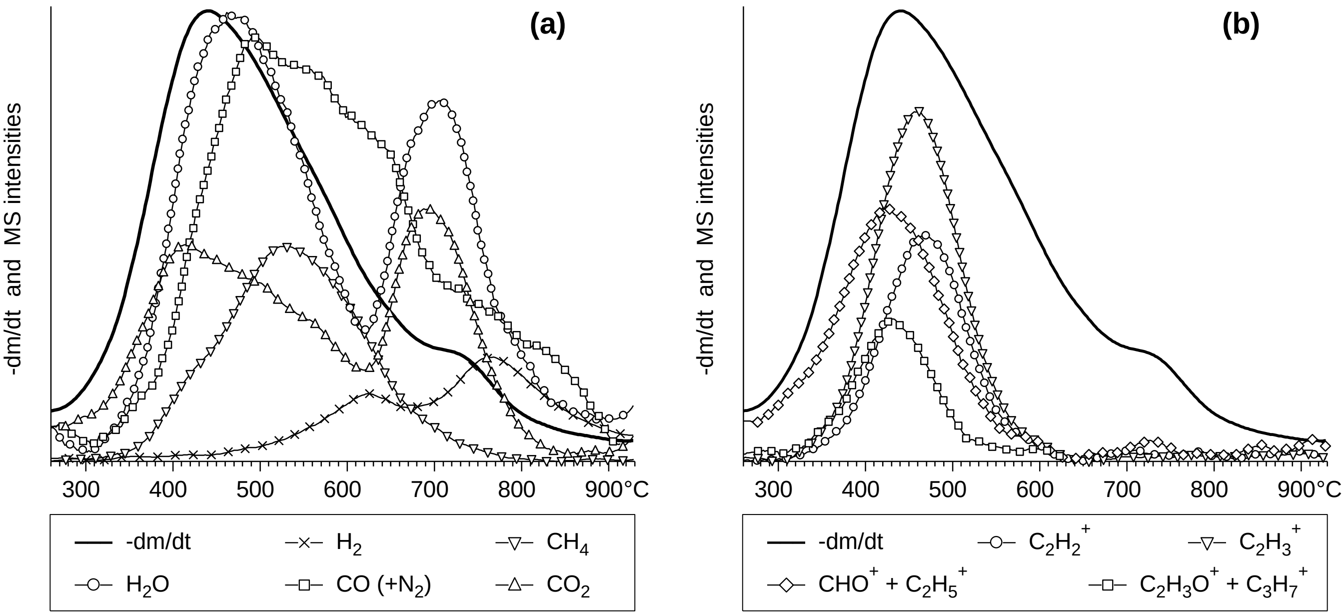

Figure 4. DTG and mass spectrometric intensity curves during the devolatilization of sample *Macadamia 1 Top* at 10ºC/min. (The scale factors of the intensity curves were chosen proportional to the molecular mass of the corresponding ions, to express better their contribution to –dm/dt. The intensities in panel (**b**) were magnified by a factor of 8.)

Controlled temperature combustion. In the presence of oxygen the mass loss of the sample has a much higher rate than in the case of inert devolatilization, even at temperatures as low as 300 - 350ºC. All samples revealed a very similar behavior at identical experimental conditions, as shown in Figure 5. The DTG curves evidence a gradually rising shoulder to 420 °C, followed by a sharp peak at about 480 °C. The reaction rate depends on the oxygen concentration of the ambient gas in both temperature domains (Figure 6).

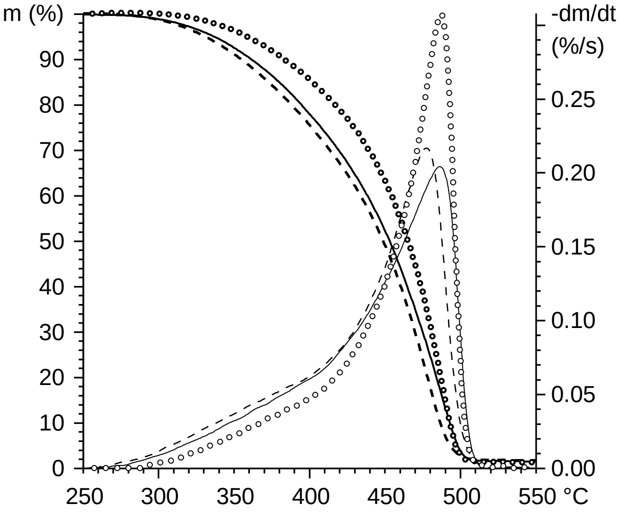

Figure 5. Temperature programmed combustion of charcoals *Eucalyptus Bottom* (○ ○ ○), *Macadamia 1 Bottom* (——) and *Macadamia 2 Bottom* (- - -). (TG and DTG curves at 10ºC/min, in an ambient of 21% O_2.)

A decrease of the oxygen concentration shifts the whole curve to higher temperatures with only minor changes in the shape of the DTG curve. In non-isothermal reaction kinetics this behavior corresponds to the change of the constant factors of the rate equations. If the partial reactions of the mass loss can be described by equations of type

$$d\alpha/dt = A' e^{-E/RT} f(\alpha) \qquad (1)$$

where α is conversion, f is a continous function and factor A' contains both the preexponential factor and the oxygen dependence of the process, then a change of A' results in the shift of the whole curve. (See e.g. Figure 4 in our earlier work on char oxidation[20].) The extent of the shift depends both on the activation energy and on the reaction order of the oxygen concentration. As Figure 6 shows, a change from 21% O_2 to 11% O_2 at a given conversion value results in roughly the same ΔT as a change from 11% to 6%. This behavior suggests a roughly first order dependence on the oxygen concentration. This issue will be examined in more details in a subsequent work dealing with the kinetic modeling of the reactions. It is interesting to note that the change of the oxygen concentration has a pronounced effect in the low temperature region, around 300°C as well as at higher temperatures. The lower temperature weight loss may be due to devolatilization of the char and oxidation of the volatile matter, that results in a carbonized residue below 430 °C. In closely related work, Shafizadeh and Sekiguchi [21] studied oxidation of cellulosic chars and concluded that weight loss below 350 °C is due to oxidation of the char's aliphatic components. However, we remark that our DTG curves most closely resemble the DSC curve for char produced at 600 °C in the work of Shafizadeh and Sekiguchi, which was almost completely aromatic. In any case, the higher temperature peak is most probably due to oxidation of the char's aromatic components.

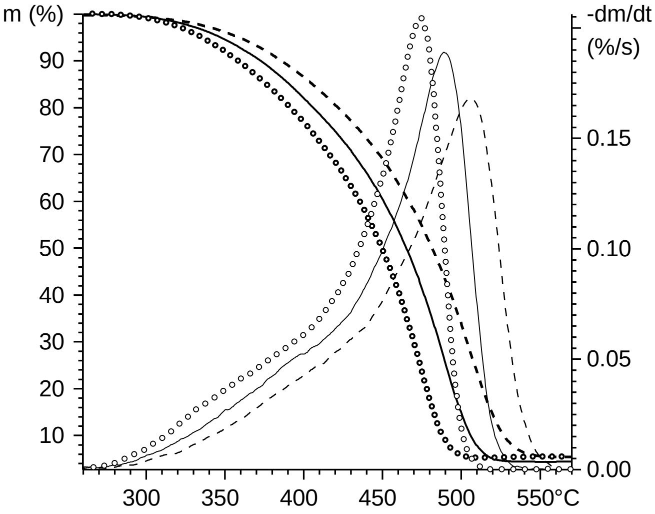

Figure 6. Effect of ambient oxygen concentration on the temperature programmed combustion of char *Macadamia 2 Bottom*. TG and DTG curves are shown at 10°C/min in oxygen concentrations of 6% (**- - -**); 11% (——); and 21% (○ ○ ○).

Formation of nitrogen oxides. It is well known that a major part of the nitrogen oxides formed during char combustion is reduced in the pores of the carbonaceous materials, resulting in N_2, CO and CO_2. Tullin et al.[22] gave a detailed overview on these reduction reactions during combustion and presented experimental data on the fate of NO and N_2O formed in a fluidized bed. A series of work dealt with NO_x

formation studied by thermogravimetry – mass spectrometry.[8-13] Wang et al.[8-9] assumed that the nitrogen present in char is gasified to NO_x at a slower rate than is the carbon, probably leading to the retention of nitrogen in the char with increasing burn-off. In the present study as well as in earlier TG-MS work on chars[8-13] quadrupole mass spectrometers were employed, allowing the characterization of all nitrogen oxides by a single ion intensity, NO^+. (In the quadruple mass spectrometry of char gasification, ions N_2O^+ and NO_2^+ are concealed by the more abundant CO_2^+ and $^{14}CO_2^+$.) NO^+ is the most abundant ion of NO and NO_2. N_2O also produces a smaller amount of fragment NO^+. Hence the intensity of ion NO^+ is a special weighted average of the formation rates of the nitrogen oxides. Contrary to other authors[8-13] we think that this fact hinders the reliable determination of ratios NO/CO_2 or NO/N_{char} during combustion. In this way the evaluation possibilities are reduced to observe and interpret the shape and position of the NO^+ intensity curves. In the domain of the devolatilization, below 400°C in Figure 7a, relatively higher NO^+ intensity appeared which might be due to the low stability of the non-aromatic nitrogen containing structures. At higher temperature, however, the intensity curve of NO^+ falls behind the mass loss rate (DTG) curves. The difference in the peak temperature is characteristic of the given sample and does not show any systematic dependence on such experimental factors as heating rate, isothermal step before the peak temperature or oxygen concentration. The results are shown in Table 2. It is interesting to note that coke and coal samples studied by the authors revealed higher ΔT_{peak} differences. As an illustration, we plotted in Figure 7b the coal sample that best matched the present biomass charcoals in temperature domain and DTG peak shape. It was a French lignite[20] of which most of the mineral matter was removed by a standard HCl – HF washing procedure.

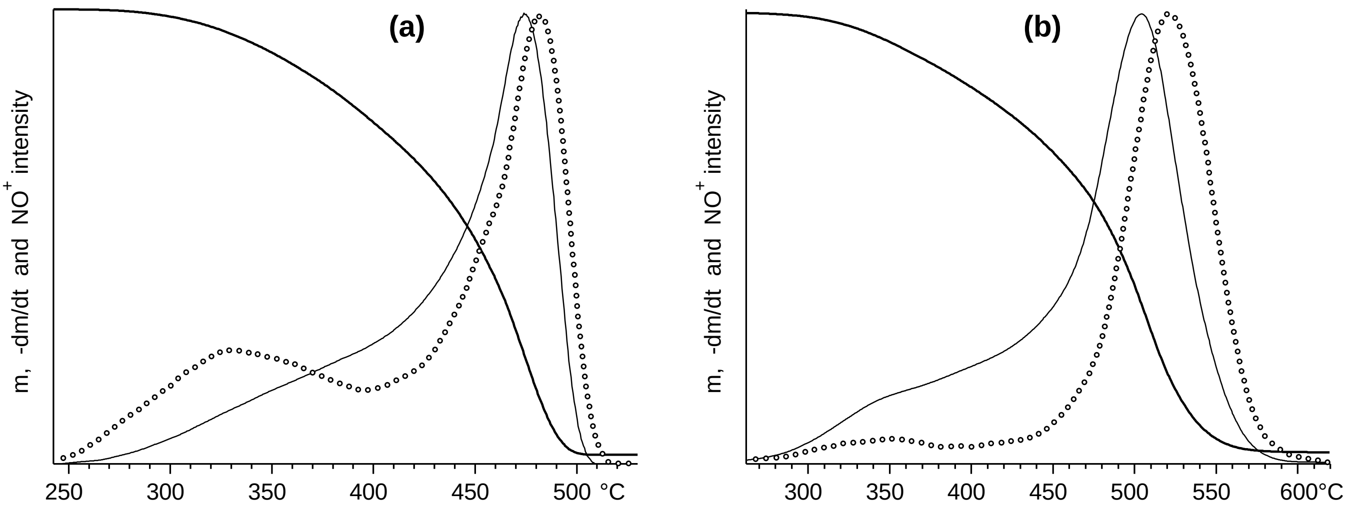

Figure 7. TG (——), DTG (——) and NO^+ (○ ○ ○) curves during the temperature programmed combustion of charcoal *Macadamia 2 Bottom* (**a**) and an acid washed lignin sample[20] (**b**).

Table 2: Average difference between DTG and NO^+ peak top temperatures.

Sample	ΔT_{peak}
Eucalyptus	3
Macadamia 1	9
Macadamia 2	9
Cokes[a]	10 – 20
Coals[a]	20

[a] Data from an unpublished work of the authors. Reference 21 contains the analysis data of the cokes and coals studied.

Elevated pressure thermogravimetry. In an earlier work we studied the influence of carbon dioxide on the temperature programmed combustion of coal chars by comparing experiments carried out in argon – oxygen and CO_2 – oxygen mixtures[20]. The experiments run from 0 to 95% CO_2 and revealed no significant effect by the presence of CO_2. Recently, we carried out similar experiments on the same chars at six bar pressure and observed that measurements carried out in flows of 95% Ar + 5% O_2 and 95% CO_2 + 5% O_2, respectively, are practically identical[23]. We also included one of the samples (Macadamia 2 top) of the present work into that series of experiments. The results are shown in Figure 8. No effect was found below 450°C, indicating that the devolatilization and oxidation processes in that region are not influenced at all by the huge (580 kPa) partial pressure of CO_2. Above 450°C, where the burning out of the carbonized residue dominates, the DTG peak is slightly wider in the CO_2+O_2 experiment. This may be due to slight differences between the transport properties of CO_2 and argon.

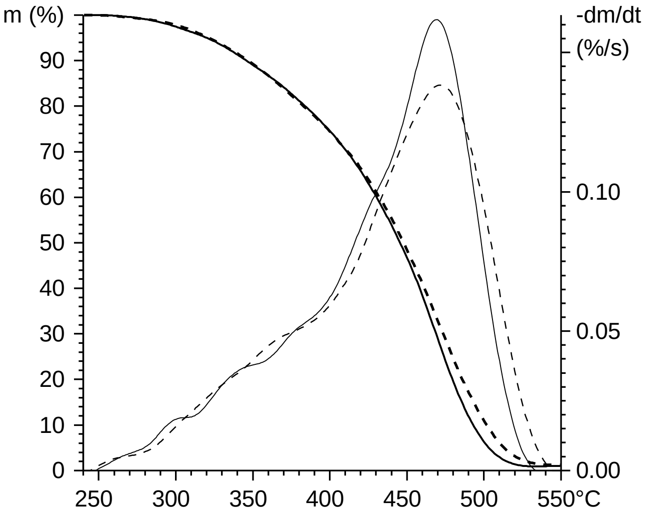

Figure 8. TG and DTG curves of char *Macadamia 2 Bottom* at 6 bar pressure in 95% Ar + 5% O_2 (——) and 95% CO_2 + 5% O_2 (- - -).

Conclusions

Thermogravimetry – mass spectrometry and FTIR analysis proved to be a useful tool for the characterization of the biomass charcoal output of a process development unit. The small sample sizes employed in this work caused no problems: pulverized samples on the order of 0.3 mg were shown to be representative to kilograms of charcoal.

Samples taken from different runs or different locations in the reactor were very similar, with minor differences due to reactor inhomogeneities and feedstock composition.

FTIR and TG-MS analysis revealed a considerable amount of oxygen containing functional groups. During devolatilization in an inert atmosphere, evolution of the oxygen containing products continued up to 800 – 850ºC, indicating the presence of heat resistant heteroaromatic structures.

In the presence of oxygen, two partially overlapping processes appeared, that represent devolatilization of the charcoal and burn-off of the resulting carbon. The rates of both processes dependend on the oxygen concentration, indicating the influence of oxidation on the low temperature devolatilization processes.

The intensity of the mass-spectrometric ion signal NO^+, which represents the formation of nitrogen oxides, was markedly different from the overall mass-loss rate curves (DTG). The peak temperatures of the NO^+ and the DTG curves differed by 3 – 9ºC. These differences were representative of the samples, and did not depend on such operating conditions as heating rate and oxygen concentration.

High partial pressure of CO_2 in the carrier gas (577 kPa) has only negligible influence on the rate of the temperature programmed combustion.

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