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CALORIMETRIC CHARACTERIZATION OF GRASS DURING ITS DECOMPOSITION

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Grass is cultivated for bioenergy purposes yet and expected to play a more prominent role as a source of renewable energy in the future. Understanding its burning characteristics is thus crucial to optimize the energetic efficiency. The aim of this study was to reveal the effect of i) microbial decomposition and ii) enzymatic depolymerisation of grass on its thermal behaviour. Thermal characteristics of grass during the course of aerobic decomposition and of fresh samples after treatment by enzymatic hydrolysis were measured by differential scanning calorimetry (DSC). Heat of reaction, 50% burnoff values and positions and areas of peaks were taken as indicators for the thermal behaviour. An increase in biochemical stability of the grass during 140 days of decomposition was indicated by an exponential mass loss and decreasing specific CO_2 respiration rates. Parameters representing the thermal stability of the materials coincided with this pattern. The relative contribution of the thermolabile fraction decreased, and 50% burnoff values increased almost steadily during decomposition from 366 to 407°C. These thermal stability parameters are thus indicators for biochemical degradation. However, peak temperatures of the individual peaks continuously decreased during decomposition. A comparison of composted and fresh, cellulase-treated samples without long-term microbial decomposition indicated that enzymatic depolymerisation rather than microbial consumption of the plant tissue led to the observed decrease in peak temperatures.

Keywords: *burning, clover, composting, depolymerisation, DRIFT, DSC, enzyme, grass*

Introduction

Bioenergy production by energy crops and agricultural and forest residues is supposed to have a great potential for primary energy substitution in Europe [1, 2]. Production of grass or grass-clover stands as leys in arable rotations or permanent grasslands is common in Switzerland mainly for feeding purposes and to a minor extent for bioenergy production. A parliamentary initiative is calling for guaranteed payments for electricity supplies from combined heat and power generation from biogas, biomass, waste wood and grasses in agricultural areas [3].

Leys and managed permanent grasslands in the temperate zone of Switzerland typically have dry matter yields of 11 to 13 Mg ha^{-1} under intensive (i.e., 5 to 6 cuts, 130–180 kg N ha^{-1}) and between 7.5 to 10 Mg ha^{-1} under moderately intensive management (i.e., 3–4 cuts, 60–110 kg N ha^{-1}) [4]. They are thus as productive as combined energy crop systems from short-rotation forestry and herbaceous energy crops in many European countries [5] and almost as productive as switchgrass systems [6]. The thermal behaviour or burning pattern of this grass-clover biomass is not well investigated and the focus of this study. Because the material is biochemically highly labile and potentially subject to rapid microbial decomposition on the field before harvest and energetic use, calorimetric characteristics were measured during decomposition and compared with enzymatic hydrolysis to identify mechanisms that alter the burning pattern.

Experimental

Materials and methods

Plant samples were harvested from an intensively managed ley in the Swiss Central Plateau (47° 17' N, 07° 44' E, altitude 450 m, mean annual temperature 9°C, mean annual rainfall 1109 mm). Species composition was dominated by *Alopecurus pratensis L.*, *Lolium perenne L.* and *Trifolium repens L.*, a typical mixture used in the temperate region of Switzerland for intensive fodder production on leys. Field-moist samples were mixed with the filtrate of a 1:10 soil suspension as an inoculum to reach a water content of around 85% ('Gras0'). Samples of 200 g each were then incubated in perforated boxes at 25°C for 1, 7, 14, 35, 70 and 140 days (hereafter referred to as Gras1–Gras6). Evolution of CO_2 was measured in an automatic static incubation chamber (Barometric Process Separation BaPS, UMS, Munich, Germany) after partitioning the respective sample into six subsamples. CO_2 concentrations in the headspace were corrected for solution and dissociation in the sample water to

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calculate the total production. Oxygen concentrations were not allowed to drop below 18% to avoid limitations in aerobic microbial activity. The specific respiration rates r_s are expressed as follows:

$$r_s = \text{mg CO}_2\text{-carbon/g organic carbon/day}$$

Curves were scanned with a differential scanning calorimeter DSC 100 (TA Instruments) at heating rates of 5, 10, 15 and 20°C min^{-1} and a flow of 50 mL min^{-1} synthetic air in open aluminium crucibles after heat flow calibration with sapphire and temperature and heat calibration with the melting of indium [7]. In a range of previous experiments, i) the linearity of the heat flow for different sample masses using a mineral soil with 24.6 mg organic carbon (OC) g^{-1} dry soil and ii) the sensitivity of the DSC parameters (heat flow Φ, onset- and peak temperatures, heat of reaction ΔH) to the OC content of the sample was tested. DSC parameters responded linearly in the range of 10 to 25 mg sample mass. Most DSC parameters (after normalisation to OC) were sensitive to the total amount of OC weighted in. From these data, an optimum OC amount of 0.2 to 0.5 mg and a ratio OC to mineral matrix of around 50–75:1 for a sample mass of typically around 15 mg was derived. Grass samples were mixed with purified quartz to achieve the optimum DSC conditions. All DSC measurements were run in triplicate for composite samples of each sampling date. Onset temperatures, peak temperatures, enthalpies of reaction and 50% burnoff values were taken as parameters to define the thermodynamic properties of the materials.

Two additional DSC experiments were carried out. First, Gras0 was depolymerised with cellulase (Sigma) for 0 to 70 h at 37°C, centrifuged and rinsed thereafter three times. These samples were measured as quartz-cellulose mixtures in the DSC with mixing ratios similar to those of the plant materials. Secondly, two different commercially available microcrystalline cellulose samples (Camag, Switzerland) were measured as quartz-cellulose mixtures in the DSC with similar mixing ratios as above to test whether the thermal behaviour of grass is similar to that of pure cellulose.

Diffuse reflectance FTIR (DRIFT) spectra were scanned for Gras0 and Gras6 both unburned and after oxidation to 350°C. Samples were prepared and measured as described previously [8]. Further characterisation of the grass samples comprised OC and N concentrations (CHN Na2000, ThermoQuest), loss on ignition and ash content (oxidation in muffle furnace at 550°C for 3 h) and pH (grass:water 1:20). Data were statistically analysed by ANOVA for effects of experimental time on sample properties.

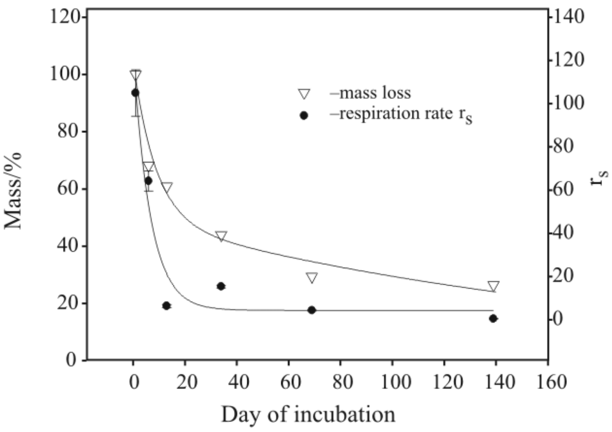

Fig. 1 Mass loss and specific respiration rate r_s (i.e. mg CO_2-carbon per gram organic carbon per day) during the course of composting. Bars are one SE (N=6)

Results and discussion

Mass loss of grass clover mixture during 140 days of incubation (m_t) followed the exponential function

$$m_t = a\mathrm{e}^{-bt} + c\mathrm{e}^{-dt} \tag{1}$$

with m_t mass remaining at any time t, a and c pool size of labile and stable organic matter and b and d decay rate constant (0.1158 and 0.0051 per day for labile and stable organic matter), respectively (R^2=0.98; Fig. 1). Each of the corresponding pools of organic matter accounted for approximately half of the total.

Specific CO_2 production rates correlated with the mass loss (r=0.91), but dropped more rapidly already between day 6 and 13. Together with the switch from the decomposition of the first, more labile pool to the second, more stable organic matter pool, OC contents increased from around 36.5% in the beginning to 40% (day 13) and then decreased to 34% at the end of the experiment. Nitrogen contents increased from 1.7 to 3.1% between day 13 and 34, resulting in smaller C/N ratios at the end of the experiment (decline from 16.8 at day 0 to 11.5 at day 140). During incubation, ash contents increased steadily from 11.3 to 26.0% and pH values increased from initially 8.3 to 9.7.

DSC curves of all samples typically showed a bimodal shape with two exotherms. These exotherms were clearly distinguished from each other and well resolved with a resolution according to [9] of more than 1.3 in any of the DSC experiments. At a heating rate of 20°C min^{-1}, the first exotherm emerged at between 222 and 253°C (i.e., onset temperatures) and the second at between 378 and 411°C, depending on the incubation time. The corresponding peak maxima occurred at around 308 to 313°C (1st peak) and 435 to 455°C (2nd peak; Fig. 2). With increasing decomposition, the contribution of the second exotherm continuously

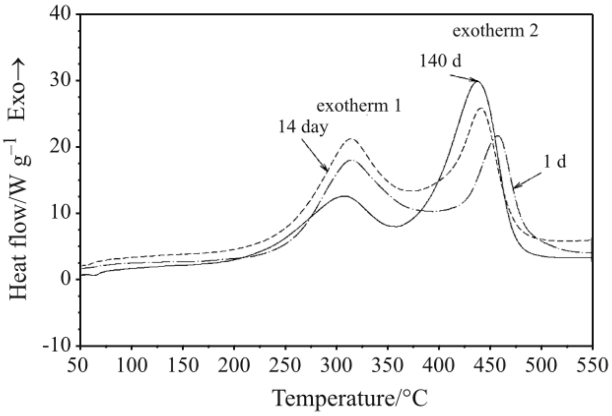

Fig. 2 DSC curves of composted grass after an incubation over 1, 14, 140 days (corresponding to grass 1, 3, 6 in the text) showing two exotherms. Conditions of measurement: heating in stream of 50 mL min^{-1} synthetic air at a rate of 20°C min^{-1}, open Al-crucible, sample mass 0.60 – 0.75 mg dry matter equivalent

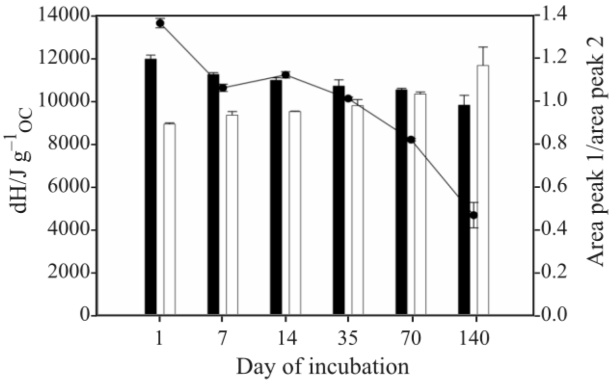

Fig. 3 Heat of reaction dH per unit organic carbon of the first peak (black) and the second peak (open bars). Ratio peak area peak 1/peak area peak 2 is represented as a line with error limits. Bars are one SE (*N*=3)

increased, while that of the first decreased. Heats of combustion for the first peak were between 9.8 and 11.9 kJ g^{-1} OC and for the second peak between 8.9 and 11.6 kJ g^{-1} OC (Fig. 3). Accordingly, the ratio peak area 1st peak/2nd peak decreased strongly during the experiment (Fig. 3) and 50% burnoff temperatures increased from 366°C at the beginning to 407°C at the end of the experiment. The effect of incubation time on the distribution of energy between the two exotherms was highly significant ($p<0.001$). However, the total heat of combustion as calculated by integrating the thermogram from 150 to 550°C showed no significant response to incubation time. Similar to peak distributions, incubation time also affected peak temperatures of both exotherms, the latter decreasing almost steadily (Fig. 4). All above data refer to combustion at heating rates of 20°C min^{-1} and any trends in peak temperatures and reaction enthalpies were similar for heating at 5, 10 and 15°C min^{-1} (data not shown).

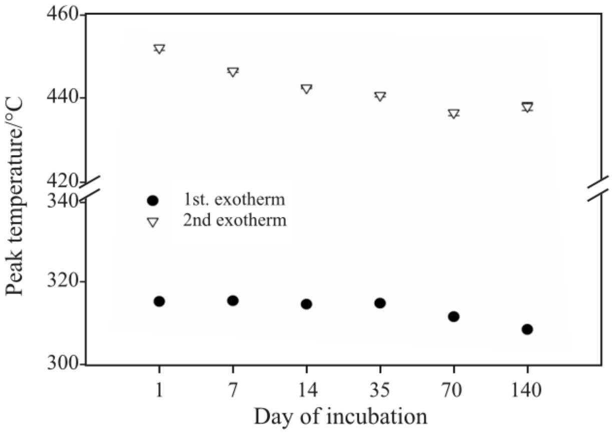

Fig. 4 Peak position (°C) of first and second exotherm during composting. Bars are one SE (*N*=3)

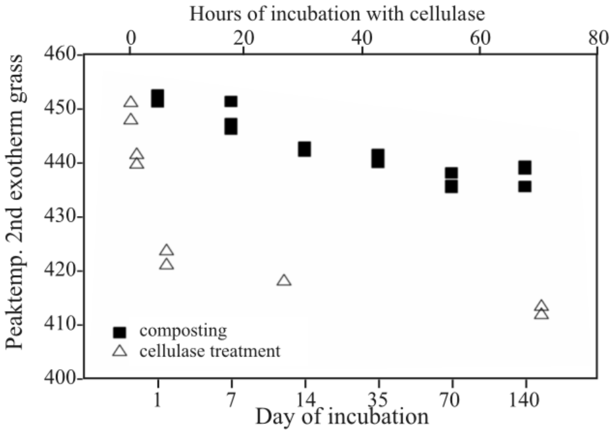

Fig. 5 Peak position (°C) of second exotherm for grass during composting (*N*=3) and during enzymatic depolymerisation (*N*=2)

During enzymatic depolymerisation of Gras0 with cellulase over 70 h, peak temperatures of the second exotherm declined even more than during composting (Fig. 5). In addition, peak temperatures of the first peak and ratios peak area 1st peak/2nd peak decreased with cellulase treatment.

DSC runs of pure microcrystalline cellulose showed exotherms at 357 and 450–470°C for the first and second peak, respectively, with a mean ratio peak area 1st peak/2nd peak of 2.2–2.7.

DRIFT spectra of samples Gras0 and Gras6 were scanned from the unaltered sample and the sample after heating to 350°C (end of reaction 1st DSC peak) (Fig. 6). Spectra of thermally untreated samples (dashed lines) were characterised by a broad band between 1036 and 1060 cm^{-1} (C–O of polysaccharides), bands at 1586 to 1590 cm^{-1} (aromatic sceleton of lignin) and aliphatic stretching between 2900 and 3000 cm^{-1}. After heating the samples to 350°C (solid lines), the polysaccharide peak largely disappeared and the lignin signature at 1586 to 1590 cm^{-1} became more

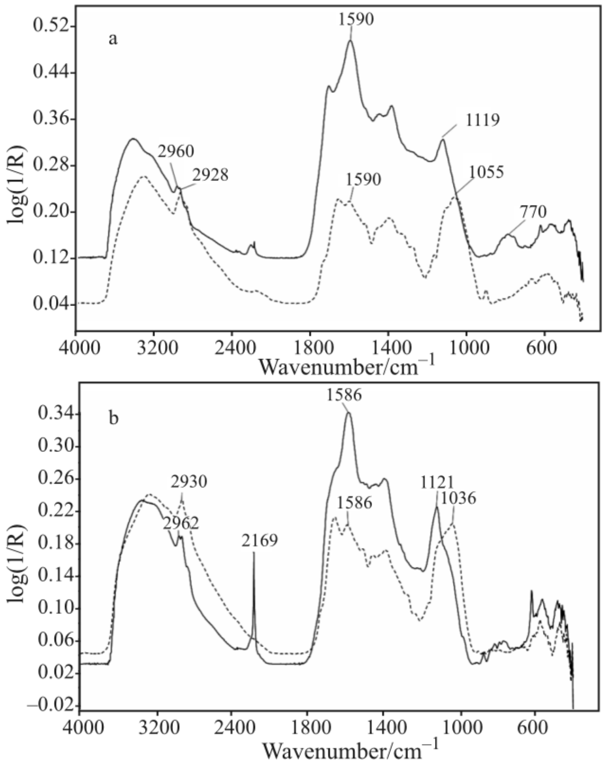

Fig. 6 DRIFT spectra of untreated grass (dashed) and grass after heating under air to 350°C (solid). a – Grass 0 at beginning of experiment, b – grass 6 after 140 days of composting

prominent, in conjunction with a signal emerging at 770 cm^{-1} characteristic for aromatic CH out of plane bending [10]. Also, a shift in the aliphatic region from 2930 to 2962 cm^{-1} is visible. Additionally, Gras6 showed the formation of a new distinct band at between 2160 and 2170 cm^{-1} that was not present in the untreated sample. A clear structural assignment by IR spectroscopy is difficult, but this band likely stems from unsaturated compounds such as terminal –C≡C–H stretching or –C=N– bonding [11].

The aerobic decomposition of the grass material showed typical composting characteristics, i.e., decreasing CO_2 production rates and exponential mass losses together with an increase in ash content and pH over time. Finally, around 75% of the initial OC mineralised. The material remaining after 140 days had a dark-green colour compared to a light green at the beginning, indicating the presence of remaining grass tissue together with an increasing contribution of microbial products and humified material. Because the starting material was comparable N-rich, pH values increased most probably due to cumulating ammonia concentrations during decomposition. This is consistent with O_2/CO_2 ratios during decomposition, which increased from around 1.0 to 1.3 during the first 14 days to 4.5 and 8.0 (day 70 and 140, respectively). Oxygen consumption by the microbial oxidation of reduced organic compounds such as polysaccharides, proteins or *n*-alkanes is expected to roughly equal CO_2 production within a range of 1±0.5, depending on the chemical composition of the organic matter. Release of excessive ammonia and its subsequent nitrification may thus have contributed to the enhanced O_2 consumption at the end of the incubation.

The thermal behaviour of the material during decomposition was characterised by two major trends, a change of energy release from the first to the second exotherm, and, for each exotherm, a decrease in thermal stability as indicated by onset- and peak temperatures. The DSC runs indicate *i*) a shift towards thermally more resistant moieties during decomposition as has been reported for composts previously [12] with *ii*) a concomitant decrease of the thermal stability of each moiety.

The assignment of chemical moieties to the energy release of fresh and biodegraded plant materials would be only possible by analytical investigations of the materials with increasing time of decomposition. An attribution of thermal to chemical or physical sample characteristics could thus not be achieved. For organic matter of soils and composts, exothermic peaks at temperatures between 200 and 350°C have been frequently assigned to the oxidative degradation and dehydration of carbohydrates including hemicellulose and cellulose, aliphatic structures and the decarboxylation of carboxylic groups [12–14]. Exothermic reactions at higher temperatures of >400°C have been assigned to the thermal degradation of aromatic, mono or polycyclic rings [15] and, more generally, to the decomposition of lignin and other aromatic and/or humic substances [16, 17]. However, the assignment of higher temperature exotherms to macromolecules such as lignin or operationally defined moieties such as humic substances appears questionable. The experiment with pure cellulose, which is a major constituent also of grass tissue, clearly showed that aromatic structures in the parent material are not needed to achieve thermal stability also at higher temperatures. Probably, the second peak in the pure cellulose experiment derived from the combustion of char formed during initial stages of heating [18]. The effect of partial combustion on char formation was investigated with infrared spectra from grass materials after heating to 350°C. They indicated the possible formation of unsaturated compounds and possible formation of aryl-C that contributed to the second exotherm.

DSC curves of cellulose were similar to that of undecomposed grass with respect to peak temperatures and shape, but the second peak was distinctly smaller than that of the plant materials, indicating that in the compost experiment, other compounds than polysaccharide derivatives contributed to the thermal stability at higher temperatures. The infrared spectra showed increasing absorption by lignin during the experiment, referring to a selective enrichment of thermally and biochemically more stable compounds. Thus, the increased thermal stability during decomposition as reflected by the peak ratios was at first place caused by selective enrichment of thermally and biochemically stable compounds, accompanied by contributions from charring of cellulose. Any quantitative interpretation of heat fluxes in these experiments is, however, impeded by the unknown contribution of endothermic processes, first and foremost the evaporation of gases. Under oxic conditions, these gaseous losses from combustion of degraded straw comprise mainly CO_2 and H_2O [19]. From the comparison of measured heats of reactions of 18.5 to 24.0 kJ g^{-1} carbon (Fig. 3, sum of both exotherms) and ΔH values for carbohydrates of approximately 35 kJ g^{-1} carbon as measured by bomb calorimetry [20] it can be deduced, that between 31 and 47% of the total heat is not captured by the DSC.

Treatment of fresh grass with cellulase was conducted to find out, whether the observed changes in the curves occurred simply due to depolymerisation rather than due to more pronounced changes in the chemical structure. This experiment acted on the assumption that microbial degradation during artificial enzymatic incubation is negligible relative to the composting experiment. These data indicated that the shift of exotherm positions towards lower temperatures was most likely caused by a smaller degree of polymerisation of the cellulose structure (cracking of the internal hydrogen bonds which compose the fibril structure) accompanied by an increase in the abundance of chain ends (breaking down of glucosidic bonds and attachment of OH).

Conclusions

The thermal stability of grass increases during composting due to selective enrichment or formation of thermally stable compounds on the expense of thermally labile material. Charring of cellulose can also form thermally stable compounds. Because the decomposition process releases most of the organic matter of the parent material by microbial respiration, the thermal stability coincides with biochemical stability. At the same time, however, depolymerisation reduces the ignition temperatures. Thus, peak ratios and 50% burnoff temperatures are valuable indicators for the thermal and biochemical stability, while peak temperatures relate to the degree of polymerisation of the tissue. The total heat of reaction per unit carbon does not correlate with changes in physical and chemical structure, implying that the caloric value of grass-clover mixtures can be estimated by means of OC contents.

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