

1 Introduction

1.1 Bioenergy production as an alternative utilization of semi-natural grassland biomass

Semi-natural grasslands are man-made habitats of high biodiversity. For their conservation they depend on a continued low-intensity agricultural management, but both intensification and abandonment of management threaten their existence in many parts of Europe (Bignal and McCracken, 1996; Ostermann, 1998). In many European regions, they are restricted to marginal sites that are characterized either by hydrological extremes or by difficulties in mechanization, for example small-structured, steep, rocky or tree-covered sites. While many semi-natural grassland communities are low-intensity pastures, others have their origin in hay-making and rely on mowing, rather than grazing, for the preservation of their specific botanical composition (Ostermann, 1998).

Both the high ecological value of semi-natural grasslands and their need for special conservation efforts have been recognized on a European level by including the majority of semi-natural grassland communities as ‘habitat types of community interest’ in Annex I of the European Habitats Directive (European Council, 1992). The directive places legal obligation on the member states to prevent loss or deterioration of Annex I habitats within designated special areas of conservation, and to report on the total area and conservation status of these habitats in regular intervals. Table 1.1 shows the reported areas for the period of 2001-2006 of those habitat types that are considered to have their origin either exclusively or partly in haymaking, or to be threatened by the abandonment of this practice. In total, they make up about 3.4 million hectares in the EU-25, nearly half of which are situated in the Continental biogeographic region (EIONET, no date). With few exceptions, the future prospects of these habitats were evaluated as ‘inadequate’ or ‘bad’ according to the three-category EIONET classification.

One major limitation for an economically viable use of the biomass produced on these grasslands as an animal forage lies in the comparatively late cutting dates that are necessary for preserving their botanical composition. Increasing maturity of grassland biomass leads to increasing fibre contents and decreasing protein contents and digestibility. As nutritional

requirements of high-performing ruminants have strongly increased over the last decades, the opportunities of using late-cut grassland herbage as a forage have become severely limited, and alternative uses for this biomass have to be found.

Table 1.1 Reported areas of grassland habitats listed in Annex 1 of the European Habitats Directive in the EU-25.

	Habitat type	Habitat area in the EU-25 (km ²) ⁽¹⁾						Sum	Origin ⁽²⁾	Threat ⁽³⁾
		ALP	ATL	BOR	CON	MED	PAN			
1630	Boreal baltic coastal meadows	–	–	214	15	–	–	229	G, H	–
6210	Semi-natural dry calcareous grasslands / scrubland	1850	2320	228	2065	>2567	134	>9164	G, H	AG
6270	Fennoscandian lowland dry to mesic grasslands	–	–	406	43	–	–	449	G, H	AG
6410	Molinia meadows on calcareous, peaty or clayey-silt-laden soils	214	>389	255	508	>86	83	>1535	H	AG, AH
6420	Mediterranean tall humid grasslands	2	–	–	13	>2456	–	>2471	H	AG
6430	Hydrophilous tall herb fringe communities	>532	>452	130	>672	>539	19	>2344	H	–
6440	Alluvial meadows of river valleys	–	–	–	86	–	553	639	H	–
6450	Northern boreal alluvial meadows	27	–	427	–	–	–	454	H	AH
6510	Lowland hay meadows	1601	>579	196	11154	>883	323	>14736	G, H	AH, AG
6520	Mountain hay meadows	543	11	3	1642	50	8	2257	G, H	AH, AG
6530	Fennoscandian wooded meadows	–	–	53	–	–	–	53	G	AG, AH
Sum		>4769	>3751	1912	>16199	>6581	1120	>34332		

(1) Assessments on the conservation status of habitat types and species of Community interest carried out in the EU-25 for the period 2001-2006, compiled as part of the Habitats Directive - Article 17 reporting process. (EIONET, no date); Biogeographic regions - ALP: Alpine; ATL: Atlantic; BOR: Boreal; CON: Continental; MED: Mediterranean; PAN: Pannonic.

(2) adapted from Ostermann (1998); G: origin in grazing; H: origin in haymaking; C: origin in crops.

(3) adapted from Ostermann (1998); AG: threatened by abandonment of grazing; AH: threatened by abandonment of hay-making; other threats not considered here

With the now widely acknowledged need to reduce greenhouse gas emissions and fossil fuel consumption, and ambitious targets for increasing the share of renewable energy in the EU (European Parliament and European Council, 2009), bioenergy generation emerges as a

promising new utilization for semi-natural grassland biomass. Using grassland biomass not currently needed as a forage, this strategy has the advantage of avoiding competition between bioenergy and food production. In contrast to many other bioenergy options, it also does not lead to a conflict, but rather to a synergy with nature conservation aims. However, it first has to be established that the bioenergy use of semi-natural grassland biomass actually leads to net energy production and net greenhouse gas savings. While semi-natural grassland biomass production involves low inputs compared to many dedicated bioenergy crops, biomass yields are also much lower. Hay moreover has a low energy density, which may lead to high energy costs if transport is necessary. A life cycle assessment (LCA) quantifying energy inputs and outputs as well as greenhouse gas emission savings is therefore the first step in evaluating the suitability of semi-natural grassland biomass for bioenergy generation.

1.2 Potential conversion technologies for semi-natural grassland biomass

A suitable conversion technology for semi-natural grassland biomass must be adapted to deal with the biomass quality that results from low-intensity management, notably the high proportion of the lignocellulosic cell wall fraction. As the low energy density leads to high transportation costs, and the often scattered occurrence of semi-natural grasslands poses considerable logistic challenges, small-scale and decentralized technologies should also be preferred.

In Germany and Austria, anaerobic fermentation for biogas generation is currently the quantitatively most important conversion technology for grassland biomass. However, the majority of currently existing biogas plants are not particularly well adapted to the utilization of more mature grassland biomass. Not only does a larger fibre content lead to reduced substrate-specific methane yields, it also has negative effects on the technical process. High fibre contents necessitate more stirring and thus lead to higher electricity use; they also increase abrasions of the feeding and stirring equipment (Prochnow *et al.*, 2009b). These effects limit the proportion of fibre-rich substrates that can be used in conventional agricultural biogas plants. An additional problem exists in the difficulty of ensiling very mature grassland herbage.

Technologies more suitable for converting lignocellulosic biomass include combustion, thermochemical gasification, pyrolysis and generation of lignocellulosic ethanol (Faaij, 2006;

Sims *et al.*, 2010). Gasification allows the generation of heat and electricity, or the production of hydrogen, methanol, Fischer-Tropsch liquids or synthetic natural gas from the syngas. Due to the lack of efficient small-scale gas cleaning equipment and consequently high fuel quality requirements of smaller-scale gasifiers, only large-scale plants of capacities well exceeding 10 MW_{th} are currently of practical relevance. Pyrolysis consist in converting biomass to charcoal, liquid and gaseous fractions at temperatures of about 500 °C in the absence of oxygen. Like hydrolysis of lignocellulosic biomass for ethanol production, it has as yet not been practically implemented on a meaningful scale (Faaij, 2006; Sims *et al.*, 2010). Combustion, on the other hand, is a comparatively well established technology with a wide range of capacities being available. Herbaceous biomass of similar properties as semi-natural grassland, such as cereal straw and perennial energy grasses, is already extensively being used as fuels. From the general suitability for using lignocellulosic fuels, the advanced stage of technical development and the availability of small-scale facilities, combustion seems currently the most promising bioenergy conversion technology for semi-natural grassland biomass, and therefore is the focus of this thesis.

1.3 Combustion technology for semi-natural grassland biomass

The basic layout of a combustion appliance is determined by the physical dimension, the form and size distribution, the bulk and particle density, as well as the moisture and ash content of the intended fuel (van Loo and Koppejan, 2008). In all these properties, grassland biomass is very similar to other herbaceous biofuels. Technologies for small- to medium-scale combustion of herbaceous biofuels in the range of some few kW_{th} to about 20 MW_{th} include pellet-fired systems, whole-bale combustion furnaces and grate furnaces.

Pellet-fired systems for residential use are available in capacities starting at 2.5 kW_{th} and offer a high degree of user convenience (Hartmann *et al.*, 2009ab). Though wood pellets are at present the most common fuel used, pelletizing is an attractive option for herbaceous biofuels as well, as it increases energy density, lowers transportation costs and facilitates fuel feeding into the burner. It is, however associated with additional monetary and energy costs (Hartmann and Witt, 2009). Thek and Obernberger (2004) calculated the production costs of wood pellets from sawdust in a large-scale pellet production plant to be 79.6-94.6 € per tonne pellets, at an energy expenditure of 460-617 MJ per tonne, or about 2.6-3.6% of the gross

calorific value. Whole-bale combustion furnaces are semi-continuous systems, into which bales are fed manually. Their batch-wise operation presents a problem as it results in temperature and CO emission peaks which cannot be adequately controlled by current process control systems (Hartmann *et al.*, 2009b). Grate furnaces are suitable for fuels with varying particle sizes and high moisture or ash contents. Although small appliances starting at about 50 kW_{th} exist, grate furnaces are also used in combustion plants of 20 MW_{th} or more (van Loo and Koppejan, 2008; Hartmann *et al.*, 2009b). Most commonly used for fuels like wood chips or bark, grate furnaces have also been adapted for herbaceous fuels. These can be automatically fed either as briquettes or loose, with a preceding bale cutter or shredder.

Pulverized fuel and fluidized bed combustion are further technologies, which only become relevant at larger plant sizes for economic reasons. In pulverized fuel combustion, fuel of maximum particles sizes of 10-20 mm is pneumatically injected into the furnace together with the primary combustion air. Capacities range from 1 MW_{th} to several hundred MW_{th}. The upper range is represented by pulverized coal-fired boilers, in which co-combustion of biomass fuels is possible. In fluidized bed combustion systems, starting at about 20 MW_{th}, the fuel is mixed with an inert, granular bed material. The bed is fluidized by the primary combustion air that enters the furnace from below. Mixtures of fuels can be burned, but particle size should not exceed 40-100 mm (van Loo and Koppejan, 2008; Hartmann *et al.*, 2009).

Production of electricity as well as heat from biomass is possible in combined heat and power (CHP) plants. Stirling engines for small-scale power production are currently in the pilot and development phase, but as they require very clean flue gas, they are not suitable for herbaceous biofuels. Among proven technologies, steam piston engines are available for smaller CHP plants, starting at capacities of 25 kW_{el} with electrical efficiencies of 4-7%. Steam turbines are typically used in large-scale CHP plants of 500 kW_{el} to 500 MW_{el}. Electrical efficiencies rise from <15% in small steam turbines to up to 40% in large ones. High electrical efficiencies, however, are linked to high steam pressure and temperature, which can lead to substantial superheater corrosion and fouling problems in biomass-fired plants (Baxter *et al.*, 1998; Faaj, 2006; van Loo and Koppejan, 2008).

In general, all the described combustion technologies are well suited to deal with the physical characteristics of herbaceous biofuels, in the case of fluidized bed and pulverized combustion

after further comminution. The main technological problems are related to the chemical composition of these fuels, and consist in harmful emissions and unfavourable ash high-temperature behaviour (Baxter *et al.*, 1998; Hartmann *et al.*, 2009b). Due to economy of scale effects, more efficient secondary measures for emission reduction are available in large-scale systems. These are consequently able to use inhomogeneous and low-quality fuels, while small-scale systems have to rely on high-quality fuels (van Loo and Koppejan, 2008). Therefore, although technical possibilities exist to use even the most difficult fuels, if semi-natural grassland biomass is to be used in smaller and more decentralized systems, higher fuel qualities with respect to emissions and ash high-temperature behaviour have to be achieved.

1.4 Challenges for grassland biomass combustion related to fuel chemical composition

1.4.1 Emissions

During the combustion of biomass fuels, and especially of herbaceous biomass fuels, relevant emissions of fly ash, nitrogen oxides (NO_x), sulphur oxides (SO_x) and hydrogen chloride (HCl) can occur. Under incomplete combustion, other pollutants, including ammonia and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF), also can be emitted. Because of their negative effects on the environment and on human health, many countries have set legal emission limits for several of these components, most notably for particle, NO_x and SO_x emissions. These limits increase in severity with plant fuel capacity, which reflects the higher difficulty of emission reduction measures in smaller plants. Emission limits for the combustion of herbaceous biofuels in Germany are listed in Table 1.2.

Table 1.2: Legislation on emission limits for the combustion of herbaceous biofuels in Germany.

Nominal fuel capacity (MW _{th})	CO (mg m ⁻³ ₀)	Particles (mg m ⁻³ ₀)	NO _x (mg m ⁻³ ₀)	SO ₂ (mg m ⁻³ ₀)	Legislation
<0.1	2500	100	–	350	1. BImSchV ⁽¹⁾
0.1 - 1	250	50	500	350	TA-Luft ⁽²⁾
1 - 50	250	20	400	350	TA-Luft ⁽²⁾

(1): at a reference O₂ concentration of 13%; 1. BImSchV (2010)

(2): at a reference O₂ concentration of 11%; BMU (2002)

m³₀: cubic metre at normal conditions (pressure of 101.3 kPa, temperature of 273 K)

Fly ash, together with organic particles from incomplete combustion, make up the particle emissions. The coarse fly ash fraction with diameters >1 μm is formed by fuel ash particles

from the fuel bed that have been entrained in the flue gas. It shows a strong relationship to fuel ash content, but is also influenced by the design of the combustion chamber (Launhardt, 2002; Johansson *et al.*, 2003; van Loo and Koppejan, 2008; Eriksson *et al.*, 2009). Fine fly ash with diameters up to 1 μm consists of aerosols that are the result of condensation and nucleation of volatile elements, such as K, Na, Cl, S, Zn and Pb. Launhardt (2002), burning biomass from nature conservation grassland with an ash content of 6.5% in a 50 kW_{th} combustor, found dust emissions of 230 mg m⁻³₀ (13 % O₂). Kaufmann (1997) reported dust emissions of 600-800 mg m⁻³₀ for the combustion of semi-natural grassland biomass with 6.9% ash in a 450 kW_{th} grate furnace. Secondary measures for particle emission reduction include cyclones, with a high collection efficiency only for larger fly ash particles, and bag filters or electrostatic precipitation, which have high collection efficiencies for the fine fly ash fraction as well. Due to their high costs, bag filters and electrostatic precipitation are only an option for large-scale appliances at present. No efficient particle control technologies are currently available for small- or medium-scale appliances (Oberberger *et al.*, 2006; van Loo and Koppejan, 2008).

During the combustion of biomass fuels, most of the fuel N is converted, over intermediates, to either N₂ or NO, which latter is converted to NO₂ in the atmosphere. The amount of NO_x emissions is influenced by fuel N content and by the concentration of O₂ in the combustion zone. While conversion rates of fuel N into NO_x decrease with increasing fuel N content, the overall NO_x emissions increase (Biollaz and Nussbaumer, 1996; Paulrud and Nilsson 2001). During the combustion of nature conservation grassland with 1.2% N, NO_x emissions of 362 mg m⁻³₀ were reported (Launhardt, 2002). NO_x formation is reduced if combustion runs at low excess air ratios, for example in fluidized bed combustion. For this reason, air staging and fuel staging can be used as primary measures for NO_x emission reduction. In air staging, primary combustion air injection is understoichiometric, increasing the proportion of N₂ formed. Secondary air is then injected in the combustion chamber to ensure complete combustion. Fuel staging consists in burning primary fuel with excess air and creating a reduction zone by feeding secondary fuel at a later stage, thus reducing the NO formed to N₂. Both measures have been shown to reduce NO_x emissions by 50-80% (Nussbaumer, 2003). Secondary measures for NO_x emission reduction include selective catalytic and non-catalytic reduction (SCR and SNCR). In these, NO_x is reduced to N₂ by urea or ammonia, either at high flue gas temperatures (SNCR) or using a catalyst (SCR; Nussbaumer, 2009).

A varying proportion of fuel S, typically 50-60%, is completely oxidized to SO₂ or SO₃ during combustion. The remainder is largely retained in the fuel ash. S retention in ash is favoured by the fuel concentration of alkaline earth metals, particularly of Ca (Knudsen *et al.*, 2004; van Loo and Koppejan, 2008). The risk of SO_x emissions above the legal limits generally exists only for very S-rich biofuels, such as rape straw (Eriksson *et al.*, 2009), and poses a comparatively small risk during the combustion of most herbaceous biofuels.

During combustion, the majority of fuel Cl will initially be released to the gas phase as HCl, Cl₂, and alkali chlorides, with subsequent reactions in the convective section (Oberberger, 1998). Kaufmann (1997), investigating a number of herbaceous biofuels with varying Cl contents, found that on average 15% of fuel Cl were emitted as HCl. Fuel Cl content is also positively related to emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF), which are formed under incomplete combustion. Because of their strong negative effects on human health PCDD/PCDF emissions will generally be more critical than HCl emissions. Apart from ensuring complete combustion, efficient dust precipitation measures are considered the best option for reducing PCDD/PCDF emissions (van Loo and Koppejan, 2008).

1.4.2 Ash high-temperature behaviour

Compared to uncontaminated wood, herbaceous biofuels generally are characterized by lower Ca and higher K and Cl contents. Ash-related problems of slagging, fouling and corrosion can be the consequence, and can have severe economic consequences (Baxter *et al.*, 1998). These problems can be traced back to two basic processes: elemental release and ash-melting behaviour.

During combustion, varying proportions of volatile elements, such as alkali metals, Cl, S and heavy metals, are released into the gas phase. The mobility of many elements is increased by the presence of Cl, due to lower evaporation temperatures of their chlorides compared to other species of the element. When the flue gas cools down in the convective section, the inorganic volatiles can condense on the heat exchanger surface forming deposits. There, they reduce heat absorption, which leads to higher flue gas temperatures, lower efficiencies and the danger of local overheating. Different forms of soot blowers are available for online cleaning of the convective section, but regular use of soot blowers increases erosive wear. In large-scale CHP plants, superheater corrosion is another highly relevant process linked to elemental release

and deposit formation. At metal temperatures above 450-500 °C, the complex process of high-temperature corrosion sets in, in which Cl plays a central role. When high-Cl fuels are burned severe superheater damage is possible (Baxter *et al.*, 1998; Knudsen *et al.*, 2004; van Loo and Koppejan, 2008).

Refractory elements, such as Si, Ca, Mg or Al, as well as certain proportions of the volatile elements, remain in the residual ash. Part of this ash can be entrained in the flue gas as well, and is either incorporated in growing convective section deposits or else emitted as coarse fly ash. In the furnace, ash melting can lead to slag formation. Partially molten particles adhere to each other or to clean furnace surfaces. Once surfaces are covered with a partially molten, sticky layer, deposition rate increases. Whereas convective section deposit formation is a slow process, slagging can proceed much faster. Excessive slag formation has a strong negative influence on boiler functioning and on the de-ashing system; it also causes difficulties in ash recycling. To address this problem, biomass firing boilers are often fitted with water- or air-cooled grates and furnace walls. In fluidized bed combustors, ash melting can have particularly severe effects, as it can lead to agglomeration of bed material. In extreme cases, bed defluidization leads to plant shut-down (Baxter *et al.*, 1998; van Loo and Koppejan, 2008; Hartmann *et al.*, 2009b).

Ash melting behaviour is the result of a complex chemistry which is still the subject of active research in the field of process chemistry. It first received attention in the context of coal combustion. Several different ash fusion tests were developed to assess the slagging potential of coal, of which the ASTM ash fusion test (ASTM, 1987) is the most widespread. It consists in forming ash cones and monitoring at which temperatures certain pre-defined stages of deformation are reached. Correlations between ash fusion test results and ash composition were used to derive a number of different slagging indices (Bryers, 1996). For biomass ashes, with lower Al and Fe but higher K contents than coal, both standard ash fusion tests and coal slagging indices have been shown to be of limited applicability (Jenkins *et al.*, 1998; Skrifvars *et al.*, 1999; Paulrud *et al.*, 2001; Fernández Lorrente and Carraso García, 2005).

The formation of low-melting silicates seems to be the most important process for ash melting. As K silicates have low melting points, ash melting behaviour is strongly linked to ash K content. However, the most common elements in ash of herbaceous biomass, Si, K, Ca and Mg form eutectic mixtures, and their interaction with each other also influences K

release, which makes the relationship between ash melting behaviour ash composition more complex (Thy *et al.*, 2000; Paulrud *et al.*, 2001; Fernández Lorrente and Carraso García, 2005; Thy *et al.*, 2006ab)

1.4.3 Fuel composition of semi-natural grassland biomass

Overviews of combustion-relevant properties of biomass fuels mostly only contain perennial energy grasses, such as miscanthus (*Miscanthus x giganteus*), switchgrass (*Panicum virgatum* L.), reed canary grass (*Phalaris arundinacea* L.) or giant reed (*Arundo donax* L.), but not semi-natural grassland biomass (Jenkins *et al.*, 1998, van Loo and Koppejan, 2008; Vassilev *et al.*, 2010). Where ‘nature conservation grassland’, ‘verge grass’ and ‘hay’ are included in such overviews, they generally show a more problematic fuel composition with higher variability than perennial energy grasses or straw (Obernberger, 1998; van der Drift *et al.*, 2001; Härdtlein *et al.*, 2004). The above-mentioned categories are rather broad and do not differentiate between different botanical composition, maturity and growing conditions of semi-natural grassland biomass. The influence of these factors on fuel quality has rarely been studied (Kasper, 1997; Florine *et al.*, 2006; El-Nashaar *et al.*, 2009). Information on combustion-relevant elements from forage quality research is also rather limited. Some important elements, particularly Cl and S, have seldom been covered (Whitehead, 2000). Moreover, mineral composition in general has mostly been studied at earlier developmental stages more relevant for animal nutrition, and information on the development of grassland biomass chemical at late cutting dates is comparatively scarce.

1.5 Research focus and objectives

Using semi-natural grassland biomass for bioenergy production would allow to combine nature conservation with bioenergy targets. Combustion currently is the best-adapted technology for the decentralized conversion of lignocellulosic biomass into energy. In spite of the considerable potential of this under-used biomass, few studies so far have dealt with the suitability of semi-natural grassland biomass for bioenergy production by combustion. This thesis focussed on the following fields of research:

Environmental impact of the combustion of semi-natural grassland biomass:

Semi-natural grasslands are biodiversity-rich and are managed under low intensity with low inputs. They are, however, characterized by low biomass yields. Due to the low energy

density of hay, energy expenditure in transport may be high. Biomass chemical composition may also lead to gaseous emissions with negative environmental impact. Paper I therefore investigates the energy use efficiency, greenhouse gas mitigation and acidification potential of the combustion of semi-natural grassland biomass, comparing it to other herbaceous biomass fuels, and considering the effect of management intensity.

Factors influencing the suitability of semi-natural grassland chemical composition for combustion:

Chemical composition of semi-natural grassland biomass is variable, but sometimes can lead to ash-related problems and high levels of pollutant emissions. Semi-natural grasslands differ widely in botanical composition, harvest date and site conditions. These factors may contribute to the observed variability of their biomass chemical composition. Paper II investigates the importance of harvest date, site effects and differences between plant functional groups in influencing fuel composition. It evaluates the suitability of semi-natural grassland herbage for combustion by comparing the experimental results to the fuel composition of other herbaceous biofuels and by discussing them in relation to knowledge of combustion technology.

Optimization of the fuel quality of semi-natural grassland biomass by on-field leaching:

In contrast to dedicated bioenergy crops, the options to influence chemical composition of semi-natural grassland biomass by management are limited, since management needs above all to be targeted to the preservation of the specific botanical composition of the grassland sward. A low-cost strategy for fuel quality optimization with minimum negative effects on biodiversity could be found in on-field leaching of problematic elements. Papers III and IV therefore assessed the effect of leaching on grassland biomass chemical composition and ash high-temperature behaviour.