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The effect of feedstock composition and taxonomy on the products distribution from pyrolysis of nine herbaceous plants

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ABSTRACT

The effect of feedstock composition and taxonomy on the products distribution from pyrolysis of nine herbaceous plants was evaluated. Specifically, eight members of the Poaceae family and one member of the Fabaceae family were pyrolyzed in a fixed bed reactor to a final temperature of 700 °C. All samples resulted in a medium-energy CO_2-rich gas and a phenol-rich liquid. The type of lignin rather than the overall lignin content was found to influence the phenols yield. All samples produced char with a suitable C/N ratio; eight plants produced char with high polarity; and only one sample (i.e., mountain brome) resulted in char with a sufficient aromaticity to be applied to soil. Low carbonization was associated with a high content of inorganic elements that were most likely deposited on the char's surface and blocked vaporization. The product distributions were dependent on (i) chemical and biochemical composition of feedstock, (ii) secondary reactions of liquid and char, and (iii) the samples' taxonomy. Red clover from the Fabaceae family was found to be the most distinct, followed by mountain brome from the Triticodae group (Poaceae family), and the remaining members of the Poodae group (Poaceae family). The least divergence was found between the hybrid samples.

1. Introduction

Fossil fuels are the main source of energy and chemicals today, however their difficult replenishment and environmental impacts of carbon dioxide (CO_2) associated with their processing increase the demands for new processing technologies and renewable energy sources. Technologies of thermochemical processing of biomass such as pyrolysis, gasification, combustion, or liquefaction are promising methods for the conversion of biomass to bio-fuels and chemicals. Woody and herbaceous plants as well as grasses are the main biomass types considered for thermochemical conversions [1]. One advantage of the exploitation of grassland biomass for thermal processing is the utilization of idle agricultural products. Grassland biomass covers up to 70.0% of agricultural land, of which about 900,000 km^2 is located in Europe [2]. According to the Commission Regulation (EC) no. 796/2004, Member States are required to maintain the specific ratio of the land under permanent pasture (grass porosity) and the total agricultural area [3], since the utilization of grasses as a fodder is no longer economically viable in most European regions [2].

Pyrolysis is a very promising thermochemical conversion method due to the fact that it is typically conducted at temperatures lower than those required in combustion or gasification and it is less complex and less expensive than liquefaction [1,4]. During pyrolysis, the biomass is converted to gas, liquid, and char in an inert atmosphere. The gas product can be combusted for energy production or converted to synthetic liquid fuels; the liquid product, also called bio-oil, can be stored and further used for the production of energy or chemicals; while the solid product termed bio-char can be combusted, applied to soil, or used as an activated carbon in industrial applications [4]. The final utilization of these products is, however, determined by their distribution and properties, which on the other hand are highly influenced by the original composition of the feedstock [5], in particular by the diverse biochemical composition.

Biomass is composed of varying amounts of three biochemical components, namely cellulose, hemicellulose, and lignin [1]. Cellulose produces the highest yield of liquid consisting mainly of anhydrosugars and the lowest yield of char; hemicellulose gives the highest yield of gas and the liquid produced is composed primarily of water, phenols, and ketones; whereas lignin generates the highest yield of char and phenols in liquids [6]. As pointed out by Burhenne et al. [7] cellulose and hemicellulose-rich herbaceous biomass decomposes faster and produces more volatiles than woody biomass with a higher content of lignin. Dorez et al. [8] found that cellulose, hemicellulose, lignin, and their degradation products interact during pyrolysis, and the manner in which the biochemical constituents influence their reaction pathway is dependent on their ratio (e.g., cellulose/lignin).

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The pyrolysis of herbaceous biomass may also be influenced by the content of ash, in particular by inorganic elements. Sodium (Na), potassium (K), magnesium (Mg) and silicates were found to be the most catalytically active constituents among plant ash [9], although their influence on the pyrolysis of individual biochemical constituents is ambiguous. Specifically, the inorganic elements have been shown to influence the rate of degradation and act as a catalyst for depolymerisation, dehydration, fragmentation, or char rearrangement reactions [10], Boudouard reaction and water–gas shift reaction [11]; and increase hydrogen (H_2), carbon oxides and char yield, while reducing the amount of liquids [12,13]. According to Collard et al. [14] one metal can promote the char rearrangement of one component and support the depolymerization of another component at the same time. Furthermore, two metals can have different catalytic effects (char rearrangement or depolymerization) on one biochemical constituent [14]. This observation was also confirmed by Lu et al. [15], who concluded that most of the inorganic compounds catalyze the biomass selectively, for instance potassium phosphate catalyzes the thermal decomposition of lignin, while the pyrolysis of holocellulose is inhibited. The knowledge of biomass composition is therefore essential for estimating the suitability of particular types of biomass for pyrolysis.

The predominance of the influence of individual biomass constituents may depend also on biomass taxonomy. Hodgson et al. [16] found a significant genotypic variation in the composition between *Miscanthus* species and genotypes, and a clear relationship between the biomass composition, yields of pyrolysis products, and the composition of the volatile fraction. Kelkar et al. [13] concluded that taxonomy does not affect the pyrolysis product composition, although they observed a discrepancy in the pyrolysis products between grasses. The difference was based on the six key chemical markers (glycolaldehyde, acetic acid, acetol, methyl glyoxal, 4-vinylphenol, and levoglucosan) of pyrolysis liquid. Conversely, Murillo et al. [17] found that products distribution is diverse and unique to the nature of the feedstock, especially in the temperature range between 450 and 700 °C. Similarly, Jeffrey et al. [18] analyzed five near-isogenic brown midrib hybrids in maize and found statistically significant differences for nine compounds, when comparing the hybrids, and 17 significant differences when comparing maize cobs with stover. The effect of genotypic differences on the products distribution from pyrolysis of switchgrass was observed by Serapiglia et al. [10] who found that pyrolysis products were most influenced by the contents of cellulose and K in switchgrass. The number of studies investigating the effect of taxonomy on the distribution of pyrolysis products, however, is still limited, although this knowledge would aid in the identification and generation of the most suitable species with improved conversion quality characteristics [10,16].

The purpose of this study was to investigate the effect of feedstock composition and taxonomy on the products distribution from pyrolysis of herbaceous species commonly grown on permanent grasslands in the Czech Republic (CZ). Specifically, five non-hybrid perennial grasses such as mountain brome, tall oat-grass, tall fescue, redtop, and reed canary grass, three hybrid grasses (crosses between Festuca × Lolium) and one leguminous plant – red clover – were selected and pyrolyzed in a fixed bed reactor. The relationships between grassland biomass composition and the yields and composition of pyrolysis gaseous, liquid, and solid products were determined using analyses commonly applied to identify commonalities and/or discrepancies between species such as cluster analysis and Pearson correlations.

2. Materials and methods

2.1. Materials

The herbaceous plants were obtained from OSEVA Research and Development Ltd. Zubří, CZ, where they were harvested in May 2013. Five samples of non-hybrid perennial grasses, three samples of hybrid grasses (crosses between fescue (*Festuca*) and ryegrass (*Lolium*)), and one sample of leguminous plant were selected. The summary of grassland biomass species and their taxonomic affiliation are presented in Table 1.

2.2. Feedstock preparation and analysis

Prior to analysis, the herbaceous plants were milled and homogenized using a vibratory sieve shaker ANALYSETTE 3 SPARTAN (FRITSCH) for 5 min. The ultimate analysis of biomass samples was conducted according to the standard test method EN 15104 using the EuroEA3000 CHNS-O analyzer (EuroVector, Italy). The proximate analysis of grassland biomass was performed using the TGA701 thermogravimetric (TG) analyzer (Leco) according to (i) the ISO 11722 standard test method to establish the content of moisture, (ii) the EN 15402 standard test method to determine the content of volatile matter (VM), and (iii) the EN 15403 standard test method to establish the content of ash. The content of fixed carbon (FC) was calculated by difference. The content of lignin was determined according to the EN ISO 13906 standard test method. The contents of cellulose and hemicellulose were established according to the method described by Kačík and Solár [19]. The content of extractives was determined according to the ASTM E1690-95 standard test method. Finally, X-ray fluorescence (XRF) was used to determine the content of inorganic elements in ash. The analysis was conducted using the SPECTRO XEPOS III HE (SPECTRO) spectrometer. The results of all analyses are presented in Table 2.

2.3. Thermogravimetric analysis (TGA)

The thermogravimetric experiments were conducted using NETZSCH STA 409 EP. Samples of approximately 10 mg were heated to a final temperature of 900 °C at a heating rate of 10 °C/min in aluminum crucibles under argon with a flow rate of 100 cm^3/min. To validate the results, the experiments were run in duplicate.

2.4. Pyrolysis experiments

The pyrolysis experiments were performed in a stainless steel fixed bed reactor. The temperature of the reactor was controlled by a PID temperature controller (Model 4836, Parr), whereas the temperature of the reaction was sensed by a K-type thermocouple. A more detailed

Table 1
Taxonomic affiliation of grassland biomass.

Common name	Binomial name	Order	Family	Subfamily	Group	Tribe
Mountain brome	*Bromus marginatus* Nees ex Steud.	Poales	Poaceae	Pooideae	Triticodae	Bromeae
Tall oat-grass	*Arrhenatherum elatius* L.	Poales	Poaceae	Pooideae	Poodae	Avenae
Tall fescue	*Festuca arundinacea* Schreb.	Poales	Poaceae	Pooideae	Poodae	Poeae
Redtop	*Agrostis gigantea* Roth.	Poales	Poaceae	Pooideae	Poodae	Avenae
Reed canary grass	*Phalaroides arundinacea* L.	Poales	Poaceae	Pooideae	Poodae	Avenae
Festulolium Perun	*Lolium multiflorum* Lam. × *Festuca pratensis* Huds.	Poales	Poaceae	Pooideae	Poodae	Poeae
Festulolium Becva	*Lolium multiflorum* Lam. × *Festuca arundinacea* Schreb.	Poales	Poaceae	Pooideae	Poodae	Poeae
Festulolium Lofa	*Lolium multiflorum* Lam. × *Festuca arundinacea* Schreb.	Poales	Poaceae	Pooideae	Poodae	Poeae
Red clover	*Trifolium pratense* L.	Fabales	Fabaceae	Faboideae		Trifolieae