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Effect of composting on the production of syngas during pyrolysis of perennial grasses

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HIGHLIGHTS

- Pyrolysis of perennial grasses and their composts is investigated.
- Composting increases syngas concentration and higher heating value (HHV).
- Composting decreases the temperature at which an explicit H_2/CO is reached.
- Composting influences contents of biochemical components, humic substances and char.

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ABSTRACT

The effect of composting on the production of syngas, a mixture of hydrogen (H_2) and carbon monoxide (CO) with an explicit H_2/CO = 2 or H_2/CO = 3 during pyrolysis of six non-hybrid grasses (NHG) and three hybrid grasses (HG) was investigated. The pyrolysis experiments were conducted in a fixed bed reactor to a final temperature of 700 °C. The experimental results obtained in this study demonstrated that composting changed the composition of biomass, significantly reduced the content of carbon dioxide (CO_2) and made H_2 and CO the primary constituents of pyrolysis gas. A significant increase in syngas concentration and a higher heating value (HHV), followed by a decrease in the temperature at which a specific H_2/CO was reached, was observed due to composting as well. The change was associated with thermal decomposition of biochemical components, formation of humic substances, and secondary reactions of char.

1. Introduction

Biomass is a clean, renewable, and CO_2-neutral material which can be converted to energy through thermo-chemical (i.e., pyrolysis) and bio-chemical/biological processes [1]. Due to its low utilization efficiency it is also one of the most abundant and at the same time readily available energy sources [2]. The biomass that can be utilized as an energy source includes but is not limited to energy crops. The energy crops are woody and grasses/herbaceous plants (all perennial crops) that can grow with a high productivity associated with lower environmental maintenance and investment costs due to the shorter time between plantation and harvesting [3–5].

Several factors are taken into consideration in determining the selection of the type of grass to be cultivated: moisture, ash, volatile matter, alkali and trace elements contents, and biochemical components [1,6]. Moisture, ash, volatile matter, alkali and trace elements contents affect the selection of thermal conversion processes [6]. As an example, biomass consists of much higher volatile matter content (80%) than fossil fuels (20%), therefore it can be easily converted through thermo-chemical processes to higher-value fuels such as hydrogen (H_2) [1]. On the other hand, biochemical structures influence biochemical fermentation processes and affect products of thermo-chemical processes [6].

Biomass is comprised of the following three basic biochemical structures: cellulose, hemicelluloses, and lignin [6–8]. Regarding the suitability of plant species for subsequent processing as energy crops, the contents of cellulose and lignin are of particular importance as they are, similarly to volatile matter, associated with the production of higher-value fuels (H_2). Perennial crops contain a lower amount of lignin compared to the contents of cellulose and

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hemicellulose [6,8]. Lignin is responsible for the highest H_2 and methane (CH_4) formation, cellulose for the highest carbon monoxide (CO) release, and hemicellulose for the highest carbon dioxide (CO_2) emission [9–12]. As pointed out by Yang et al. [10] lignin releases four times more H_2 than cellulose and three times more than hemicellulose. To alter the biochemical composition of perennial crops and therefore increase the release of H_2 (i.e., increase the content of lignin) pretreatment methods such as composting can be applied [13–16].

Composting is a naturally occurring, biological decomposition process in which bacteria, fungi, and other microorganisms brake down the existing organic matter into a more stable form called compost [13–15]. Barneto et al. [15] reported a 24–30% increase in the lignin content and 8–17% and 28–44% decreases in the contents of hemicellulose and cellulose, respectively due to composting of Leucaena (tree) and Tagasaste (shrub). Corsaro et al. [17] investigated the effect of composting on the composition of perennial grasses and found that composting increases the contents of lignin and cellulose (by 461% and by 35%, respectively) and reduces the content of hemicellulose (by 89%).

A number of studies have examined the utilization of grasses through pyrolysis for bio-oil or char production as a result of their greater conversion to these fractions (i.e., 13–76% for bio-oil and 6–42% for char) [18,19]. However, there is a dearth in the literature regarding utilization of pyrolysis gas, even though the yields reported in the literature for this fraction are smaller (i.e., between 13% and 28%) [19]. The commercialization of any laboratory or pilot plant process expects possible utilization of each of the products including minor products such as gas from of grass.

The utilization of biomass to energy through pyrolysis gas depends primarily on the ratio of released H_2 to CO (syngas), but pyrolysis gas consists in majority of CO and CO_2 [9,20]. Hydrogen and lower hydrocarbons (C_1–C_3) are presented in significantly lower amounts [9,20]. The specific ratio of H_2/CO is essential due to the fact that the processes utilizing syngas for energy generation involve (i) synthesis of liquid hydrocarbons from methanol or through Fischer–Tropsch synthesis ($H_2/CO = 2$), or (ii) synthesis of natural gas ($H_2/CO = 3$) [19,21]. Both ratios are not attained without problems and depend on several factors such as the composition of raw material, operating conditions [22,23] and/or cleaning and processing [14,24]. Since composting changes the composition of biomass making H_2 and CO the primary constituents of pyrolysis gas, its effect on the production of syngas and the H_2/CO ratios needs to be adequately examined. The novelty of this research is the investigation of the effect of composting on the production of syngas during pyrolysis of perennial grasses. Six non-hybrid grasses (NHG) and three hybrid grasses (HG) are investigated and the main objective is selective formation of syngas with an explicit H_2/CO ratio in the amount of 2:1 or 3:1.

2. Materials and methods

2.1. Materials and sample preparation

Perennial grasses (six NHG and three HG) were supplied by OSEVA Research and Development s.r.o., Zubří, Czech Republic (CZ) and divided into halves. Half of each sample was subjected to composting and then to pyrolysis, whereas the other half was subjected only to pyrolysis. The grasses' sprouts were finely chopped to a size below 2 cm and then ground to a particle size below 2 μ. Similarly, the compost samples were ground to a particle size below 2 μ. Grinding was performed in the Thermomix (Vorwerk) and the Vibratory Micro Mill PULVERISETTE 0 (FRITSCH). The names and abbreviations of the grasses and their composts are listed in Table 1.

Table 1
Names and abbreviations of grasses and their composts.

Grass type	Grass name	Grass abbreviation	Compost abbreviation
Non-hybrid	Redtop – Rožnovský (*Agrostis gigantea Roth*)	R-G	R-C
	Reed canarygrass – Chrastrava (Phalaris arundinacea L.)	RC-G	RC-C
	Tall fescue – Kora (*Festuca arundinacea* Schreb.)	TF-G	TF-C
	Tall oatgrass – Rožnovský (*Arrhenatherum elatuis* L.)	TO-G	TO-C
	Mountain brome – Tacit (*Bromus marginatus* Nees ex Steud.)	MB-G	MB-C
	Mixture of clover (*Trifolium pratense*)	MC-G	MC-C
Hybrid	Festulolium Perun	FP-G	FP-C
	Festulolium Becva	FB-G	FB-C
	Festulolium Lofa	FL-G	FL-C

2.2. Composting

The composting experiments were conducted in a microcomposter (NM125, NatureMill) in the Institute of Geological Engineering, VŠB – Technical University of Ostrava (VŠB – TU Ostrava), CZ. To obtain the appropriate C/N ratio perennial grasses were mechanically mixed with spruce sawdust (Sawmill Ostravica, CZ) and garden soil (AGRO) in the ratio of 21–30/1 and placed in a mixing chamber. Consequently, the blend was continuously stirred by a mixing bar and the decomposition process took place in the presence of heat and air drawn into the mixing chamber by the air pump. The temperature during the composting process reached 60 °C. The composting of each blend (perennial grass, sawdust, and soil) was carried out for 10 days, whereas the maturation of composts was carried out for 14 days in the cure tray located just below the mixing chamber. The maturity of composts was assessed by dissolved organic carbon (DOC) using the Apollo 9000 Total Organic Carbon (TOC) analyzer (Teledyne Tekmar). All composts resulted in DOC below 17 g/kg of dry matter which was suggested as a cutoff of compost maturity by Bernal et al. [25].

2.3. Chemical characterization

The grass and compost samples were subjected to proximate and ultimate analyses. The following standard test methods were applied: EN 15402 (volatile matter), EN 15403 (ash), EN 15104 (carbon (C), nitrogen (N), and hydrogen (H)), and EN 15400 (higher heating value (HHV)). The biochemical components were determined according to the EN ISO 13906 standard test method (lignin) and the method described by Kačík and Solár [26] (cellulose and hemicellulose). Humic acids (HA) and fulvic acids (FA) were extracted from composts according to the method recommended by the International Humic Substances Society (IHSS) [27]. In addition, the X-ray fluorescence (XRF) was used to determine the contents of ash elements. The analysis was conducted using the SPECTRO XEPOS III HE (SPECTRO) spectrometer in the laboratories of the Institute of Public Health in Ostrava, CZ.

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. More detailed description of the set-up has been described elsewhere [28]. Two sets of experiments were conducted. The first