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Research article

The impact of dry torrefaction on the fast pyrolysis behavior of ash wood and commercial Dutch mixed wood in a pyroprobe

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ABSTRACT

In this study torrefied feedstocks, consisting of mixed wood and wood residues torrefied at 300 °C and ash wood torrefied at 250 and 265 °C, were pyrolyzed in a pyroprobe at five pyrolysis temperatures (600–1000 °C) and a fast heating rate (600 °C·s^{-1}) to investigate the effect of torrefaction on the formation of volatiles and their evolution in a 100 kW circulating fluidized bed gasifier. Results showed that torrefaction converted mostly the hemicellulose content of feedstocks. Furthermore, torrefaction resulted in decreasing the bio-oil and gas yields, increasing the char and phenol yields and not affecting the polyaromatic hydrocarbons yield. Phenol and naphthalene showed the largest yield at 600–700 °C and 800–1000 °C, respectively. At such high temperatures, the rest polyaromatic hydrocarbons showed yields similar to phenol's. At 900 °C torrefaction affected mainly the phenolic species, with 4-propyl-phenol being the dominant species of its group for mixed wood and wood residues feedstock. In the gasifier, H_2 and CO_2 yields increased, CH_4 yield remained constant, and CO yield depended on tar conversion and oxidation and steam reactions. The phenol and naphthalene yields further decreased and increased, respectively, whereas, polyaromatic hydrocarbons did not change in the gasifier.

1. Introduction

Biomass conversion to electricity and biofuels has become attractive due to its potential carbon neutrality and its benefits regarding the global warming impact. However, there are aspects of biomass that inhibit its use in different applications, such as its heterogeneous nature (even for the same species), its high moisture content that results in low energy density. Therefore, pretreatment technologies were developed to address such issues. Among the various biomass kinds, wood has gained attention as it is considered second generation biomass and it has a low ash content.

Torrefaction is a promising pretreatment technology which converts biomass to a more coal-alike fuel. It is a mild thermochemical process occurring between 200 and 300 °C in an inert atmosphere. During torrefaction biomass devolatilizes partially, becomes more brittle, hydrophobic, less prone to microbial and fungal degradation and increases its energy density [1]. Torrefied biomass is a potential coal-replacement fuel for boilers with a much lower carbon footprint considering its life cycle [2]. In addition, torrefaction has shown to lower the oxygen content of the biomass and to increase the aromatic fraction of the condensable species during fast pyrolysis for bio-oil production [3,4].

Hemicellulose, cellulose and lignin are the main biocomponents of biomass. These chemical components decompose at different temperature ranges. Hemicellulose is the least thermally stable component due to its amorphous nature, cellulose thermal behavior is due to its relatively strong intramolecular bonds and lignin is a complex, highly branched and heavily crosslinked polymer and therefore it is more thermally stable than the other two components. Hemicellulose decomposes in the temperature range of 200 to 315 °C and its typical products are acetic acid, acetone, furfural, CO, CO_2 and CH_4 [5]. Hemicellulose decomposition is mainly responsible for the release of CO_2. This is mainly due to its higher carboxyl content in comparison to cellulose and lignin which are mainly responsible for CO and H_2 – CH_4 production, respectively [3]. Cellulose decomposition starts approximately at 230 °C and ends at 400 °C and it produces mainly

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levoglucosan which at temperatures exceeding 500 °C vaporizes to contribute almost exclusively to the gas and liquid yields [4]. At lower temperatures active cellulose is generated with a comparatively low degree of polymerization [6]. Due to the action of radicals and increasing temperature, active cellulose undergoes further degradation to generate tar, char and light gases [7–9]. During torrefaction the active cellulose undergoes crosslinking. Severe carbon–carbon crosslinking of cellulose hinders the production of volatiles and results in increasing char production [5]. Thermal degradation of lignin starts at approximately 200 °C, but the main part of its conversion typically occurs at higher temperature, between 400 and 750 °C [10]. Lignin decomposition leads to mainly char and, secondarily, volatiles [11]. At temperatures higher than 500 °C the aromatic rings of lignin rearrange and condense releasing H_2. CO is produced both at higher and lower temperatures from ether groups. CH_4 is mainly produced from a weakly bonded methoxy group, at somewhat lower temperatures [12].

Several researchers [3,13–18] performed fast pyrolysis using a pyroprobe and focussed their studies on the effect of torrefaction of wood, agricultural residues or fractionated bio-polymers on bio-oil components production. These researchers compared torrefied and untreated biomass, but only Neupane et al. [13] and Yang et al. [20] used feedstocks with different degrees of torrefaction. On the other hand, there are researchers [21,22] who focused on investigating high temperature fast pyrolysis, but used a fixed bed reactor, a design that is similar to the pyroprobe's design (see Table 1).

Ojha and Vinu [14] pyrolyzed cellulose at 500 °C in a pyroprobe and reported mainly yields of aldehydes/ketones, furans and anhydrosugars. Srinivasan et al. [15] pyrolyzed, at 600 °C, cellulose and torrefied cellulose (at 225 °C for 30 min) in a pyroprobe. They reported no significant mass loss during the torrefaction process, rather than an effect of the process on the structure of the cellulose. They commented that torrefaction modified cellulose structure by altering the C–O–C and glycosidic bonds and reported no phenol yield in both feedstocks pyrolysis tests, and an aromatics yield only during the pyrolysis test of the torrefied cellulose. Wu et al. [18] pyrolyzed three mixtures (two personally prepared mixtures and one natural mixture) of cellulose and hemicellulose at 500–700 °C in a pyroprobe to investigate possible interactions between the polymers. They concluded that for all mixtures, the main condensable products were anhydrosugars, mainly levoglucosan, and acetone and the only quantified non-condensable gas was CO_2. The latter was quantified in larger yields in the mixture with the largest content of hemicellulose. Neupane et al. [13] performed fast pyrolysis of pine wood at 550 °C. They reported an increase in phenol and a minor increase in aromatic hydrocarbons (HC), such as benzene, naphthalene, anthracene, phenanthrene and fluorene, with increasing torrefaction level (225, 250 and 275 °C and 15, 30 and 45 mins). In an earlier study of the same authors [3], they reported a much larger increase of some aromatic HC (such as benzene, toluene, xylenes, indene and styrene) and no influence on the phenolic and naphthalene species upon torrefaction during fast pyrolysis at 650 °C of untreated and torrefied pine wood. Thangalazhy-Gopakumar et al. [17] performed fast pyrolysis of pine wood; they concluded that the bio-oil yield showed a maximum at 550 °C with levoglucosan and other anhydrous sugars being the major compounds. They also reported increasing phenols and toluene yields with increasing temperature, from 550 to 750 °C. Yang et al. [20] reported mainly oxygenated polar species from fast pyrolysis at 500–700 °C of untreated and torrefied switchgrass in a pyroprobe. Torrefaction promoted the production of the anhydrous sugars and, to a slight extent, the phenols, but apart from toluene the authors did not report other aromatics.

Mazlan et al. [21] investigated the effect of fast pyrolysis temperature, from 450 to 650 °C, on two types of untreated hardwood residues in a fixed bed drop-type pyrolyzer under a fast heating rate. They concluded that both feedstocks produced the same maximum amount of bio-oil but at slightly different temperature. When bio-oil yield decreased, non-condensable gases yield increased due to the secondary reactions. The main analyzed constituents of the bio-oil were acetic acid, tetrahydrofuran, and benzene. Zhou et al. [22] performed fast pyrolysis of lignin at 500–900 °C in a fixed bed reactor using a rapid heating rate. They reported that lignin pyrolysis results mainly in solid residue (char), except at 900 °C, where the gas yield exceeds the solid residue yield. The main heavy organic species analyzed were naphthalene and acenaphthylene, especially at 900 °C their yields increased significantly. Previous researchers investigated the effect of torrefaction of wood on fast pyrolysis and focused on selecting these process conditions that would optimize bio-oil production. Furthermore, authors put emphasis on bio-oil constituents, such as anhydrosugars, furans, etc. Therefore, literature is scarce concerning investigating on fast pyrolysis as the first chemical step at high temperature thermochemical reactors. Louwes et al. [23] investigated on fast pyrolysis of one of the two woody feedstocks used in our study, but these authors focused on bio-oil properties and supply chain analysis while using an entrained down-flow reactor.

The aim of this study is to characterize the effect of wood torrefaction on the formation of volatiles during fast pyrolysis, as the latter is the first chemical conversion step of thermochemical-converting technologies. In addition, to our knowledge this is the first time when a commercially available, severely torrefied fuel is characterized, and various non-condensable gases and PAH species are quantified under fast pyrolysis conditions. Furthermore, the pyrolysis volatiles were selected in order to be relevant to gasification's volatiles generated by mixed reactions. Therefore, the results of this study are compared with published results of O_2-steam blown circulating fluidized bed (CFB) gasification using exactly the same feedstocks [24,25] in order to show

Table 1
Literature review of similar pyroprobe research. Only the major identified compounds are reported.

Reference	Feedstock	Temperature (°C)	Heating rate (°C·s^{-1})	Holding time (s)	Non-condensable gases	Oxygenated hydrocarbons	Non-oxygenated hydrocarbons
[14]	Cellulose	500	20,000	50	CO_2	Acetaldehyde, 5-hydroxymethylfurfural	–
[15]	Torrefied and untreated cellulose	600	n.d.	n.d.	–	Levoglucosan	Aromatics[a]
[18]	Cellulose-hemicellulose mix	500–700	20,000	15	CO_2	Levoglucosan, acetone	–
[17]	Pine wood	450–750	100	30	–	Guaiacols, phenols	Toluene
[13]	Torrefied and untreated pine wood	550	2000	90	–	Phenols, guaiacols	Naphthalene, anthracene, phenanthrene and fluorene
[3]	Torrefied and untreated pine wood	650	2000	n.d.	–	Phenols, guaiacols	Naphthalene
[20]	Torrefied and untreated Kanlow switchgrass	500–700	1000	n.d.	–	Benzofuran, phenols	Toluene, benzene

[a] No species are reported, however they concern non-oxygenated hydrocarbons with one or two rings structure.