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# The effect of torrefaction on the chlorine content and heating value of eight woody biomass samples

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#### ABSTRACT

This study examined and compared the effect of torrefaction on the heating value, elementary composition, and chlorine content of eight woody biomasses. The biomass samples were torrefied in a specially constructed batch reactor at 260 °C for 30, 60, and 90 min. The original biomasses as well as the solid, liquid, and gaseous torrefaction reaction products were analyzed separately. The higher heating values (HHV) of dry samples increased from 19.5–21.0 MJ  $\text{ kg}^{-1}$  to 21.2–23.2 MJ  $\text{ kg}^{-1}$  during 60 min of torrefaction. In all samples, the HHV increased 9 % on average. Furthermore, the effect of torrefaction time on the biomass HHV was studied. Measurements showed that after a certain point, increasing the torrefaction time had no effect on the samples' HHV. This optimal torrefaction time varied considerably between the samples. For more reactive biomasses, i.e., birch and aspen, the optimal torrefaction time was close 30 min whereas the HHV of less reactive biomasses, e.g., stumps, increased markedly even after a 60-min torrefaction. Another significant observation was that torrefaction reduced the chlorine content of the biomass samples. The chlorine concentration of the solid product dropped in most samples from the original by half or even as much as 90 %. The highest relative chlorine decrease was observed in the Eucalyptus dunnii sample, which also had the highest chlorine content of all the studied biomasses. The relative carbon content of the biomass samples increased during torrefaction as the average elementary composition changed from CH\_0.123O\_0.827 to  $CH_{0.105}O_{0.674}$  after a 60-min torrefaction.

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## 1. Introduction

The growing world population and accelerating industrialization keep increasing the energy demand. The concurrent global warming and concerns about the depletion of fossil fuel reserves necessitate the development of sustainable ways to produce energy. Because biomass is considered a carbonneutral source of energy, partial replacement of coal with

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biofuels in commercial combustion units lowers the carbon dioxide emissions [1]. However, biomass properties, such as heterogeneous and tenacious structure, hydrophilic nature, and high moisture content are posing challenges to using biomass for energy production.

Torrefaction, i.e., thermal treatment at temperatures ranging from 200 to 300 °C in the absence of oxygen, transforms biomass properties close to those of fossil coal [2,3]. Torrefaction increases biomass bulk density and improves its

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storage and handling properties [4]. Furthermore, torrefaction reduces the biomass moisture content in two ways. First, increasing temperature evaporates the free water in biomass, and at above 200 °C releases the physically bound water [5]. Moreover, biomass loses partly its hydrophilic property as the hydroxyl groups decompose [1]. Torrefaction decreases the biomass oxygen content and increases the relative proportion of carbon, thus improving biomass fuel properties [2]. The vaporization of water and stripping of carbon dioxide (both with zero heating value) increase the biomass heating value. Even a 20-% increase in the biomass heating value during torrefaction has been observed [6]. Torrefaction has also shown to improve the grindability of biomass in terms of lowered energy demand and more spherical particles produced [7,8,9].

Arias et al. [10] have studied the effect of torrefaction on the reactivity and combustion properties of woody biomass and found out that torrefaction affects only to the most reactive hemicellulose components. Because of the low volatile content of torrefied biomass, the activation energy of the first stage of combustion increases [10]. Generally, hardwoods show better reactivity during torrefaction than softwoods because of their higher content of the most reactive hemicellulose component, i.e., glucuronoxylan, or xylan [6]. Compared to coal, the crucial problem in torrefied biomass use is its explosibility and higher flame speed referring to the ignition sensitivity of combustible dust and air mixture and the higher burning velocity of this powder, respectively [11].

This study focused on comparing the behavior of eight woody biomasses during torrefaction. Elementary analyses were conducted on the samples to better understand the changes in biomass during torrefaction. The effect of torrefaction on the biomass chlorine content was examined because fuel derived chlorine compounds may heavily corrode boilers [12,13,14,15] and in flue gas mitigate to the environment. Hydrogen chlorine (HCl) cause acidification [16] and dioxins are a risk to the human health because of their persistence, toxicity, and bio-accumulation resulted from their lipophilicity [17,18]. The effect of torrefaction on biomass chlorine content has not been studied commonly; however, methyl chloride has been detected in the volatile torrefaction products [19]. The torrefaction device in this study is a batch reactor with a relatively large sample particle size and sample volume together with slow torrefaction. Kim et al. [20] and Na et al. [21] have reported similar experimental set-ups.

## 2. Experimental

### 2.1. Materials

The experiments were run with eight woody biomass samples shown in Table 1. The chosen Eucalyptus samples represent globally important wood species and the other biomass samples represent common wood species in Finland.

The biomasses have been chipped, or crushed in the case of stumps, as a part of wood processing and the sample chip

Table 1 – Biomass s	amples.							
Sample	Euca d.	Euca g.	Birch	Aspen	Pine	Spruce	Residue	Stumps
Species	Eucalyptus dunnii	Eucalyptus grandis	Betula pubescens	Populus tremula	Pinus sylvestris	Picea abies	97% pine 3% birch	100% spruce
Type	Hardwood	Hardwood	Hardwood	Hardwood	Softwood	Softwood	Softwood	Softwood
Geographic location	Forestal oriental	Forestal oriental	South-East	South-East Finland	South-East Finland	Eastern Finland	Finland	South-East Finland
	plantation, Uruguay	plantation, Uruguay	Finland					
Date sample obtained	Spring 2012	Spring 2012	15.6.2012	15.6.2012	Spring 2012	27.3.2012	28.3.2012	5.6.2012
Diameter of original	Not known	Not known	1-15 cm	1–15 cm	15-30 cm	Ι	<7 cm	I
cross-section								
Age	9–11 years	9–11 years	Not known	Not known	70–80 years	Not known	30–40 years (first	60–70 years
					(final felling)		thinning)	
Storage conditions	Shipped in a	Shipped in a	Outdoors	Outdoors	Not known	In forest	In forest	In forest
before sampling	container to Finland	container to Finland						
Content	Stem wood	Stem wood	Stem wood,	Stem wood,	Stem wood from	Logging waste	Stem wood, bark,	Roots, foreign matter
			sticks, bark	sticks, bark	surface, no bark		pine needles	(soil, stones)
Maximum chip dimension	4 cm	4 cm	15 cm (sticks)	15 cm (sticks)	8 cm	12 cm	12 cm	12 cm
Moisture content, % (mass fraction)	31.8	39.5	31.7	47.1	51.4	57.2	48.2	44.8

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