

Characterization of different wood species as potential feedstocks for gasification

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Abstract. This paper provides an extended overview of the chemical characteristics of 19 different wood species originating from Estonia. The variation of chemical composition in wood and bark was investigated using a variety of analytical techniques including WD-XRF, ICP-MS, and elemental analysis. Principal component analysis (PCA) was used to observe clustering in the sample set. It revealed a clear data clustering in terms of the wood and bark samples. Wood characteristics exhibit quite narrow ranges, on the other hand the composition of wood bark samples is significantly different and more distributed. The correlations and associations among 27 chemical parameters, including 16 ash-forming elements, were studied. Several significant positive correlations between Cr-Ni-Fe, Ca-Sr, Al-Na-Si-Ti, K-Mg-P, Fe-Zn-Cr-Ni-Cu, Ash-Ca, N-S-P and O-volatile matter were found. Most of the metallic components are negatively correlated with volatile matter, C, H, O and heating value and are positively related to each other, or no significant correlation was identified. Results are compared to literature data and technical quality standards for biomass. Biomass feedstocks availability and composition for gasification process was discussed. Wood samples had higher volatiles content than in bark which is an indication that higher conversion rate and lower gasification temperature can be used. Spruce, pine and black alder barks have higher fixed carbon content than other common species that may increase biochar yield. Commonly available woods like Scots pine, Norway spruce, aspen, birch, black alder and grey alder may considered as suitable feedstocks for gasification because of their low N, S, Cl, and ash content together with high volatile matter, however, relatively high total heavy metals content were found from birch and grey alder barks compared to other hardwoods.

Key words: biomass, biomass ash, chemical composition.

INTRODUCTION

In order to reduce the share of oil shale in the Estonian energy sector, renewable fuels like woody biomass are increasingly becoming a prospective alternative to produce energy and reduce environmental impacts like greenhouse gas (GHG) emissions and the amount of ash in landfills (Konist et al., 2013). Moreover, renewable energy directive sets targets for EU Member States to raise the share of renewable sources to at least 32% by 2030 (Official Journal of the European Union, 2009; Amanatidis, 2019). There is a huge perspective for increasing natural biomass use and for co-gasification with solid

fossil fuels in the energy sector (Vassilev et al., 2013). Via gasification, biomass can be converted to synthesis gas (syngas) which is a platform for heat and power production and an intermediate to produce chemicals. The co-gasification of many biomass/coal combinations were investigated by Koppejan & van Loo (2016), Thengane et al. (2019), Ma et al. (2019), Mallick et al. (2020). For Estonian, biomass co-combustion with oil shale would be a great alternative and offers near-term solutions to cut down CO₂ emissions.

Biomass is considered a highly reactive fuel (Koppejan & van Loo, 2016) and is easy to ignite at relatively low temperatures (García et al., 2012), however in industrial plants fuel feeding requires special measures (Caillat & Vakkilainen, 2013). From previous work of our research group (Maaten et al., 2019), biomass co-combustion with oil shale was found to be technologically promising. However, the characteristics of woody biomass and the possible effects of its composition on gasification were not included in the previous work.

Biomass composition is highly variable and depends on many factors, like the type of biomass, plant species and part of the plant; growth, transport and deposition conditions; geographic location; harvesting time and technique; pick-up of extraneous material (dust, dirt, soil) etc (Vassilev et al., 2010). A lot of different data about biomass composition are available, especially about major species in Nordic countries (Eriksson et al., 2004; Antero, 2006; Werkelin et al., 2010, 2011; Pesonen et al., 2014), but there is a lack of information involving Estonian biomass characteristics that may influence thermochemical biomass conversion processes like gasification. In order to estimate the Estonian renewable energy potential, it is necessary to investigate and map biomass characteristics that are related to regional biomass including all major species in Estonia. Furthermore, the present work includes also trace elements in local wood species which is important because Estonia is one of the major wood pellets exporters (Kaup, 2018).

A direct link exists between the chemical composition of biomass and the gas obtained by gasification. For example, the calorific value of syngas depends on the heating value and moisture content of the fuel (Kirsanovs & Žandeckis, 2015). Gil et al. (2019) statistically analysed biomass properties that influence gasification and found that carbon and hydrogen contents and the heating value of the biomass promote gas production. Also, important constituents that should be considered in gasifier selection are silica, chlorine, sulphur and alkali metals, which can cause slagging, fouling, hazardous emissions and high-temperature corrosion.

The gasification process is strongly influenced or controlled by the catalyst, which leads to high selectivity towards desired products. Catalysts can be expensive and rapidly deactivated when in direct contact with biomass, and therefore, are not in common use in industrial biorefineries. Using biomass with a suitable mineral composition that acts as a catalyst may improve the syngas composition. It is reported that alkali and alkaline earth metals are the best catalysts for promoting char gasification (Nzihou et al., 2013). K and Ca in feedstocks may exhibit a catalytic effect, enhancing the char gasification reactivity and leading to a higher carbon conversion rate. Early work on the importance of alkali catalysts was done by Elliott et al. (1984), who claimed the optimum concentration of catalyst to be 3×10^{-4} – 1.5×10^{-3} mol of alkali per gram of biomass. Sueyasu et al. (2012) soaked feed biomass in a K solution before gasification to minimize tar emissions. Also, transition metals can participate as catalysts: Fe accelerates gasification and Ni prevents carbon deposition, which helps in conditioning biomass-derived syngas. Many studies have reported Ca to be a promising catalyst for increasing the gasification

rate of the char (Nzihou et al., 2013; Perander et al., 2015; Link et al., 2018). On the other hand, high alkali contents are considered a serious problem in biomass gasification due to contamination of equipment and increase maintenance costs (Ren et al., 2019).

The aim of this study was to analyse different types of wood species harvested from Estonia and analyse their suitability as gasification feedstock based on their characteristics and chemical composition. The selection of wood species was based on the principle that all dominant species harvested in Estonia should be covered in this study. Dominant wood species in Estonia are Scots pine (36%), silver birch (25.6%), Norway spruce (19.7%), aspen (7.0%), grey alder (6.8%) and black alder (3.8%) (Raudsaar et al., 2018). Additional tree species like common laburnum, hawthorn, European crab apple, blackthorn, common lilac, European ash, Norway maple, common plum, rowan, white willow, bird cherry, wych elm and common juniper were also selected for the current study. These generally have a small volume (1.2%) of the total growing stock compared to the dominant species. However, the wider selection of wood species gives a more detailed overview of biofuel characteristics and their relationships.

It is known that physicochemical properties of bark and wood differ (Olanders & Steenari, 1995; Frandsen et al., 2007; Vassilev et al., 2010; Werkelin et al., 2010; Johansson et al., 2016; Koppejan & van Loo, 2016); therefore, a comparison between bark and wood was made. Most studies have focused only on common wood species or analysed whole tree parts that contains both wood and bark and limited information on the separate components. Wood species were characterized by proximate and ultimate analysis, like ash content, heating value, volatile matter, C, H, N, S, Cl content and concentration of microelements/trace components. The data were compared to literature sources where possible. The results are compared with the data of Technical Specification (ISO 17225), which defines the biomass requirements and typical values and ranges for coniferous and broad-leaf wood and bark (results are obtained from a combination of research from Sweden, Finland, Denmark, Netherland and Germany). This study enhances our understanding of biomass composition as feedstock for gasification and will be beneficial to developing energy efficient processes.

MATERIALS AND METHODS

In total, 19 different wood species were investigated. These include 16 broad-leaf species: common laburnum (*Laburnum Anagyroides*), hawthorn (*Crataegus*), European crab apple (*Malus sylvestris*), blackthorn (*Prunus spinosa*), common lilac (*Syringa vulgaris*), European ash (*Fraxinus excelsior*), Norway maple (*Acer platanoides*), common plum (*Prunus domestica*), rowan (*Sorbus aucuparia*), white willow (*Salix alba*), bird cherry (*Prunus padus*), wych elm (*Ulmus glabra*), grey alder (*Alnus incana*), silver birch (*Betula pendula*), aspen (*Populus tremula*), black alder (*Alnus glutinosa*). 3 coniferous wood species were also included: common juniper (*Juniperus communis*), Scots pine (*Pinus Sylvestris*), Norway spruce (*Picea abies*). Samples originated from northern and southern Estonia in order to represent a wider population of tree species.

Wood samples were provided as air-dried logs. Wood and bark were separated mechanically before further analyses. The wood and bark ratios were determined gravimetrically after drying. Samples were grinded with a cutting mill and homogenized according to ISO 14780 solid biofuel sample preparation standard.

Wood samples were dried at 105 °C to a constant weight (ISO 18134-3). Ash content was determined at 550 °C (ISO 18122). Volatile matter was determined by burning the sample in a muffle furnace at 900 °C, following the procedure described in ISO 18123. Fixed carbon is the mass remaining after volatilization, excluding ash and moisture component. It can be calculated as subtracting from 100% the sum of the volatile matter and ash in percentage (Telmo et al., 2010).

Gross calorific value at constant volume ($q_{v,gr}$) was measured with IKA C2000 and IKA C5000 bomb calorimeters (ISO 18125). Gross calorific value on a dry basis ($q_{v,gr,d}$) includes the condensation enthalpy of water. Net calorific value, also called the lower heating value ($q_{p,net,d}$), is obtained when the condensation enthalpy of water is not included.

A Vario MACRO CHNS Elementar Analyser System was used to measure the C, H and N contents of the dry matter (ISO 16948). Oxygen content was calculated from the C, H, N, S, Cl and ash. Cl and S contents were measured with a Dionex 1000 ion chromatograph (ISO 16994). A Rigaku WD-XRF and Thermo Scientific iCAP Qc ICP-MS were used to determine ash forming elements and trace components in the biomass (ISO/TS 16996, ISO 16968).

Analysis results are presented according to the requirements of ISO standards. Uncertainties for every method is determined by the Nordtest (Magnusson et al., 2017) or ISO GUM method (Joint Committee For Guides In Metrology, 2008) or the relative standard deviation is given. Uncertainty estimations according to (a) the Nordtest approach ($U_c, k = 2$): HV – 3.9%; Ash – 43.0%; S – 3.2%, Cl – 4.2%, Volatiles – 4.6%; C – 1.10%; H – 4.1%; N – 19.1%; Mg – 9.4%; Fe – 9.1%; Mn – 5.4%; Zn – 11.4%; Cr – 14.8%; Ni – 16.4%; Sr – 6.6%; Ti – 11.3%; Cu – 7.4%; Pb – 8.1%; K – 19.8%; Na – 75.5% (b) ISO GUM approach ($U_c, k = 2$): O – 3.0%, FC – 27.7% and (c) RSD (rel%): Ca – 1.1%; Al – 29.2%; P – 2.2%; Si – 14.8%.

PCA was carried out with the aim of highlighting possible clusters of wood types characterized by similar properties. PCA is a chemometric technique for analysing the structure of the observations (wood and bark samples) and the variables (proximate, ultimate and trace metal analyses). PCA finds lines, planes and hyperplanes in the K-dimensional space that approximate the data as well as possible (Jackson, 1991; Jolliffe & Cadima, 2016). PCA was conducted via XLSTAT Statistical Software for MS Excel.

Chemical correlations between variables were determined in order to understand some of the fundamental relationships and trends. Data from the analysed woody biomass were subjected to the Pearson's correlation test (Plata, 2006) to calculate correlation coefficient values between 26 characteristics. The calculated correlation coefficient values include the statistically significant as well as statistically insignificant R^2 relationships, at a 95% confidence level.

RESULTS AND DISCUSSION

Proximate, ultimate analysis and heating value results are presented in Table 1. Minor and trace elements are shown in Table 2. Overall, 26 different parameters were measured for every sample. For better understanding, results are grouped as common and all wood species. Scots pine, silver birch, Norway spruce, aspen, grey alder and black alder are largely the most available resource in Estonia (Raudsaar et al., 2018), and therefore, some special attention is given to them.

Table 1. Proximate and ultimate analysis and heating value of different wood species. Literature data is included and refer to the wood type in the row above. (A – ash; VM – volatile matter; FC – fixed carbon; C – carbon; H – hydrogen; N – nitrogen; S – sulfur; O – oxygen; Cl – chlorine; HHV – higher heating value; LHV – lower heating value, wt% db – weight percent of dry basis)

Feedstock Wood	Content of wood or bark, %				Proximate analysis (wt% db)				Ultimate analysis (wt% db)				Heating value (MJ kg ⁻¹)		
	A	VM	FC	%	A	VM	FC	C	H	N	S	O	Cl	HHV	LHV
1. Broad-leaf wood (BLW)															
Aspen	87.2	0.4	87.0	12.6	50.2	6.2	0.1	0.01	43.1	< 0.01				20.07	18.72
Pesonen et al. (2014)		0.8			47.8	5.9	-							20.04	18.76
Bird cherry	90.1	0.5	86.4	13.1	48.1	6.5	0.1	< 0.01	44.8	0.01				19.11	17.69
Black alder	86.9	0.4	86.1	13.5	50.6	6.2	0.2	0.03	41.8	< 0.01				19.79	18.45
Blackthorn	81.9	0.6	84.4	15.0	48.4	6.3	0.2	< 0.01	44.5	0.01				19.24	17.86
Common laburnum	90.1	0.5	81.2	18.3	47.8	6.6	0.3	0.07	44.6	0.02				19.59	18.15
Common lilac	89.4	0.5	85.0	14.5	48.7	6.5	0.2	< 0.01	44.2	0.01				19.55	18.14
Common plum	57.9	0.5	83.2	16.3	49.5	6.4	0.2	< 0.01	43.4	0.01				19.65	18.26
European ash	94.9	0.4	84.9	14.7	49.1	6.5	0.1	< 0.01	43.8	0.01				19.44	18.03
European crab apple	96.3	0.8	83.5	15.8	47.0	6.5	0.1	0.02	45.6	0.01				19.22	17.81
Grey alder	90.8	0.4	85.7	13.9	49.9	6.6	0.2	< 0.01	43.0	< 0.01				19.95	18.52
Pesonen et al. (2014)		0.33			48.5	6.1	0.2							20.44	19.11
Hawthorn	92.9	1.6	81.6	16.8	48.1	6.5	0.2	0.05	43.6	0.01				19.82	18.40
Norway maple	92.7	0.6	86.2	13.3	48.7	6.5	0.1	< 0.01	44.1	0.01				19.36	17.95
Rowan	92.4	0.8	85.0	14.2	48.5	6.5	0.1	< 0.01	44.1	< 0.01				19.07	17.65
Silver birch	87.3	0.3	86.9	12.8	49.3	6.6	0.1	< 0.01	43.7	0.01				19.94	18.10
Pesonen et al. (2014)		0.4			48.2	6.1	-							19.80	18.46
White willow	92.7	0.5	85.2	14.3	48.4	6.5	0.1	< 0.01	44.5	< 0.01				19.72	18.31
Wych elm	89.8	1.8	79.9	18.4	49.6	6.5	0.2	< 0.01	42.1	0.01				19.69	18.29
Common BLW															
Mean	88.0	0.4	86.4	13.2	50.0	6.4	0.2	0.02	43.1	< 0.01				19.94	18.45
Minimum	86.9	0.3	85.7	12.6	49.3	6.2	0.1	0.01	42.6	< 0.01				19.79	18.10
Maximum	90.8	0.4	87.0	13.9	50.6	6.6	0.2	0.03	43.7	0.01				20.07	18.72
All BLW															
Mean	87.8	0.7	84.5	14.8	48.9	6.5	0.2	0.01	43.9	0.01				19.58	18.15
Minimum	57.9	0.3	79.9	12.6	47.0	6.2	0.1	0.01	42.1	< 0.01				19.07	17.65
Maximum	96.3	1.8	87.0	18.4	50.6	6.6	0.3	0.03	45.6	0.01				20.07	18.72

Table 1 (continued)

Feedstock	Content of wood or bark, (wt% db)		Proximate analysis (wt% db)				Ultimate analysis (wt% db)				Heating value (MJ kg ⁻¹)	
	%	A	VM	FC	C	H	N	S	O	Cl	HHV	LHV
2. Coniferous wood (CW)												
Common juniper	86.2	1.2	82.3	16.6	48.8	6.8	0.2	< 0.01	43.1	0.01	20.65	19.16
Norway spruce	92.2	0.3	85.5	14.2	50.3	6.6	0.1	< 0.01	42.7	0.01	19.79	18.35
Scots pine	89.3	0.3	85.2	14.5	50.1	6.6	0.2	< 0.01	42.8	0.01	20.04	18.61
Mason et al. (2015)		2.0	82.5	17.5	47.4	5.3	1.3		45.9		18.6	
Common CW												
Mean	90.7	0.3	85.4	14.3	50.2	6.6	0.1	0.01	42.7	0.01	19.92	18.48
All CW												
Mean	89.2	0.6	84.3	15.1	49.8	6.7	0.1	0.01	42.8	0.01	20.16	18.71
Minimum	86.2	0.3	82.3	14.2	48.8	6.6	0.1	0.01	42.7	0.01	19.79	18.35
Maximum	92.2	1.2	85.5	16.6	50.3	6.8	0.2	0.01	43.1	0.01	20.65	19.16
Bark												
Broad-leaf wood (BLW)												
Aspen	12.9	3.5	79.8	16.7	53.4	6.4	0.9	0.07	35.8	< 0.01	21.37	19.99
Bird cherry	9.9	4.9	72.8	22.4	48.6	5.9	1.0	0.06	39.7	0.01	19.36	18.07
Black alder	13.1	3.2	71.3	25.5	55.1	5.9	1.3	0.05	34.4	0.02	21.97	20.69
Blackthorn	18.2	6.8	76.3	16.9	52.6	6.7	0.9	0.06	33.0	0.03	22.77	21.32
Common laburnum	9.9	2.7	77.0	20.3	49.2	6.4	2.5	0.10	39.0	0.02	21.02	19.62
Common lilac	10.6	3.2	76.3	20.5	48.6	6.1	0.9	0.07	41.1	0.01	19.85	18.52
Common plum	42.1	5.9	67.5	26.6	48.6	5.5	1.0	0.05	38.9	0.01	19.58	18.37
European ash	5.1	9.3	74.8	15.9	45.0	5.5	0.6	0.06	39.6	0.01	17.86	16.66
Zajac et al. (2018)		9.14										
European crab apple	3.7	16.9	69.2	13.9	44.1	5.2	1.0	0.07	32.8	0.01	16.47	15.34
Grey alder	9.2	2.7	74.0	23.4	53.5	6.5	1.1	0.05	36.2	< 0.01	22.27	20.86
Hawthorn	7.1	13.7	68.8	17.5	47.9	5.7	0.9	0.11	31.6	0.03	19.46	18.22
Norway maple	7.3	10.4	74.0	15.6	43.9	5.5	0.8	0.03	39.4	0.01	17.14	15.94
Bryers, (1996)		4	76.6	19.4	52	6.2	0.4	0.11	41.3			
Rowan	7.6	4.1	77.9	18.0	49.4	6.5	0.6	0.04	39.4	0.01	20.63	19.22

Table 1 (continued)

Feedstock	Content of wood or bark, (wt% db)		Proximate analysis (wt% db)				Ultimate analysis (wt% db)					Heating value (MJ kg ⁻¹)	
	%	A	VM	FC	C	H	N	S	O	Cl	HHV	LHV	
Silver birch	12.7	1.4	80.1	18.5	56.3	7.0	0.4	0.02	34.8	0.02	24.18	22.66	
Bryers, (1996)		2.1	78.5	19.4	57.0	6.7	0.5	0.10	35.7				
White willow	7.3	9.0	69.6	21.4	45.8	5.4	0.6	0.08	39.1	0.01	18.48	17.30	
Wych elm	10.2	13.4	72.0	14.6	44.8	5.5	0.9	0.07	35.4	0.01	17.31	16.12	
Bryers, (1996)		8.1	73.1	18.8	50.9	5.8	0.7	0.11	42.5				
Common BLW													
Mean	12.0	2.7	76.3	21.0	54.6	6.4	0.9	0.05	35.3	0.01	22.45	21.05	
Minimum	9.2	1.8	71.3	16.7	53.4	5.9	0.4	0.02	34.4	<0.01	21.37	19.99	
Maximum	13.1	3.5	80.1	25.5	56.3	7.0	1.3	0.07	36.3	0.02	24.18	22.66	
All BLW													
Mean	11.5	6.8	73.5	19.8	49.3	6.0	0.9	0.06	37.0	0.01	19.97	18.68	
Minimum	3.7	1.4	67.5	13.9	43.9	5.2	0.4	0.02	31.7	<0.01	16.47	15.34	
Maximum	42.1	16.9	80.1	26.6	56.3	7.0	2.5	0.11	41.2	0.03	24.18	22.66	
Coniferous wood (CW)													
Common juniper	13.8	7.2	73.0	19.8	49.2	6.0	0.6	0.07	37.0	0.03	19.66	18.35	
Norway spruce	7.9	7.9	71.1	21.0	48.4	5.6	0.6	0.02	37.6	0.01	18.72	17.50	
Frandsen et al. (2007)		4.9			49.9	5.8	0.5	0.04					
Antero (2006)		2.3	77	23	51.1	6	0.4	0.03			20.3	19.0	
Brunner et al. (2013)		4.8			49.8	5.7	0.34	0.03	40.8	0.01			
Scots pine	10.7	3.1	70.1	26.9	52.8	6.1	1.2	0.05	36.9	0.01	21.40	20.08	
Jerzak, (2020)		1.56	67.98		55.95	5.29	0.05	0.03	37.03	0.012			
Antero (2006)		2.3	74.3	25.7	53.4	5.8	0.4	0.03			21.3	20.0	
Vassilev et al. (2010)		1.9	73.7	24.4	53.8	5.9	0.3	0.07	39.9	0.01			
Common CW													
Mean	9.3	5.5	70.6	24.0	50.6	5.8	0.9	0.04	37.2	0.01	20.06	18.79	
All CW													
Mean	10.8	6.0	71.4	22.6	50.1	5.9	0.8	0.05	37.2	0.01	19.93	18.64	
Minimum	7.9	3.1	70.1	19.8	48.4	5.6	0.6	0.03	36.9	0.01	18.72	17.50	
Maximum	13.8	7.9	73.0	26.9	52.8	6.1	1.2	0.07	37.6	0.03	21.40	20.08	

Table 2. Minor and trace elements (ppm, db)

Feedstock	Al	K	Na	Ca	Si	Mg	Fe	P	Mn	Zn	Cr	Ni	Sr	Ti	Cu	Pb
Wood																
Broad-leaf wood (BLW)																
Aspen	51	479	20	890	51	648	47	100	3	6	-	0.2	2.3	-	0.9	<0.1
Werkelin et al. (2010)	6	1,370	15	998	63	286	5	49	49	5	1.5	0.2	2.3	2.7	0.4	0.1
Bird cherry	22	547	17	1,482	68	280	46	98	9	5	-	0.1	2.9	-	1.5	-
Black alder	17	354	6	1,171	35	354	43	104	10	6	-	0.1	7.6	0.5	0.4	-
Blackthorn	23	779	29	1,920	55	415	40	96	1	2	1.1	0.1	4.8	-	0.6	-
Common laburnum	29	766	32	1,146	95	338	41	139	2	3	0.4	0.1	3.3	-	0.1	-
Common lilac	24	693	34	1,127	61	388	41	194	2	15	0.1	-	3.4	1.9	1.8	-
Common plum	23	699	31	1,060	66	297	43	143	1	3	0.2	0.1	3.0	-	1.5	-
European ash	17	597	114	891	46	360	40	81	0.2	2	0.1	0.4	10.1	2.4	0.8	-
European crab apple	29	869	41	2,551	58	365	42	124	1	5	0.2	0.1	2.2	-	0.9	0.3
Grey alder	19	496	12	1,091	35	268	41	137	8	8	0.4	0.1	6.9	0.9	2.9	-
Hawthorn	40	1,124	232	5,522	100	394	45	372	2	12	0.5	0.2	1.4	0.1	0.4	-
Norway maple	20	769	22	1,316	48	417	40	162	13	2	0.2	0.2	3.1	1.1	0.4	0.4
Rowan	17	1,093	40	1,692	38	513	41	79	114	7	1.3	1.0	2.5	2.1	0.2	0.5
Silver birch	14	473	12	1,036	21	421	39	51	44	14	0.3	0.3	2.2	2.4	1.0	-
Werkelin et al. (2010)	2	315	4	636	77	92	6	102	2	17	0.1	0.1	10.4	0.3	2.0	-
White willow	28	1,192	31	975	51	333	43	288	2	2	0.2	0.0	2.5	2.4	2.0	-
Wych elm	21	4,847	47	3,371	175	391	43	172	1	2	0.2	0.0	2.5	2.1	1.5	0.5
Common BLW																
Mean	25	451	13	1,047	36	423	43	98	16	8	0.2	0.2	2.5	0.5	0.9	0.2
Minimum	14	354	6	890	21	268	39	51	3	6	0.0	0.1	2.2	0.0	0.2	0.0
Maximum	51	496	20	1,171	51	648	47	137	44	14	0.4	0.3	2.9	2.1	1.5	0.5
All BLW																
Mean	25	986	45	1,703	63	386	42	146	13	7	0.4	0.2	4.3	0.9	1.0	0.1
Minimum	14	354	6	890	21	268	39	51	0	2	0.0	0.0	1.4	0.0	0.1	0.0
Maximum	51	4,847	232	5,522	175	648	47	372	114	17	1.5	1.0	10.4	2.7	2.9	0.5

Table 2 (continued)

Feedstock	Al	K	Na	Ca	Si	Mg	Fe	P	Mn	Zn	Cr	Ni	Sr	Ti	Cu	Pb
Coniferous wood (CW)																
Common juniper	30	591	43	5,817	49	371	42	181	5	5	0.4	0.2	3.0	1.7	0.9	-
Norway spruce	14	246	13	1,118	26	233	38	17	11	5	0.3	0.2	8.9	1.2	0.3	1.4
Werkelin et al. (2010)	3	235	7	752	93	99	5		100							
Scots pine	16	530	16	718	28	241	41	103	6	6	0.3	0.1	1.4	-	1.0	0.1
Werkelin et al. (2010)	4	407	15	641	123	189	8		81							
Common CW																
Mean	15	388	15	918	27	237	40	60	9	5	0.3	0.1	5.2	0.6	0.7	0.7
All CW																
Mean	20	456	24	2,551	34	282	40	100	7	5	0.3	0.2	4.5	1.0	0.7	0.5
Minimum	14	246	13	718	26	233	38	17	5	5	0.3	0.1	1.4	0.0	0.3	0.0
Maximum	30	591	43	5,817	49	371	42	181	11	6	0.4	0.2	8.9	1.7	1.0	1.4
Bark																
Broad-leaf wood (BLW)																
Aspen	70	4,727	86	9,527	164	1,618	55	812	25	123	-	0.1	14.1	0.3	2.1	-
Bird cherry	316	1,787	142	22,762	616	645	391	589	215	108	254.7	128.5	27.8	14.5	36.3	3.5
Blackthorn	84	1,959	125	26,708	222	1,268	65	615	11	13	1.4	0.9	87.4	3.5	6.2	0.2
Black alder	85	122	66	13,191	255	470	60	195	75	27	1.0	0.5	26.8	1.6	9.5	1.2
Common laburnum	154	5,468	73	6,479	431	1,451	115	1381	11	52	3.7	0.8	22.1	6.0	3.9	0.4
Common lilac	209	3,972	197	10,259	659	1,154	167	757	21	119	1.5	37.6	24.0	9.2	3.4	0.6
Common plum	209	2,968	120	29,078	492	934	261	490	18	38	78.7	44.6	66.3	14.5	20.8	1.2
European ash	605	1,503	359	34,067	2,930	962	1377	300	103	960	407	236.7	64.1	37.5	41.6	2.7
European crab apple	393	4,039	297	63,910	1,379	1,434	125	985	28	135	9.9	1.7	189.6	31.6	6.7	1.8
Grey alder	393	1,414	63	8,715	247	476	494	404	62	109	191.7	92.3	14.3	7.1	26.7	4.5
Hawthorn	2,810	2,432	1,204	38,453	9,487	946	581	777	61	139	8.2	2.0	48.4	160	14.8	4.6
Norway maple	343	3,817	181	43,797	3,068	1,198	154	619	233	99	3.3	1.9	29.3	9.4	6.1	0.8
Rowan	117	3,131	123	15,863	345	1,246	120	505	833	139	6.9	2.7	21.7	2.8	9.6	0.8
Silver birch	102	606	38	4,489	163	703	184	195	201	157	59.9	31.0	10.5	2.4	5.2	0.4

Table 2 (continued)

Feedstock	Al	K	Na	Ca	Si	Mg	Fe	P	Mn	Zn	Cr	Ni	Sr	Ti	Cu	Pb
Werkekin et al. (2010)	19	1,710	14	7,860	114	323	24	534								
White willow	146	5,741	289	33,966	910	1,481	71	800	16	332	0.3	0.2	24.2	2.6	4.6	0.1
Wych elm	153	5,067	149	49,587	4,140	1,102	73	870	11	13	1.8	1.2	138.3	8.7	8.6	0.6
Common BLW																
Mean	163	1,717	63	8,981	207	817	198	402	91	104	84.2	31.0	16.4	2.9	10.8	1.5
Minimum	70	122	38	4,489	163	470	55	195	25	27	1.0	0.1	10.5	0.3	2.1	0.0
Maximum	393	4,727	86	13,191	255	1,618	494	812	201	157	191.7	92.3	26.8	7.1	26.7	4.5
All BLW																
Mean	356	2,800	207	25,421	1,416	995	250	598	116	152	70.7	37.9	54.1	17.7	12.6	1.4
Minimum	70	122	38	4,489	163	470	55	195	11	13	0.3	0.1	10.5	0.3	2.1	0.0
Maximum	2,810	5,741	1,204	63,910	9,487	1,618	1,377	1,381	833	960	407.2	236.7	189.6	160	41.6	4.6
Coniferous wood (CW)																
Common juniper	405	1,574	302	27,033	1,094	566	151	424	41	39	5.3	1.2	15.4	18.5	4.0	3.1
Norway spruce	79	786	86	32,175	193	795	114	333	193	231	98.5	45.3	188.9	2.8	14.3	0.7
Frandsen et al. (2007)	616	2,493	103	13,196	3,866	781	377	361	428							
Werkekin et al. (2011)	98	2,030	26	8,350	171	865	39	452	714							
Antero (2006)		3,003	89													
Brunner et al. (2013)		1,825	79	13,450	1,810	822		338		85						
Scots pine	87	2,095	29	12,947	102	459	186	310	48	50	138.2	91.4	15.7	3.5	14.4	0.2
Ragland et al. (1991)	2,149	1,333	280	5,282	5,278	1,137	609									
Werkekin et al. (2010)	908	3,180	22	6,350	60	874	52	343								
Common CW																
Mean	83	1,441	58	22,561	148	627	150	322	120	141	118.4	68.3	102.3	3.2	14.3	0.4
All CW																
Mean	190	1,485	139	24,052	463	607	150	356	94	107	80.7	45.9	73.3	8.3	10.9	1.3
Minimum	79	786	29	12,947	102	459	114	310	41	39	5.3	1.2	15.4	2.8	4.0	0.2
Maximum	405	2,095	302	32,175	1,094	795	186	424	193	231	138.2	91.4	188.9	18.5	14.4	3.1

It is noticeable that in most of the species bark is less than 10% of the overall stem wood (Table 1). However, there are some exceptions like common plum where the bark ratio reached over 42%. This result may be explained by the factors that affect bark thickness: wood species, the age and growing conditions (Sonmez et al., 2007; Koman & Feher 2015). It should be considered that wood chips are generally produced from whole trees; therefore, the prominent component is wood and bark makes only a small contribution to the average. However, bark is a main source of ash, different extractives and elements that may affect the biomass gasification process and need careful consideration.

Ash yield

Ash content is an important quality parameter of biomass. A high content of ash is undesirable in most conversion processes as it causes problems related to utilization and process design, reduces the heating value (Elbersen et al., 2017) and affects dust emission (Koppejan & van Loo, 2016). Biomass with an ash content over 10% is considered to have a high risk of slag formation (Ren et al., 2019). However, there is no evidence that the ash content in a gasification process directly influences gas composition, although ash can cause a variety of problems like slagging, which is influenced by the presence of alkaline metals in biomass.

Results show that the wood part of most of the species has a relatively low ash content ranging between 0.3 to 1.8%. Only hawthorn and wych elm have a higher ash content, 1.56% and 1.75%, respectively, compared to typical broad-leaf wood values (0.2–1.0%). The ash content of pine and spruce (0.2–0.3%) matches standardized values of 0.1–1.0% according to ISO 17225. However, common juniper has a higher ash content than other softwoods. Mason et al. (2015) report much higher ash values for pine and willow, 1.9% and 2.0%, respectively. On the other hand, the alder ash content is similar to that from Pesonen et al. (2014). It is stated that the ash content in untreated wood of different species is 0.1% to 0.6% and in bark 3% to 5% (Ragland et al., 1991), but it can reach up to 20% for some biomasses (Caillat & Vakkilainen, 2013). In gasification mostly a mixture of bark and wood is used; therefore, ash content is primary dependent on the bark content of the feedstock. Results show that broad-leaf trees have higher ash contents than coniferous wood, which is similar to earlier findings (Alakangas et al., 2016).

The ash content of bark (1.4–16.9%) was significantly higher than that of stem wood (0.3–1.8%). Silver birch, alder and common laburnum have the lowest ash contents in the bark: 1.4%, 2.7% and 2.7%, respectively. These values lie between the typical broad-leaf wood bark ash content values of 0.8–3.0% according to ISO 17225. The bark ash content of birch and European ash, 1.4 and 9.3%, respectively, are similar to the values of 2.1% (Bryers, 1996) and 9.14% (Zajac et al., 2018) reported in previous studies. However, most of the analysed Estonian hardwood barks have higher ash values than typical hardwood. The wood species with the highest bark ash content are European apple tree 16.9%, hawthorn 13.7%, wych elm 13.4% and Norway maple 10.4%. High ash content may be due to mossy bark. Contaminants from soil can lead to severe problems like fouling and slagging (Caillat & Vakkilainen, 2013). The ash content of 3.1% for pine bark was within the typical range of values for softwood bark (< 1.0–3.0%) and comparable to the value reported by Antero (2006) (2.3%). Norway spruce and common juniper have higher ash contents of 7.9 and 7.2%, respectively.

A high ash content is normally undesirable since it complicates the operational process. Moreover, it is stated that higher ash content promotes the growth of CO and H₂ concentration in the syngas and the decrease of CH₄ content (Kirsanovs & Žandeckis, 2015). On the other hand, it is possible to use biomass with a suitable ash composition that may act as a natural catalyst for char gasification and tar removal. Therefore, ash yield alone is not a sufficient parameter for estimating the suitability of different woody samples. The chemical composition, especially alkali and alkali-earth metals concentrations, should additionally be considered (discussed in the following paragraphs).

Heating value

Heating value (HV) is an expression of the energy content released when burnt in air (McKendry, 2002). HV is not highly variable from one tree species to another (Table 1). The HHV of wood lays between 19.07 and 20.65 MJ kg⁻¹. These results are similar to earlier findings, where no significant differences in HVs of different wood species and barks were found (Pesonen et al., 2014). On contrary, HHV of bark is much more distributed and values range between 16.47 and 24.18 MJ kg⁻¹. Moreover, silver birch bark has the highest HV of 24.18 MJ kg⁻¹ exceeding a typical hardwood bark HV of 20.0 MJ kg⁻¹ (according to ISO 17225). This result may be explained by the fact that birch bark is rich in extractives and suberin (Pinto et al., 2009) that may contribute to higher HV. Also, it is reported that lignin content has strong positive correlation to HV (Demirbaş, 2001). However, Pesonen et al. (2014) states that the HV of silver birch wood HV is much lower, 18.46 MJ kg⁻¹, but aspen and alder have very similar results to current results. The lowest HV determined was for European crab apple bark, 16.47 MJ kg⁻¹, where a negative correlation is seen between ash content (16.91%) and HV. The HV of the pine bark analysed is similar to those reported by Antero (2006), McKendry (2002) and Phyllis2 Database. In contrast, spruce bark has a lower HV than reported by Antero (2006) and the Phyllis2 Database, but still lies between values that are typical for softwood barks. Overall, the mean HVs of hardwood and softwood are very similar, although softwood samples tend to have a slightly higher HV, as supported by previous findings (Ragland et al., 1991; Nurmi, 2000).

The HHV of the biomass along with C and H content were found to promote the concentrations of CO and combustible gas, the calorific value of the product gas and the gasification conversion (Gil et al., 2019). Therefore, bark samples that have much higher HHV than wood samples may appear to be more suitable feedstocks for gasification.

Volatile matter

Data for the volatile matter (VM) of the biomass samples indicates that there is no significant difference between broad-leaf and coniferous wood. The same trend is seen in bark samples. Wood samples have higher VMs compared to barks (79.9–86.6% versus 67.5–80.1%). According to the literature, VM in woody biomass lies between 70.20 and 93.99% (Miles et al., 1996; Koziński & Saade, 1998; McKendry, 2002; Cuiping et al., 2004; Demirbas, 2004; Eriksson et al., 2004; Grammelis et al., 2006; Saidur et al., 2011; García et al., 2012; Miccio et al., 2012; Rizvi et al., 2015; Lu et al., 2018). The VM of willow and pine wood is similar to that result reported by Mason et al. (2015). Silver birch bark had the highest VM among all barks, similar to results obtained by Bryers (1996). The VM content of Norway spruce coincides with the content reported by Antero (2006).

According to the literature, a higher volatile matter increases the biomass conversion rate in comparison to biomasses with higher fixed carbon content (Roldan, 2018). Therefore, the conversion rate of wood samples in thermochemical processes should be much higher than bark samples. Kurkela (1996) found that a lower volatiles content decreases the reactivity of pine bark compared to wood, and therefore, pine bark gasification needs an extra 100 °C increase in the temperature. These findings suggest that samples with higher VM matter, like wood samples, are preferred for gasification when a lower gasification temperature is required.

Fixed carbon

Fixed carbon (FC) is the carbon found in the material that remains after volatile materials are emitted. FC content is linked to the biochar yield which is reported to be higher for biomasses with high FC (Roldan, 2018). FC in wood and bark samples varies between 12.6–18.4% and 13.9–26.9%, respectively. It is possible to hypothesise that gasification of bark samples yields more biochar. Biochar may be a valuable by-product that can be used as a soil amendment or in carbon sequestration applications (Hansen et al., 2015). Therefore, from the analysed data set the most suitable samples for a high biochar yield would be spruce and black alder bark that have by far the highest FC, low ash content and belong to prevalent wood species in Estonia.

Carbon

The typical range of carbon (C) content in softwood is between 47–54% and in hardwood 48–52%, on a dry basis, according to ISO 17225. The present study shows that there is no significant difference in C content between hardwood and softwood wood, as in hardwood it varies between 47.0 to 49.9% and in softwoods from 48.8 to 50.3%. On the other hand, bark samples have a much higher variation between different species – 43.9 to 56.3%. Silver birch bark stands out as having the highest C content of 56.3%, which is similar to results reported in the literature (Bryers, 1996). Wych elm, white willow, European ash, European crab apple and Norway maple have C content below the typical hardwood bark range of 47 to 55% (ISO 17225). Norway spruce, however, has a lower C content than Scots pine, 48.4% and 52.8%, respectively. In the literature the same pattern is apparent between pine and spruce bark (Antero, 2006; Frandsen et al., 2007; Vassilev et al., 2010; Brunner et al., 2013; Jerzak, 2020).

Hydrogen

Hydrogen (H) is one of the parameters that has a higher influence on the heating value along with carbon, oxygen and sulfur (Telmo et al., 2010). According to the results, most of the species have higher H content in the wood than the bark with a few exceptions like silver birch, blackthorn, rowan and aspen. The H content of the analysed samples in broad-leaf wood is slightly higher than reported in the literature (Pesonen et al., 2014; Mason et al., 2015) lying between 6.3 and 6.6%. Hardwood wood, on the other hand, have a wide distribution in H content, varying between 5.2–7.0%. The H content of softwood bark is similar that reported in the literature (Antero, 2006; Vassilev et al., 2010; Brunner et al., 2013; Phyllis2 Database).

A higher H content is preferred in biomass as it results in a higher concentration of H₂ and a higher H₂/CO ratio in the gasification outlet gas according to hierarchical cluster and principal component analyses conducted by Gil et al., (2019).

Oxygen

Lignocellulosic fuel has a comparatively high oxygen (O) content that contributes to low heating values. Oxygen content is one of the most significant parameters along with gasification temperature, that determine the chemical efficiency of the gasification (Schuster et al., 2001). O content is very similar in all woods and ranges between 42.1 to 45.6%, but in bark samples it lies between 31.6 and 41.3%. O content in the literature is reported mostly on the basis of the whole wood and the content varies between 40.6 and 44.6% among different wood species (Miles et al., 1996; Koziński & Saade, 1998; Cuiping et al., 2004; Demirbas, 2004; Eriksson et al., 2004; Saidur et al., 2011; García et al., 2012; Miccio et al., 2012; Brunner et al., 2013; Lu et al., 2018; Phyllis2 Database). Kirsanovs & Žandeckis (2015) point out that lower O content in the feedstock necessitates a higher amount of air to be injected into the gasifier in order to achieve the required equivalent ratio. In addition, a higher C/O mass ratio in the fuel increases the heating value of the syngas. Therefore, common hardwood barks like grey alder, black alder, silver birch and aspen that have higher C/O mass ratios, ranging between 1.43 to 1.62, may be a more suitable feedstock when the highest HV of syngas is required.

Nitrogen

Results show that nitrogen (N) content in bark is remarkably higher than in wood, varied from 0.1 to 0.3% and 0.4 to 2.5%, respectively. Typical N content in hardwood and softwood lays between < 0.01 to 0.5% (ISO 17225). Common laburnum bark differs greatly from other species and the N content reaches 2.5%. A relatively high N content (1.2%) was also found in Scots pine bark. On the one hand, this is similar to the result for pine wood, which has a N content of 1.3%, as reported by Mason et al. (2015). However, Brunner et al. (2013), Frandsen et al. (2007), Antero (2006) report much lower N contents in softwood bark ranging between 0.05–0.5%. N is an important characteristic that should be considered in gasification and design of gas cleaning section. N is converted into N₂, NH₃ and HCN during gasification. The N₂ content in the syngas decreases the calorific value of the syngas produced. Ammonia can be eliminated from product gas by increasing the gasification temperature so it decomposes to nitrogen (Devi et al., 2003). Also, NH₃ can be separated from the gas flow by adding H₂SO₄ (Zisopoulos et al., 2018), where the product ammonium sulphate can be further used as fertilizer. Samples that have a higher N value should be avoided if possible, e.g. common laburnum, black alder and Scot's pine bark.

Sulphur and chlorine

The advantage of untreated woody biomass is the low content of sulphur (S) and chlorine (Cl). The presence of Cl and S in the feedstock often leads to the formation of sulphates and facilitates fouling (Miles et al., 1996). The problem is that HCl formation and condensation can occur on the cooler parts of equipment, often on heat exchangers, which will lead to corrosion of the metal surface. In gasification, S is transformed to H₂S or COS, but as the concentrations are low, the issue is not very common in biomass gasification. It is seen that most of the sulphur originates from the bark as a majority of wood samples have an S content below 0.01%. Common laburnum, hawthorn and European crab apple stand out as they have relatively high S contents both in wood and bark compared to other tree species, and in order to avoid S and Cl related problems, these samples can be excluded from the selection of possible feedstocks for gasification.

The S content of fuel increases when the bark content is higher. Cl content in barks is slightly higher compared to woods, $\leq 0.01\%$ and $0.01\text{--}0.03\%$, respectively. Higher Cl contents can be found when woody biomass contains needles or leaves (Alakangas et al., 2016), however these parts of the tree were out of the scope of this study.

Minor and trace elements

According to Zevenhoven & Kilpinen (2001), the elements can be classified as follows: major ($> 1.0\%$), minor ($0.1\text{--}1.0\%$) and trace ($< 0.1\%$) elements. The present results show that elemental classification is slightly different and changeable in the case of wood and bark. Major elements in both are C, H, N, O, but also Ca can be classified as a major component in bark where its concentration may exceed 6% . However, in stem wood Ca is a dominant minor element and all other determined elements: Al, Na, Si, Mg, Fe, P, Cu, Mn, Ni, Zn, Sr, Cr, Ti, Pb, belong to the trace elements range. K is found as either a minor or trace element depending on the wood type. In the bark samples, there is variation between different species and K, Mg, Si can be classified as minor elements. All in all, the major and minor elements in biomass, in decreasing order of abundance, are $C > O > H > N > Ca > K > Mg > P > S > Cl > Si > Na > Fe > Al > Mn > Zn > Sr > Cr > Ni > Ti > Cu > Pb$.

Many of the tested wood and bark samples contain high concentrations of Ca, K, Mg and Na that, according to different studies, improve the gasification process (Elliott et al., 1984; Sueyasu et al., 2012; Perander et al., 2015; Ren et al., 2019). These results support earlier findings that the majority of ash forming elements are found within the bark (Kleinhans et al., 2018). Also, Werkelin et al. (2011) investigated the chemical composition of different parts of Norway spruce and reported lower Al, K, Si and Mn in wood than in the present work and much higher values of Mn and K in bark. Scots pine and silver birch, on the other hand, show small amounts of Al, Na and Si. Generally, common wood species stand out as having relatively low contents of ash-forming elements compared to all analysed species.

Ca is the dominate ash forming element in biomass, especially in bark samples where concentrations were up to twelve times higher than those of the wood samples. Similar findings have been reported by Kleinhans et al. (2018). The Ca content of the wood species ranged within rather wide limits, $718\text{--}63,910$ ppm, depending on the wood type. The highest Ca content of $63,910$ and $49,587$ ppm was found from the European crab apple and wych elm bark samples, respectively. The lowest Ca content was observed in Scots pine, aspen and European ash wood samples: 718 , 890 and 891 ppm, respectively. A higher Ca content in the feedstock is advantageous. In some cases, limestone as a source of calcium is added because it acts as a sulphur capture technique and prevents agglomeration (Miles et al., 1996). Koppejan & van Loo (2016) indicate that ashes of agricultural crops with low concentrations of Ca and high concentrations of potassium (K) start to sinter and melt at significantly lower temperatures than woody biomass. In this study, the Ca content of most of the samples outweigh K content, but there are two exceptions: willow and wych elm wood – these samples have a much higher probability to cause lower ash melting behaviour.

K is the second most abundant alkali element in biomass. K is stated as one of the elements that in high concentrations together with the high silica and chlorine content, is known to create ash deposit problems (Kurkela, 1996). K is detected as KCl , K_2SO_4 , K_2CO_3 , K_3PO_4 in biomass ash (Mlonka-Mędrala et al., 2020). Results show that broad-leaf

wood species tend to have higher K contents than softwood. On the other hand, K is reported as an effective catalyst in gasification and it enhances tar reforming (Sueyasu et al., 2012; Nzihou et al., 2013). Gil et al. (2019) also found that a high H₂ content and high H₂/CO ratio in the gas product are related to the higher H/O ratio and K₂O in biomass. Therefore, samples that have a higher K content may be favoured instead, when a low content of tar in the syngas is required, although sintering problem should be considered.

It has been found that the Si content in hardwood bark may reach up to 2% and in case of softwood up to 0.5% (ISO 17225). Interestingly, all analysed samples had lower Si content than typical values, from 0.002 to 0.41% (except hawthorn bark with 0.9% Si). Although, a similar pattern exists where bark has majority of Si content compared to the whole wood. These results seem to be consistent with other research which found that the silica content of clean bark is higher than that of wood (Ragland et al., 1991). The high silica content in bark or wood originates from soil components and sand.

Iron (Fe) content varied between 38 ppm and 1,377 ppm. It is stated that the typical Fe content in woods lies between 0–100 ppm and in bark it may reach up to 800 ppm (ISO 17225). European ash wood was enriched in Fe (1,377 ppm), but all other samples are comparable to typical values.

Al content in most of the woods and barks are in accordance to technical standard, that propose values of < 10 to 1,200 ppm (ISO 17225). Smallest amount of Al is found from common species (< 393 ppm). On the other hand, hardwood barks show higher concentrations than recommended values in standard, from 70 to 2,810 ppm. Na content in woods and barks are below 200 ppm and 1,200 ppm, respectively and are in accordance to typical values.

Woody biomass has higher amounts of heavy metals than annually harvested crops because wood has a longer rotation period for accumulation of heavy metals (Koppejan & van Loo, 2016). Barks of hawthorn, European ash, bird cherry, and rowan stand out as they have relatively high amount of Mn, Zn, Cr, Ni, Sr, Ti, Cu and Pb. Silver birch and grey alder have higher concentration of heavy metals than other common hardwoods. In addition, Norway spruce bark has twice as high of a heavy metals concentration as Scots pine bark.

Correlations between characteristics

The Pearson correlation coefficient was used to assess linear associations between biomass parameters in order to elucidate which feedstock features have an impact on each other (Table 3). The strength of the correlation is described using the guide that Evans (1996) suggests for the absolute value of *r*: 0.40–0.59 as 'moderate'; 0.60–0.79 as 'strong'; 0.80–1.0 as 'very strong'. Knowing correlations between variables gives the opportunity to predict biomass composition without a need to carry out a full set of analyses.

The present data show very strong positive correlations ($r \geq 0.8$) between the following characteristics: Cr-Ni-Fe, Ca-Sr, HV-C, Al-Na-Si-Ti, K-Mg-P, Fe-Zn-Cr-Ni-Cu, Ash-Ca, N-S-P and O-VM. Most of the ash forming elements like Si, Ca, K, P, Al, Mg, Fe, S, Sr, Na and Ti have moderate to very strong correlations with ash. Also, Mn is classified as an ash-forming element according to Werkelin et al., (2011). Cr and Ni together with Ca, Fe and Cu are non-volatile metals that are found to exit principally in equal concentrations in the bottom ash and the fly ash (Nzihou & Stanmore, 2013). However, this was not supported in the present study where no significant relationships between ash yield and Mn, Cr and Ni were determined.

Table 3. Pearson's correlation matrix between any two variables ($P \leq 0.05$)

	Ash	VM	FC	C	H	N	S	O	Cl	HHV	Al	K	Na	Ca	Si	Mg	Fe	P	Mn	Zn	Cr	Ni	Sr	Ti	Cu	Pb
Ash	1.0	-0.8	0.2	-0.5	-0.8	0.5	0.7	-0.7	0.5	-0.5	0.6	0.6	0.7	1.0	0.7	0.7	0.4	0.7	0.1	0.4	0.2	0.2	0.8	0.6	0.4	0.5
VM	-0.8	1.0	-0.7	0.1	0.8	-0.7	-0.8	0.8	-0.5	0.1	-0.5	-0.6	-0.5	-0.8	-0.5	-0.6	-0.4	-0.7	-0.2	-0.4	-0.4	-0.4	-0.6	-0.4	-0.6	-0.5
FC	0.2	-0.7	1.0	0.3	-0.3	0.6	0.4	-0.5	0.3	0.3	0.1	0.2	0.1	0.3	0.0	0.2	0.2	0.3	0.2	0.2	0.3	0.3	0.3	0.1	0.5	0.3
C	-0.5	0.1	0.3	1.0	0.5	0.1	-0.1	-0.2	0.1	0.9	-0.2	-0.3	-0.3	-0.5	-0.4	-0.2	-0.2	-0.3	0.0	-0.3	0.0	0.0	-0.4	-0.2	-0.1	0.0
H	-0.8	0.8	-0.3	0.5	1.0	-0.4	-0.6	0.5	-0.1	0.6	-0.4	-0.5	-0.5	-0.8	-0.5	-0.5	-0.4	-0.5	0.0	-0.5	-0.3	-0.3	-0.7	-0.4	-0.5	-0.4
N	0.5	-0.7	0.6	0.1	-0.4	1.0	0.8	-0.7	0.4	0.2	0.3	0.6	0.3	0.5	0.3	0.6	0.3	0.8	0.1	0.2	0.2	0.2	0.4	0.2	0.4	0.4
S	0.7	-0.8	0.4	-0.1	-0.6	0.8	1.0	-0.8	0.5	-0.1	0.6	0.7	0.6	0.7	0.6	0.8	0.4	0.9	0.1	0.4	0.2	0.2	0.4	0.5	0.4	0.5
O	-0.7	0.8	-0.5	-0.2	0.5	-0.7	-0.8	1.0	-0.6	-0.2	-0.5	-0.4	-0.5	-0.7	-0.5	-0.6	-0.3	-0.6	-0.2	-0.3	-0.2	-0.2	-0.6	-0.5	-0.4	-0.5
Cl	0.5	-0.5	0.3	0.1	-0.1	0.4	0.5	-0.6	1.0	0.2	0.5	0.1	0.6	0.4	0.5	0.3	0.2	0.4	0.0	0.1	0.0	0.0	0.3	0.5	0.1	0.4
HHV	-0.5	0.1	0.3	0.9	0.6	0.2	-0.1	-0.2	0.2	1.0	-0.1	-0.2	-0.2	-0.5	-0.3	-0.1	-0.1	-0.1	0.1	-0.2	0.0	0.0	-0.4	-0.2	-0.1	0.0
Al	0.6	-0.5	0.1	-0.2	-0.4	0.3	0.6	-0.5	0.5	-0.1	1.0	0.2	1.0	0.4	0.9	0.2	0.5	0.3	0.1	0.3	0.2	0.2	0.2	1.0	0.4	0.7
K	0.6	-0.6	0.2	-0.3	-0.5	0.6	0.7	-0.4	0.1	-0.2	0.2	1.0	0.3	0.5	0.3	0.8	0.1	0.8	0.1	0.2	0.0	0.0	0.3	0.1	0.1	0.1
Na	0.7	-0.5	0.1	-0.3	-0.5	0.3	0.6	-0.5	0.6	-0.2	1.0	0.3	1.0	0.6	0.9	0.4	0.5	0.4	0.1	0.3	0.1	0.1	0.3	1.0	0.3	0.6
Ca	1.0	-0.8	0.3	-0.5	-0.8	0.5	0.7	-0.7	0.4	-0.5	0.4	0.5	0.6	1.0	0.6	0.7	0.4	0.6	0.2	0.4	0.3	0.2	0.8	0.5	0.5	0.5
Si	0.7	-0.5	0.0	-0.4	-0.5	0.3	0.6	-0.5	0.5	-0.3	0.9	0.3	0.9	0.6	1.0	0.3	0.5	0.4	0.1	0.3	0.1	0.1	0.3	0.9	0.3	0.6
Mg	0.7	-0.6	0.2	-0.2	-0.5	0.6	0.8	-0.6	0.3	-0.1	0.2	0.8	0.4	0.7	0.3	1.0	0.2	0.9	0.3	0.4	0.1	0.1	0.5	0.2	0.2	0.1
Fe	0.4	-0.4	0.2	-0.2	-0.4	0.3	0.4	-0.3	0.2	-0.1	0.5	0.1	0.5	0.4	0.5	0.2	1.0	0.2	0.1	0.9	0.9	0.9	0.2	0.5	0.8	0.7
P	0.7	-0.7	0.3	-0.3	-0.5	0.8	0.9	-0.6	0.4	-0.1	0.3	0.8	0.4	0.6	0.4	0.9	0.2	1.0	0.1	0.2	0.0	0.0	0.5	0.3	0.2	0.3
Mn	0.1	-0.2	0.2	0.0	0.0	0.1	0.1	-0.2	0.0	0.1	0.1	0.1	0.1	0.2	0.1	0.3	0.1	0.1	1.0	0.2	0.2	0.1	0.1	0.0	0.3	0.2
Zn	0.4	-0.4	0.2	-0.3	-0.5	0.2	0.4	-0.3	0.1	-0.2	0.3	0.2	0.3	0.4	0.3	0.4	0.9	0.2	0.2	1.0	0.7	0.8	0.3	0.3	0.7	0.4
Cr	0.2	-0.4	0.3	0.0	-0.3	0.2	0.2	-0.2	0.0	0.0	0.2	0.0	0.1	0.3	0.1	0.1	0.9	0.0	0.2	0.7	1.0	1.0	0.2	0.1	0.9	0.5
Ni	0.2	-0.4	0.3	0.0	-0.3	0.2	0.2	-0.2	0.0	0.0	0.2	0.0	0.1	0.2	0.1	0.1	0.9	0.0	0.1	0.8	1.0	1.0	0.2	0.1	0.9	0.5
Sr	0.8	-0.6	0.3	-0.4	-0.7	0.4	0.4	-0.6	0.3	-0.4	0.2	0.3	0.3	0.8	0.3	0.5	0.2	0.5	0.1	0.3	0.2	0.2	1.0	0.2	0.3	0.2
Ti	0.6	-0.4	0.1	-0.2	-0.4	0.2	0.5	-0.5	0.5	-0.2	1.0	0.1	1.0	0.5	0.9	0.2	0.5	0.3	0.0	0.3	0.1	0.1	0.2	1.0	0.3	0.7
Cu	0.4	-0.6	0.5	-0.1	-0.5	0.4	0.4	-0.4	0.1	-0.1	0.4	0.1	0.3	0.5	0.3	0.2	0.8	0.2	0.3	0.7	0.9	0.9	0.3	0.3	1.0	0.7
Pb	0.5	-0.5	0.3	0.0	-0.4	0.4	0.5	-0.5	0.4	0.0	0.7	0.1	0.6	0.5	0.6	0.1	0.7	0.3	0.2	0.4	0.5	0.5	0.2	0.7	0.7	1.0

Strong positive correlations ($0.60 \leq r \leq 0.79$) occurred also between Ash-Na-Si-Mg-P-Sr-Ti, VM-H, N-Mg, S-Ash-K-Na-Ca-Si-Mg, HV-H, K-P-Pb, Ca-Si-Mg-P. Compared to previous studies there were similar findings, for example strong positive correlation for Al-Ti-Si, N-S-P and K-Mg-P (Vassilev et al., 2010), S-N-Cl (Jenkins et al., 1998), Ash-Ca-Na-Si, K-P-Mg, Ca-S-P (Monti et al., 2008).

Very strong negative relationships occur between Ash-VM, Ash-H, VM-Ca and Ca-H. Strong negative correlations are mainly associated with VM, C, H, O and HV which are mostly negatively correlated with trace elements. VM has a negative correlation with most of the parameters, except with O, H, C and heating value. Same pattern is seen with O, where a positive correlation is only observed with volatiles and a moderate correlation with H. This finding was also reported by Vassilev et al. (2010) who stated there is a strong negative relationship between ash-O, O-N, O-S, O-P. In contrast to earlier findings, however, no evidence of negative correlations between trace elements (e.g. Si-Ca, Si-Mg, Si-K, Si-Mn, Ca-K, Ca-Al, K-Al, Ca-Al, Fe-Ca) was detected. In this study, several strong correlations between metallic elements were found, for example Al-Na-Si-Ti, Ca-Sr, Ca-Si, Ca-Mg, Si-Pb, Fe-Pb, Zn-Cr-Ni, Cu-Pb. According to Vassilev et al. (2012) the Si-Al-Fe-Na-Ti association is related mostly as detrital silicates and oxyhydroxides, excluding authigenic opal and Ca-Mg-Mn is commonly related to authigenic oxalates and carbonates.

VM correlates with H content in the data set, which is in agreement with the conclusion of Caillat & Vakkilainen (2013) that a higher VM content is due to a high hydrogen content and depends on the nature of the material and thermochemical process conditions. It has also been suggested that a high VM and fixed carbon content increase the heating value (Saidur et al., 2011). This does not appear to be the case and no correlation between VM and HV was detected in the current study.

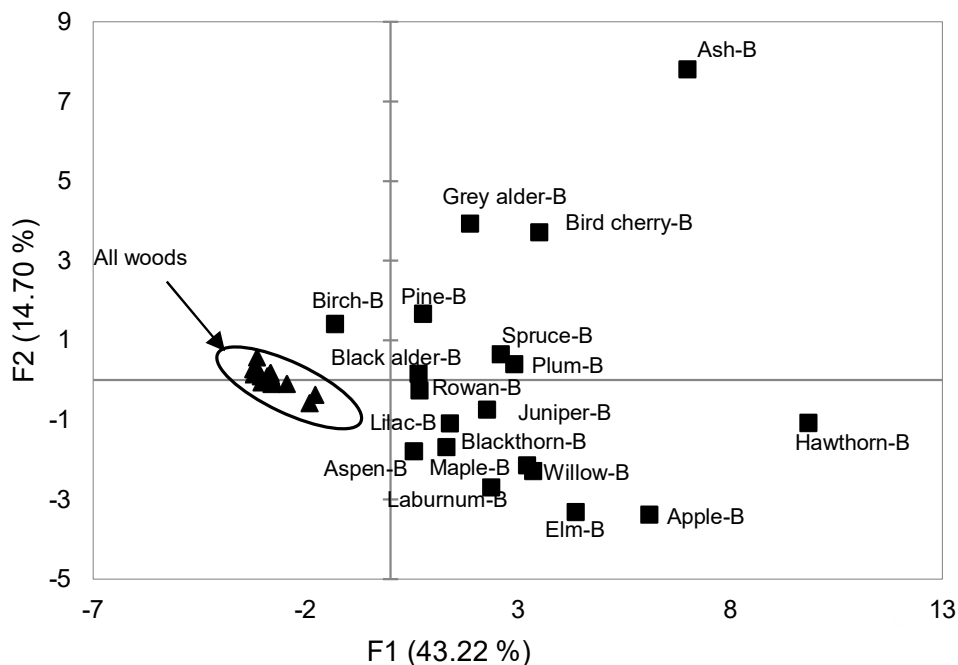


Figure 1. Graphical dispersion based on the PCA obtained from 26 variables (autoscaled): B – bark; W – wood.

A principal component analysis (PCA) was conducted on the variables studied in order to observe possible groupings and/or separation among wood species. PCA scatter plot (Fig. 1) revealed a clear data clustering in terms of the sample type using the scores of the first two principal components with a total variance of 57.9%. Generally, a total variance of 70% is considered as satisfactory in PC analysis. In this case, a lower total variance was accepted as satisfactory because descriptive purpose was desired, and it gave sufficient interpretation and scattering of the samples. Wood samples form a relative compact cluster that is characterized by high O, H, VM and HHV and low ash, while the bark samples are much more diverse and distributed over a wider range that is characterized by high ash and ash-forming element concentration. This suggests that different woods have similar compositions and there is no significant difference between species. It is possible, therefore, that the grouped biomass samples will show similar behaviours even if they are namely different. This means that if the process conditions are similar, the same behaviour can be expected among wood samples. However, the layout of bark samples reflects their variability and differences in composition. Interestingly, birch bark belongs to the wood cluster. This can be explained by the very high heating value (24.18 MJ kg⁻¹), volatiles content (80.1%) and carbon content (56.34%), makes it similar to wood samples. Results show that there are some significant differences and exceptions between wood species. For instance, hawthorn bark had remarkably high Al, Na, Ca and Si content compared to others.

The loading plot (Fig. 2) illustrates the connections of the variables to each other and gives an impression about correlations between features. The loading unravel the magnitude (large or small correlations) and in which way (positive or negative correlation) the variables contribute to the scores (Jackson, 1991; Jolliffe & Cadima, 2016). Sample distributions follow the loading values that wood samples spread in horizontal direction due to contents of volatiles, hydrogen, oxygen, Al, Ti, Na, Si, Ca, S and ash, and in the vertical direction due to mainly Cr, Ni, K content.

It reveals that VM, H and O exhibit negative loadings in the negative side of the first principal component (F1). On the other hand, Al, Ti, Na, Ca, S and ash show significant positive loading contributions to the first principal component (F1).

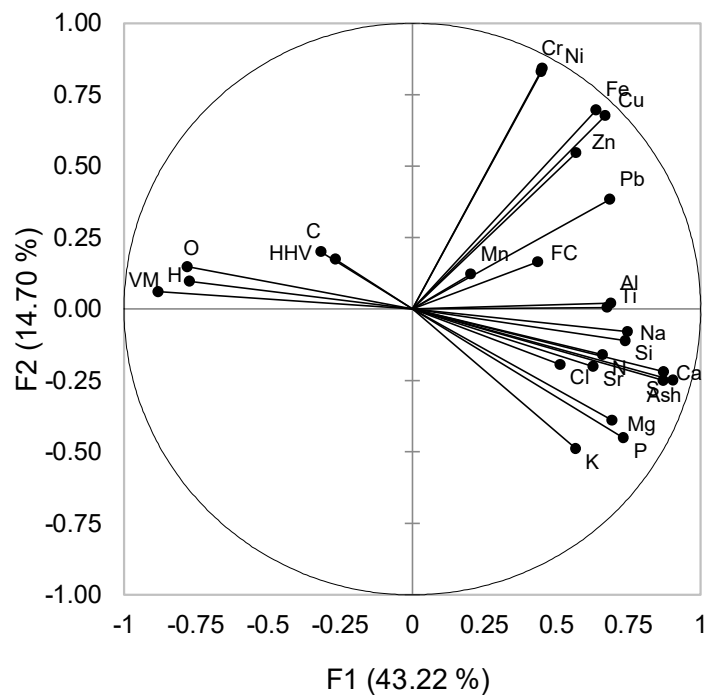


Figure 2. Correlations between variables according to PCA.

CONCLUSIONS

Based on results obtained experimentally and information available in the literature, this paper gives an overview of the characteristics of different Estonian wood species.

Statistical analysis supports the knowledge that woody biomass is heterogenous and its composition depends on its origin, growing environment and wood-specific mineral uptake.

Some conclusions based on complete proximate, ultimate and ash analyses of 19 different wood and bark samples can be made:

1) Wood samples have a relatively predictable composition where parameters vary in a narrow range. On the other hand, wood bark composition is more diverse and depends on the wood species.

2) Birch bark composition is more similar to wood samples than other bark samples, mainly due to its very high heating value, high content of C, H and volatiles and low ash content.

3) Main parameters that cause wood and bark samples clustering are volatiles, hydrogen, oxygen, ash, Al, Ti, Na, Si and Ca.

4) Very strong positive correlations were found, namely: Cr-Ni-Fe, Ca-Sr, HV-C, Al-Na-Si-Ti, K-Mg-P, Fe-Zn-Cr-Ni-Cu, Ash-Ca, N-S-P and O-VM.

5) Strong positive correlations occurred between Ash-Na-Si-Mg-P-Sr-Ti, VM-H, N-Mg, S-Ash-K-Na-Ca-Si-Mg, HV-H, K-P-Pb, Ca-Si-Mg-P.

6) Most of the ash forming elements have moderate to very strong correlation with ash, except Mn, Cr, Ni.

7) Very strong negative relationships occur between Ash-VM, Ash-H, VM-Ca and Ca-H.

8) Results show that not all wood species coincide with typical wood or bark. Most of the analysed hardwood barks have higher ash yields compared to a typical hardwood.

9) Gasification feedstock should be chosen considering the aim of gasification. To increase the yield of biochar, bark should be used because of the high content of fixed carbon. When a high reactivity and conversion rate is required, the wood part should be used because of its high volatile matter content.

10) Common wood species (Scots pine, Norway spruce, aspen, birch, grey alder and black alder) are perspective feedstock for gasification because of the low S, N, Cl, and ash content and high volatile matter.

11) Hardwood species have higher heavy metal contents (Mn, Zn, Cr, Ni, Sr, Ti, Cu, Pb) than softwoods. Of the common species, birch and grey alder have over three times higher total heavy metal content than other common hardwoods. In addition, spruce bark has more than two times higher total heavy metals content than pine bark.

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