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Fast Pyrolysis of Forestry Residue. 2. Physicochemical Composition of Product Liquid

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In this second article on fuel oil, use of forestry residue pyrolysis liquids, their physicochemical properties, and the behavior of these liquids are described. Understanding of the chemical composition of forestry residue liquids enables the selection of correct handling and storage conditions. Forestry residue is one of the most viable biomass feedstocks for liquid production in Northern softwood forest zone. A 10–25 wt % top phase with a high heating value is produced from forestry residue due to the high content of extractives and low water content. However, it has high solid and ash contents. The main product, bottom phase, is similar to bark-free wood pyrolysis liquid: volatile acids 8–10 wt %; aldehydes and ketones 10–15 wt %; water 25–30 wt %; “sugar constituents” 30–35 wt %; water-insoluble, mainly lignin-based constituents 15–20 wt %; and extractives (2–6 wt %). Its physical properties (water 28 wt %, pH 3.0, viscosity at 40 °C 15 cSt, LHV 14 MJ/kg, solids < 0.05 wt %), making it suitable for fuel oil use. The solids content is typically lower than in pine liquids. Needles and bark in forestry residue, especially in fresh green feedstock, yields high alkali metal (400–1000 mg/kg), ash (0.1–0.2 wt %), and nitrogen (0.1–0.4 wt %) contents of the liquid compared to pine (50 mg/kg, 0.02–0.03 wt %, < 0.1 wt %, respectively) liquids. This results in higher NO_x and particulates emissions in combustion. In pyrolysis of forestry residue attention should be paid on solids/alkali removal and decrease in nitrogen content.

Introduction

Biomass pyrolysis liquids have a potential to be used as fuel oil substitute both in heavy fuel oil^{1,2} and light fuel oil^{2–5} use. Combustion tests¹ in an 8 MW test furnace of Oilon Oy's Research and Development Centre have shown that the oils can be burnt efficiently in standard or slightly modified⁴ equipment. However, these tests also identified several challenges in the pyrolysis liquid applications resulting from their properties. The liquids have heating values of only 40–50% of those for hydrocarbon fuels. A high water content is detrimental for ignition rates. Organic acids cause corrosiveness of the liquids to some common construction materials. Solids (char) can block injectors or erode turbine blades. The reactivity of some components leads to the formation of larger molecules, which results in high viscosity and in slower combustion chemistry. For improving the fuel oil quality of pyrolysis liquids, the

understanding of physicochemical properties of pyrolysis liquids is of utmost importance.

Forestry residue (FR), besides sawdust, is one of the most feasible biomass feedstocks for liquid fuel production in Northern softwood forest zone. The majority of forestry residue in the Finnish market comprises spruce (50–90%) and pine (10–30%) from final cutting. The amount of hardwood (birch) is 10–20%. Logging residue can be collected either as “green” (moisture about 55%) with needles or as “brown” after seasoning (moisture about 35%), when around half of needles and a small amount of thin branches remain at the logging site. Green residue of spruce contains on average 40% of wood, 23% of bark, and 37% of needles. The corresponding composition of brown residue is more than 60% of wood, less than 30% of bark, and less than 10% of needles.^{6,7} Bark and needles in forestry residue increase the nitrogen content due to chlorophyll and proteins. In Scandinavian wood, the protein content is low. A high content of certain soluble constituents such as pectin and phenolic compounds as well as suberins is typical of bark. The mineral content of bark is also much higher than that of wood. The lignin in inner bark is claimed to be similar to wood lignin, whereas the outerbark lignin is of unknown structure but significantly differs from innerbark lignin.⁸

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Table 1. Chemical Composition of Pine and Spruce in Percentages⁷

pine	stem wood	needles	bark
extractives	3	12.6	4.5
lignin	28.1	28.4	29.2
carbohydrates	67.9	54	62.4
cellulose	40.8	29.1	36.2
glucmannane	15.4	11.8	5.2
galactose	1.1	3.7	4.2
arabinose	0.8	3.4	9.2
xylane	7.7	3.9	5.5
uronic acid	2.1	2.1	2.1
unknown	1	5	4
spruce			
extractives	0.8	6.1	3.8
lignin	28.2	35.3	35.9
carbohydrates	70	53.6	56.3
cellulose	42.7	28.2	35.9
glucmannane	16.1	12.5	3.8
galactose	1.2	2.8	3.3
arabinose	0.5	3.4	6.1
xylane	7.4	4.6	5
uronic acid	2.1	2.1	2.1
unknown	1	5	4

There is variation in composition within various softwood species (Table 1).⁹ Spruce contains more lignin in bark and needles than pine. The extractive content of spruce fractions is less than for pine.

The forestry residue pyrolysis liquid separates immediately after condensation to a polar, liquid bottom phase (80–90 wt %) and a hydrophobic viscous top phase (10–20 wt %). The amount and composition of top phase are affected by the feedstock (wood species, amount of needles, feedstock storage time), pyrolysis, and recovery of product.¹⁰ This article describes in detail the composition and properties of pyrolysis liquid produced from green forestry residue. In addition, major differences of forestry residue liquids produced from green and brown feedstocks and pine are compared. This is the second part of a series of publications, which focus on giving an insight on physicochemical properties, behavior, and storage properties of forestry residue liquids in order to understand their behavior in handling, storage, and combustion in various applications. This article is an essential part of the next one describing the storage properties of forestry residue liquids. The understanding of the chemical composition of pyrolysis liquids enables the choice of correct storage conditions and appropriate handling of pyrolysis liquid.

Experimental Section

Feedstock Analyses. Feedstock analyses were carried out employing standard methods: moisture according to DIN 51718, volatiles (volatiles = material evaporated at 900 °C for 7 min protected with a cover) according to DIN 51720, ash according to EN 7 (at 815 °C), elemental analysis CHN

according to ASTM D 5373, and heating value according to DIN 51900. Alkaline metal analysis was carried out using wet oxidation for sample preparation and AAS (atomic absorption spectrometry) for determination. Chlorine content was determined by capillary electrophoresis technique after combusting the sample in an oxygen bomb according to ASTM D 4239. Extractives were determined using acetone and continuing the extraction by dichloromethane. Lipids were analyzed by the method described in Ekman and Fagernäs.¹¹

Analyses of typical wood fuels are presented in Table 2. Analyses of needles and bark are included for comparison. The feedstocks differ clearly from each other. The presence of needles and bark in forestry residues increases ash, nitrogen, alkali metal, and extractive contents and decreases the amount of volatiles. There is an about 10 μm layer of hydroxylated fatty acids on the waxy surface of needles.¹² This can be seen in the extractive composition of green forestry residue (Figure 1). Forestry residue is mainly composed of spruce wood. The stem wood of spruce contains less extractives than that of pine (Table 1). Hence, the presence of needles and extractives of bark raises the level of brown forestry residue to the same level as with pine.

Liquid Production. Pyrolysis was carried out at a 20 kg/h capacity in the Process Development Unit (PDU) of VTT.¹⁰ The ground, sieved, and dried (moisture 4–11 wt %) feedstock was fed to the reactor. Pyrolysis temperature was about 520 °C and residence time for pyrolysis vapors 1–2 s in all experiments. The product vapors were condensed using liquid scrubbers. Liquid yields (organics + water) from forestry residue ranged from 59 to 64 wt % of dry feed and for pine sawdust about 74 wt % (Figure 2).

Liquid Analyses. Physical characterization of liquid products was carried out using modified standard and new methods.^{13,14} The average molecular weight (MM) by GPC (gel permeation chromatography) was carried out for forestry residue liquid and its fractions.

Chemical characterization was carried out according to Oasmaa et al.¹⁰ The liquid samples were washed with water (Figure 3). The water-insoluble fraction was removed by filtration and the dried residue was weighed. The residue was further extracted with dichloromethane. Dichloromethane-solubles and -insolubles were evaporated (≤ 40 °C), and the dried residues were weighed.

The water-soluble fraction was further extracted with diethyl ether and dichloromethane. These fractions are called "diethyl-ether-solubles" and "diethyl-ether-insolubles" in the text. Diethyl-ether-solubles and -insolubles were evaporated (≤ 40 °C) and residues were dried and weighed. In the determination of evaporation residue, a part of the small low molecular mass compounds evaporated. Part of low molecular mass compounds evaporate during drying of the fraction as azeotropes (acetic and formic acids) with water. These compounds were analyzed separately by using headspace GC/MSD. The compounds were mainly small aldehydes (acetaldehyde, 2-furaldehyde, 5-methylfurfural, glycolaldehyde), and ketones (1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 2-cyclopenten-1-one, 1-acetyloxopropan-2-one, and 5H-furan-2-one). These compounds are mainly ether-soluble and hence are included in that fraction in the composition diagramme. They were analyzed also separately quantitatively by GC/MSD for the water-soluble fraction.

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Table 2. Feedstock Analyses

	method	unit	pine: ^a	spruce: ^b	forestry residue		spruce	
			Pinus sylvestris	Picea Abies	brown ^c	green ^d	needles ^e	bark
moisture as received	DIN 51718	wt %	3.3	7.0	4.9	8.1	50.8	0
ash, d.m.	DIN 51719	wt %	0.2	0.5	3.8	2.1	6.7	2.3
volatiles, d.m.	DIN 51720	wt %	82.5	n.d.	73.2	76.7	—	75.2
carbon, d.m.	ASTM D 5373	wt %	50.3	53.4	51.1	51.4	48.4	49.9
hydrogen, d.m.	ASTM D 5373	wt %	6.0	6.0	5.9	6.0	6.1	5.9
nitrogen, d.m.	ASTM D 5373	wt %	<0.1	0.2	0.5	0.5	0.6	0.4
oxygen, d.m.	as difference	wt %	43.5	40.4	38.7	40	38.3	41.4
sodium	AAS	mg/kg			80	250	67	90
potassium	AAS	mg/kg	600		1800	1523	5960	3000
calcium	AAS	mg/kg	1200		4800	5332	13560	8500
magnesium	AAS	mg/kg	200		660	642	450	800
chlorine, d.m.	ASTM D4208+CEF	mg/kg	<50			220		280
sulfur, d.m.	ASTM D 4239	wt %				0.04		0.03
HHV, d.m.	DIN 51900	MJ/kg	20.6		20.5	20.8		19.8
LHV	DIN 51900	MJ/kg	17.6		18.2	17.7		18.5
LHV, d.m.		MJ/kg	19.2		19.3	19.5		
extractives, d.m.	solvent extractives ^f	wt %	5.9		5.4	10.5	20.3	21–24

^a Felling 3–4.5.95, drying 8–9.5.95. ^b Literature data. ^c 80% spruce, 10% pine, 10% birch, Vapo. Approximately 7 wt % needles. Cutting 7-8/99, felling 3/00. Moisture 52.3 p %. ^d 86% spruce, 9% pine, 5% birch, Kymenlaakso. Approximately 25 wt % needles. Cutting 27-29.4.95. ^e Air-dried spruce needles. ^f Solubles in acetone and dichloromethane. d.m. = dry matter. CEF = capillary electrophoresis

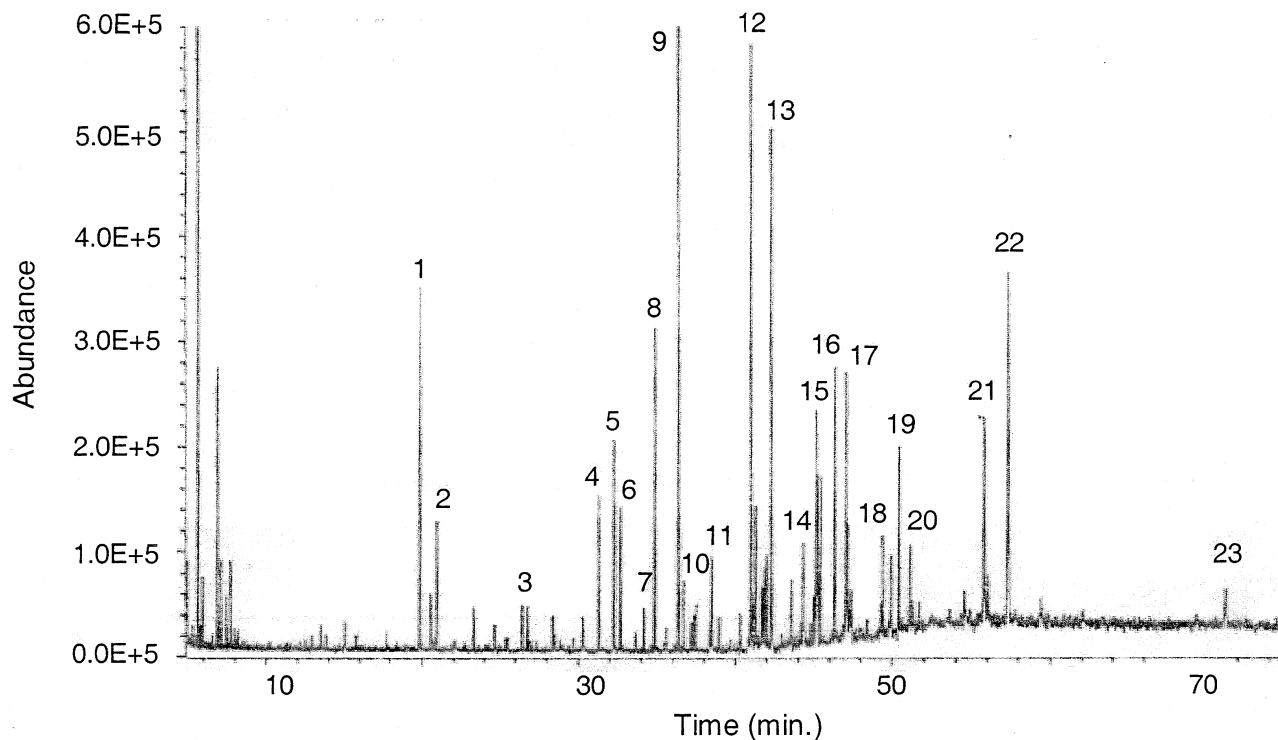


Figure 1. Total ion chromatogram of free and esterified lipids in green forestry residue as silylated and methylated derivatives. Peak identification: (1) dodecanoic acid, (2) nonane-1,9-dioic acid, (3) tetradecanoic acid, (4) 12-hydroxydodecanoic acid, (5) hexadecanoic acid, (6) 12-dodecanediol, (7) heptadecanoic acid ai., (8) heptadecanoic acid, (9) 14-hydroxytetradecanoic acid, (10) 9-octadecenoic acid, (11) octadecanol, (12) 16-hydroxyhexadecanoic acid, (13) dehydroabietic acid, (14) abietic acid, (15) 7-oxodehydroabietic acid, (16) docosanoic acid, (17) 16-hydroxydehydroabietic acid, (18) 20-hydroxyeicosanoic acid, (19) tetracosanoic acid, (20) tetracosanol, (21) matairesinol acid, (22) matairesinol, (23) beta-sitosterol.

The quantitative analysis of low-molecular carboxylic acids,¹⁵ alcohols, and other low-molecular compounds (acetaldehyde and 1-hydroxy-2-propanone) in the water fraction was carried out by GC/FID (for alcohols using an HP-Innowax cross-linked polyethylene glycol capillary column, 60 m × 0.25 mm i.d., and film thickness 0.25 μm.) Quantitative determination of other forestry residue liquid compounds was carried out GC/MSD at IWC (Germany). The compounds of various fractions were identified by GC/MSD (using an HP Ultra 1 fused silica capillary column, 50 m × 0.32 mm i.d., film

thickness 0.52 μm). The interpretation of the spectra obtained by GC/MS-spectrometry was based on automatic library search and literature data.^{16–21} The derived compounds were identified using model compounds and own library.

Extractives were determined as *n*-hexane-soluble material. Acetone was not used for the feedstocks, because the pyrolysis liquid is dissolved almost totally in acetone. Quantitative

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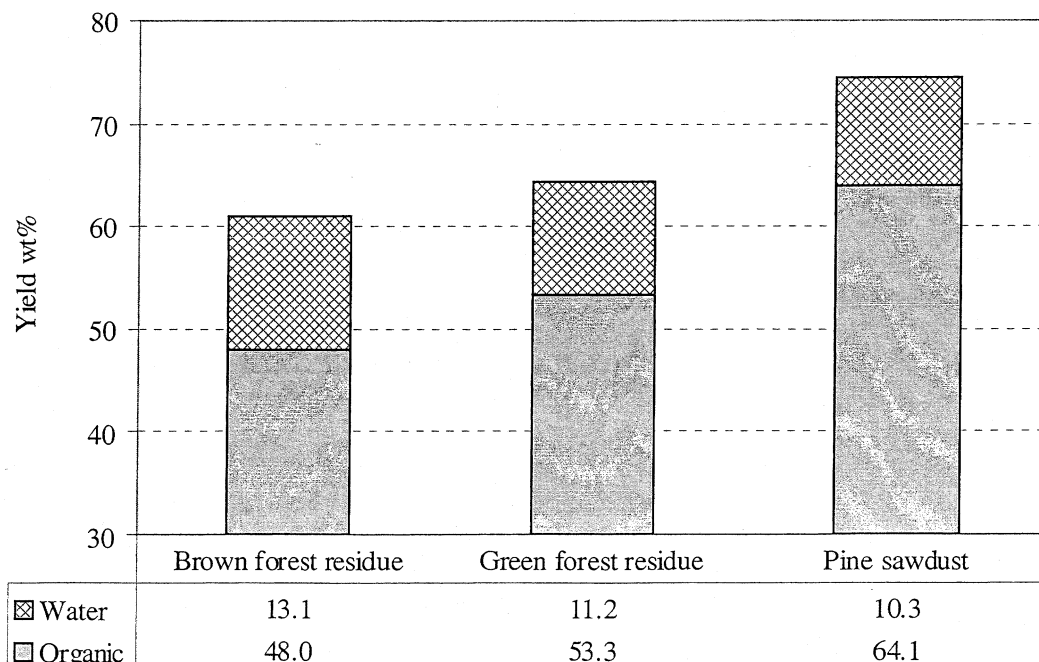


Figure 2. Organic yield and pyrolysis water for pyrolysis liquids from brown and green forestry residue and pine. Comparable conditions in each run.

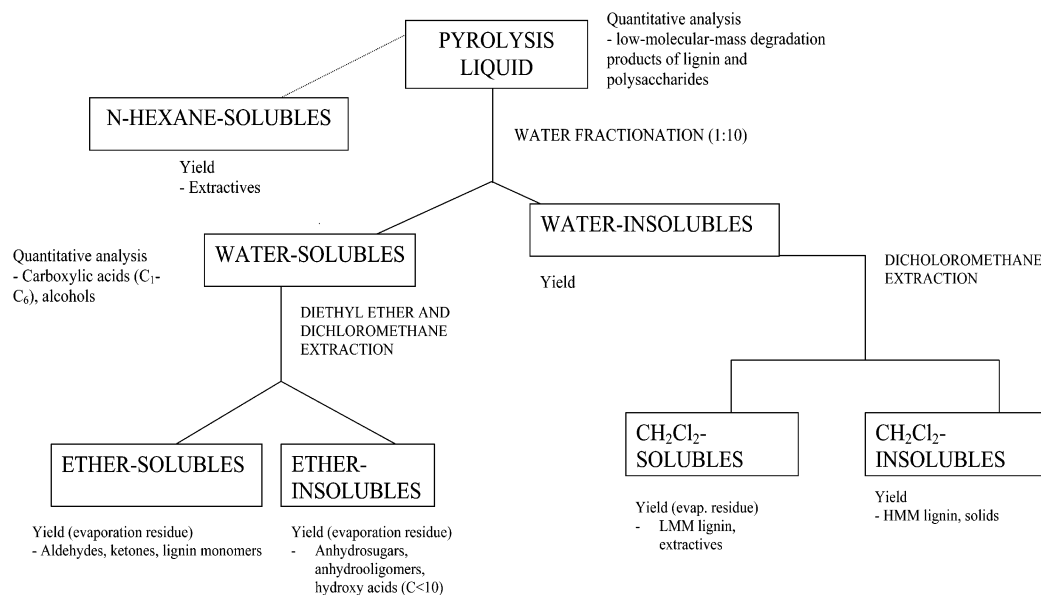


Figure 3. Fractionation scheme for chemical characterization.

analysis was carried out according to Ekman and Ketola.²² Lipids were analyzed by the method described in Ekman and Fagernäs.¹¹

Terminology. In this article, the following terminology is used:

Pyrolysis Liquid. Liquid product obtained from fast heating of biomass in the absence of air. Synonyms are pyrolysis oil and bio-oil.

Forestry Residue Liquid. Forestry residue liquid means the bottom phase, which comprises majority (80–90 wt %) of the product liquid.

Top Phase of Forestry Residue Liquid. The top phase of forestry residue liquid is the extractive-rich fraction of product (10–20 wt %) that separates out of the product liquid during condensation.

Water-Insolubles. The water insoluble fraction of pyrolysis liquid is composed of degraded lignin (HMM lignin material and LMM lignin material), extractives, and solids (char). The lignin material has a wide molecular size distribution. In the literature, there is great variation in the amount of water insolubles ("pyrolytic lignin") even for the same pyrolysis liquid.²³ This is due to the method used and to the complex solubility behavior of pyrolysis liquid.²⁴ Part of the LMM lignin material may form an emulsion with water under suitable

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Table 3. Physical Properties of Forestry Residue Liquids

(week-year): feedstock:	exptl value								
	forestry residue						pine		
	14-1999 green	17-2000 green	41-2000 green	24-2001 green	44-2002 green	10-2001 brown	12-1997 pine	26-1998 pine	43-1998 pine
solids, wt %	0.1 ^a	0.02 ^b	0.11 ^b	0.09 ^b	0.03 ^b	0.02 ^b	0.03 ^a	0.20 ^a	0.29 ^a
pH	3.1	3.2	3.3	n.d. ^c	2.97	2.9	2.4	2.6	n.d.
water, wt %	24.9	29.4	32.0	25.5	28.9	24.1	17.0	21.4	16.3
viscosity at 40 °C, cSt	15	17	13	24	13	29	n.d.	35	n.d.
density (15 °C), kg/dm ³	n.d.	1.21	1.20	1.21	1.21	1.22	1.24	1.22	1.24
HHV, MJ/kg	16.9	n.d.	15.8	16.7	15.7	17.4	18.7	17.8	19.0
LHV, MJ/kg	15.3	16.2	14.1	15.2	14.1	15.8	17.2	16.3	17.6
LHV, MJ/kg, dry	20	23	21	20	20	21	21	21	21
ash, wt %	0.06	0.24	0.1		0.16	0.08	0.03	0.02	0.03
C, wt %	43.9	38.8	38.2	41.2	38.7	43.0	45.7	43.5	46.7
H, wt %	7.5	7.5	7.8	7.0	7.4	7.4	7	7.1	6.7
N, wt %	<0.1	0.4	0.4	0.3	0.3	0.1	<0.1	<0.1	0.1
O (difference)	48	53	53	52	53	49	47	49	46
Na, ppm	2	5	n.d.	n.d.	8	n.d.	6	n.d.	n.d.
K, ppm	120	130	n.d.	n.d.	89	n.d.	16	n.d.	n.d.
Mg, ppm	170	150	n.d.	n.d.	110	n.d.	5	n.d.	n.d.
Ca, ppm	710	630	n.d.	n.d.	200	n.d.	23	n.d.	n.d.

^a Determined as being ethanol insoluble. ^b Determined as being methanol–dichloromethane-insoluble. ^c n.d. = not determined.

Table 4. Physical Properties of the Top Phase of Forestry Residue Liquids

(week-year): feedstock:	exptl value					
	14-1999 green	17-2000 green	41-2000 green	24-2001 green	44-2002 green	10-2001 brown
solids, ^a wt %	1.0 ^b	2.66	0.66	1.96	1.05	0.90
pH	n.d. ^c	3.3	n.d.	n.d.	3.1	2.9
water, wt %	8.3	13.8	13.3	7.0	7.8	15.2
viscosity at 40 °C, cSt	n.d.	153	n.d.	n.d.	n.d.	n.d.
density (15 °C), kg/dm ³	n.d.	n.d.	1.11	n.d.	1.11	1.14
HHV, MJ/kg	28.1	27.0	25.4	30.3	29.0	23.7
LHV, MJ/kg	27.9	25.3	23.7	28.7	27.3	22.0
LHV, MJ/kg, dry	30	29	27	31	30	26
ash, wt %	0.22	0.37	0.13	n.d.	0.29	0.25
C, wt %	61.7	59.9	57.9	66.2	64.3	54.5
H, wt %	7.8	7.8	7.7	7.5	7.8	7.8
N, wt %	<0.1	0.2	0.3	0.1	0.2	0.2
O (difference), wt %	30	32	34	26	27	37
Na, ppm	n.d.	n.d.	n.d.	n.d.	11	n.d.
K, ppm	n.d.	n.d.	n.d.	n.d.	77	n.d.
Mg, ppm	n.d.	n.d.	n.d.	n.d.	35	n.d.
Ca, ppm	n.d.	n.d.	n.d.	n.d.	290	n.d.

^a Determined as being methanol–dichloromethane-insoluble. ^b Determined as being ethanol-insoluble. ^c n.d. = not determined.

conditions (high efficient mixing and presence of surface active extractives) and a small water insoluble fraction is obtained. In this study, all fractions were characterized and the water-soluble fraction contained only a small amount of lignin monomers.

High Molecular Mass (HMM) Lignin Material. Dichloromethane-insolubles of water-insoluble fraction. Powder-like high-molecular-mass (MM = 1050 Da; pd = 2.3) lignin-derived material. There are no GC-eluted compounds. Solids are included in this fraction. Except the solids, this fraction dissolves in methanol.

Low Molecular Mass (LMM) Lignin Material (MM = 400 Da; pd = 1.7). Dichloromethane-solubles of the water-insoluble fraction. GC-eluted compounds of this fraction are poorly water-soluble lignin monomers (guaiacol and catechol derivatives) and lignin dimers (stilbenes). The fraction reminds so-called guaiac wood oil.²⁵ The fraction is of thick, viscous liquid. It is crystalline at normal temperatures, agreeable violet, soluble in alcohol, ether, and chloroform, poorly soluble in water.

Extractives. (MM = 460 Da; pd = 1.9) *n*-Hexane-soluble compounds of pyrolysis liquid dissolve in dichloromethane with

LMM lignin material and their amount is analyzed by *n*-hexane extraction for the original pyrolysis liquid.¹⁰ Besides extractives given in Table 7, pyrolysis liquids contain triglycerides. *n*-Hexane also dissolves small amounts of lignin monomers.

Sugar Constituent. Diethyl ether insoluble material of the water-soluble fraction. Syrup-like fraction containing anhydrosugars, anhydrooligomers, and monosaccharides. The amount of GC-eluted compounds, mainly anhydrosugars, is insignificant.

Results and Discussion

Physical Properties of Forestry Residue Liquid.

Solubility. The solubility of forestry residue liquid is similar to that of bark-free wood pyrolysis liquids. It dissolves well in polar solvents, like alcohols (methanol). Because of a small amount of extractives, an addition of a neutral solvent (for example dichloromethane) improves the solubility.¹⁴

Fuel Oil Analyses. Physical properties of forestry residue and pine liquids are presented in Table 3. Density, heating value and viscosity of forestry residue and pine liquids are similar when water content is

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Table 5. Elemental Analysis, Average Molecular Mass, and Polydispersity (Pd) of a Green Forestry Residue Fractions (Dried Evaporation Residues)

	elemental, wt % of dry matter					MM, Da	Pd
	C	H	N	O	S		
bottom phase						350	1.92
ether-insolubles ("sugars")	46.0	6.3	0.3	47.4	n.d.	240	1.58
water-insolubles	66.2	6.6	0.3	26.9	n.d.	670	2.05
CH ₂ Cl ₂ -solubles ("LMM lignin material", extractives)	68.1	6.7	0.4	24.7	0.06	410	1.73
"LMM lignin material"	65.6	7.6	0.2	26.2	n.d.	400	1.73
extractives	77.4	10.4	0	12.2	n.d.	460	1.88
CH ₂ Cl ₂ -insolubles ("HMM lignin material", solids)	64.1	5.9	1.5	28.4	0.12	1050	2.25

Table 6. Quantified *n*-Hexane Soluble Extractives in a Green Forestry Residue

<i>n</i> -hexane solubles, wt %	5.5
identified compounds, wt %	
mono-, seskviterpenes	0.1
fatty acids	0.2
hydroxy fatty acids	0.27
dicarboxylic acids	0.1
fatty alcohols	0.06
hydrocarbons	0.02
resin acids	0.48
sterols	0.01
other di- and triterpenoids	0.03

Table 7. Acid Composition of Green Forestry Residue and Pine Liquids

feedstock:	exptl value, wt %			
	green FR	green FR top ^a	green FR whole	pine: <i>Pinus sylvestris</i>
acid				
formic	1.66	0.74	1.52	2.60
acetic	4.15	2.04	3.83	3.10
propionic	0.17	0.18	0.17	0.20
isobutyric	0.0166	0.07	0.02	0.02
glycolic	0.33	0.07	0.29	0.36
<i>n</i> -butyric	0.08	0.13	0.09	0.13
lactic	0.08	0.00	0.07	0.03
allyl acetic	0.0249	0.02	0.02	0.01
<i>n</i> -valeric	0.0166	0.00	0.01	0.00
caproic	0.0249	0.07	0.03	0.05
total, wt %	6.56	3.32	6.07	6.50

^a 15 wt % of whole liquid.

catered.^{10,13,14} The pH of forestry residue liquid is a little higher than that for pine liquid due to a lower ratio of formic and acetic acids. Ash content is higher for forestry residue liquid due to higher amount of alkali metals from needles, and bark.

Physical Properties of Top Phase. *Solubility.* The top phase contains most of the feedstock neutral extractives and does not dissolve totally in polar solvents. A mixture of polar and neutral solvents is needed for good dissolution.¹⁴ When the extractive content increases, the proportion of neutral to polar solvent should be larger. For the top phase containing 25 wt % extractives, the best solvents tested were mixtures (1:1) of dioxane-methoxypropanol, dioxane-industol (ethanol with small amount of acetone), or dioxane-*iso*-propanol.

Fuel Oil Analyses. Table 4 presents the properties of the top phase of forestry residue liquid. Properties of the two phases of forestry residue liquid differ from each other mainly due to the effect of extractives. Neutral extractives that concentrate in the top phase are hydrophobic rejecting water and water-soluble compounds (carboxylic acids, alcohols, aldehydes, ketones, and "sugar" constituents). The oxygen content of the top

phase is much lower than that for the forestry residue liquid. High-melting extractives with a low water content of the top phase cause its high viscosity at room temperature.¹⁰ When heating above 40 °C, the viscosity of the top phase decreases significantly.¹⁴ Due to the high heating value (LHV of oleinic acid is 38.7 MJ/kg df) and the low density (density of oleinic acid is 0.8935 kg/dm³ at 20 °C) of extractives, the top phase has a higher heating value and lower density compared to those of the forestry residue liquid.¹⁰ Most of the solids and ash of the liquid are found in the top phase.

The Composition of Forestry Residue Liquid and Its Top Phase. For detailed chemical characterization, one forestry residue liquid from green forestry residue was chosen (Figure 4). The proportion of the top phase in this experiment was 20 wt %. The liquid was divided into water-soluble and -insoluble fractions (Figure 3). Low-molecular-mass ($C \leq 6$) carboxylic acids and alcohols were analyzed quantitatively for the aqueous phase. The water-soluble fraction was divided further by solvent extractions into ether-soluble (aldehydes, ketones, and lignin monomers) and -insoluble fractions ("sugars": anhydrosugars and anhydrooligomers). The water-insoluble fraction was divided further to dichloromethane-soluble ("LMM lignin material", extractives) and -insoluble ("HMM lignin material") fractions. Elemental analyses were performed and the average molecular mass was analyzed for the fractions (Table 5).

Chemical Composition of Forestry Residue Liquid. *Water-Soluble Fraction (80 wt %).* Water-soluble fraction (22 wt % water) of green forestry residue liquid contained about 1 wt % alcohols (methanol) and 6 wt % low-molecular-mass carboxylic acids, of which the share of acetic and formic acids was 90% (Figure 5, Table 8).

Diethyl-ether-solubles of the water-soluble fraction (about 15 wt % of forestry residue liquid) contained low-molecular and volatile compounds. For example, the boiling point of acetaldehyde is 20 °C. In addition, acetic and formic acids form azeotropes with water and hence evaporate during drying of residue. This fraction contains the main part of GC-eluted compounds in the forestry residue liquid. The evaporation residue of ether soluble fraction was characterized by GC/MSD (Figure 6). For determining the volatile compounds, a headspace GC/MS was carried out. Quantitative GC/MS was performed for the original whole liquid.

The main groups of ether solubles were aldehydes (50% of the fraction), ketones (25% of the fraction), and lignin degradation products (25% of the fraction). The aldehydes were composed of straight-chain aldehydes (main compound hydroxyacetaldehyde, 7 wt %) and furan derivatives (2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, and 5H-furan-2-one, in total 2 wt %).

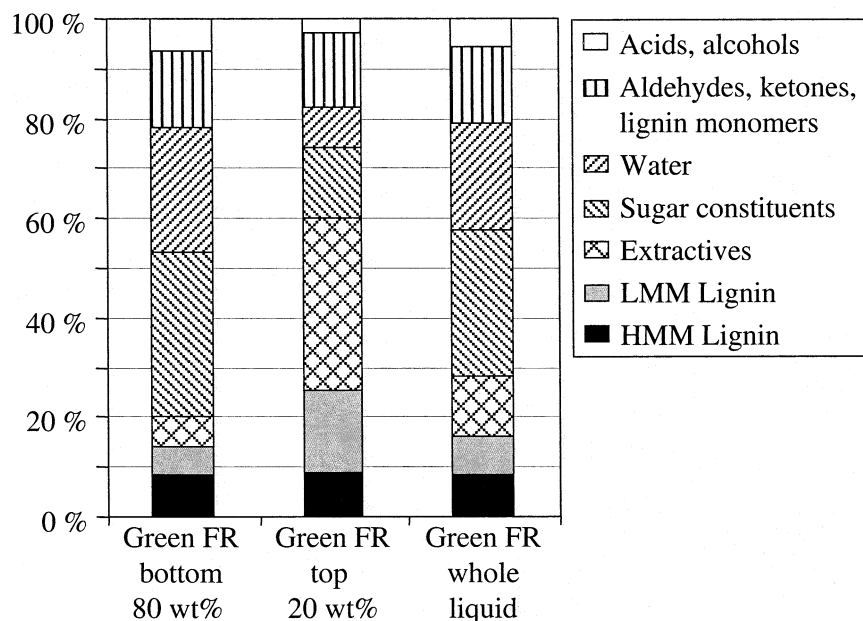


Figure 4. The composition of a green forestry residue (G FR) liquid and its top phase (20 wt % of whole liquid product). The whole liquid calculated based on 80 wt % bottom and 20 wt % top phase.

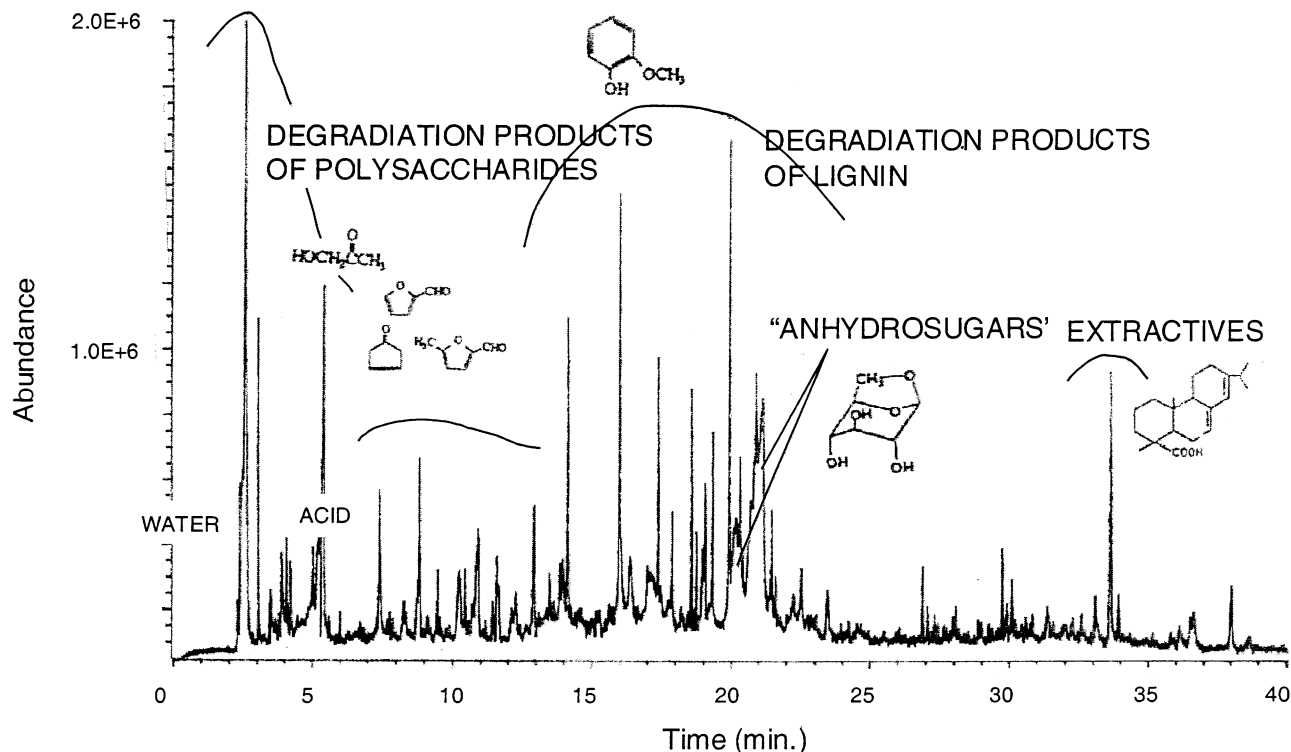


Figure 5. Total ion chromatogram of the bottom phase of a green forestry residue liquid.

Ketones were composed of straight-chain (hydroxypropanone, 5 wt %) and ring-ketones. The main groups of lignin derivatives were guaiacols (guaiacol and 4-methylguaiacol, and isoeugenols, in total 3 wt %), phenols (phenol and cresols, in total 0.56 wt %) and catechols (catechol and 4-methylcatechol).

Diethyl ether-insolubles of water-soluble fraction (33 wt % of forestry residue liquid), syrup-like "sugar fraction", consisted of degradation products of cellulose and hemicelluloses: GC-eluted anhydrosugars (levoglucosan and cellobiosan), and hydroxy acids ($C < 10$). The proportional amount of GC-eluted compounds in this fraction is very small. The fraction was identified mainly

as "sugars" on the bases of solubility, behavior (syrup-like), TGA, C^{13} -NMR, and pyroprobe-GC/MSD analysis.

Water-Insoluble Fraction. The water-insoluble fraction (20 wt % of original liquid) was divided into dichloromethane soluble (12 wt %) LMM lignin material and extractive (Table 6) fractions and dichloromethane insoluble (8 wt % of liquid) HMM lignin material fraction.

Chemical Composition of Top Phase. The top phase (20 wt % of liquid product) differs significantly from the main product, forestry residue liquid. Most of hydrophobic extractives are stratified on the top phase, and hence its water content and the amount of water-

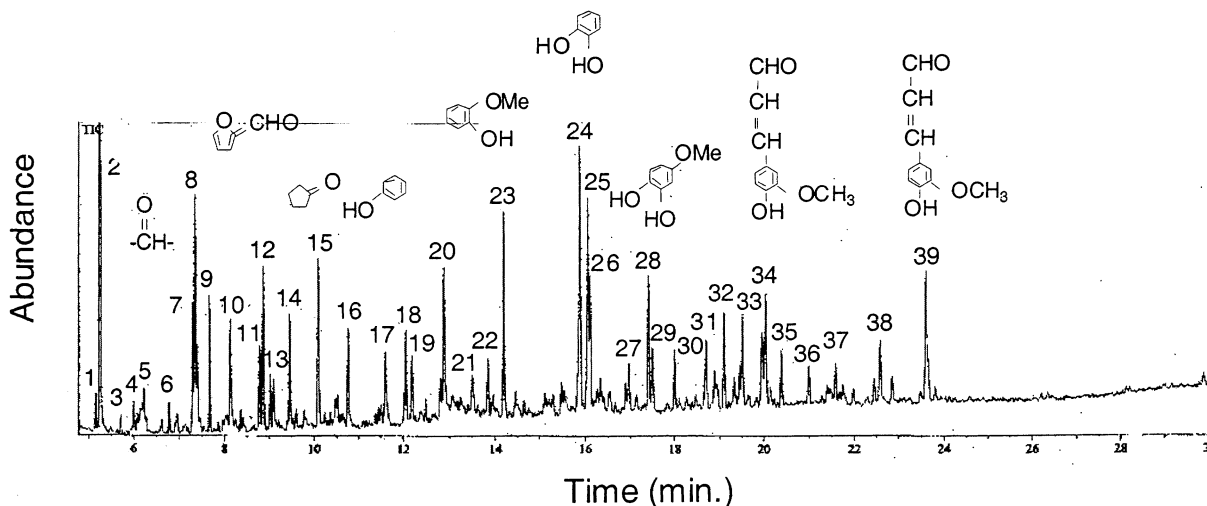


Figure 6. Total ion current chromatogram (TIC) of diethyl ether-soluble fraction of fresh forestry residue liquid. Peak identification: (1) 2-butenal, (2) 1-hydroxy-2-propanone, (3) 2-methyl-1-buten-3-one, (4) 2,3-pentanedione, (5) tetrahydrofuran-3-one, (6) pent-3-en-2-one, (7) 3-hydroxypropanal, (8) 1-hydroxubutan-2-one, (9) purvic acid methyl ester, (10) 2-methoxytetrahydrofuran, (11) 2-cyclopenten-1-one, (12) 2-furaldehyde, (13) 4-methyltetrahydrofuran-3-one, (14) 1-acetyloxypropan-2-one, (15) (5H)-furan-2-one, (16) 2,3-dihydro-5-methylfuran-2-one, (17) 5-methyl-2-furaldehyde, (18) phenol, (19) 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one, (20) 2-hydroxy-3-methyl-2-cyclopenten-1-one, (21) 2-methylphenol, (22) 3- or 4-methylphenol, (23) guaiacol, (24) catechol, (25) 4-methylguaiacol, (26) 5-hydroxymethyl-2-furaldehyde, (27) 3-methylcatechol, (28) 4-methylcatechol, (29) 4-ethylguaiacol, (30) 4-vinylguaiacol, (31) eugenol, (32) vanillin, (33) isoeugenol (cis), (34) isoeugenol (trans), (35) acetoguaiacone, (36) coniferyl alcohol, (37) propionylguaiacol, (38) dihydroconiferyl alcohol, (39) coniferaldehyde.

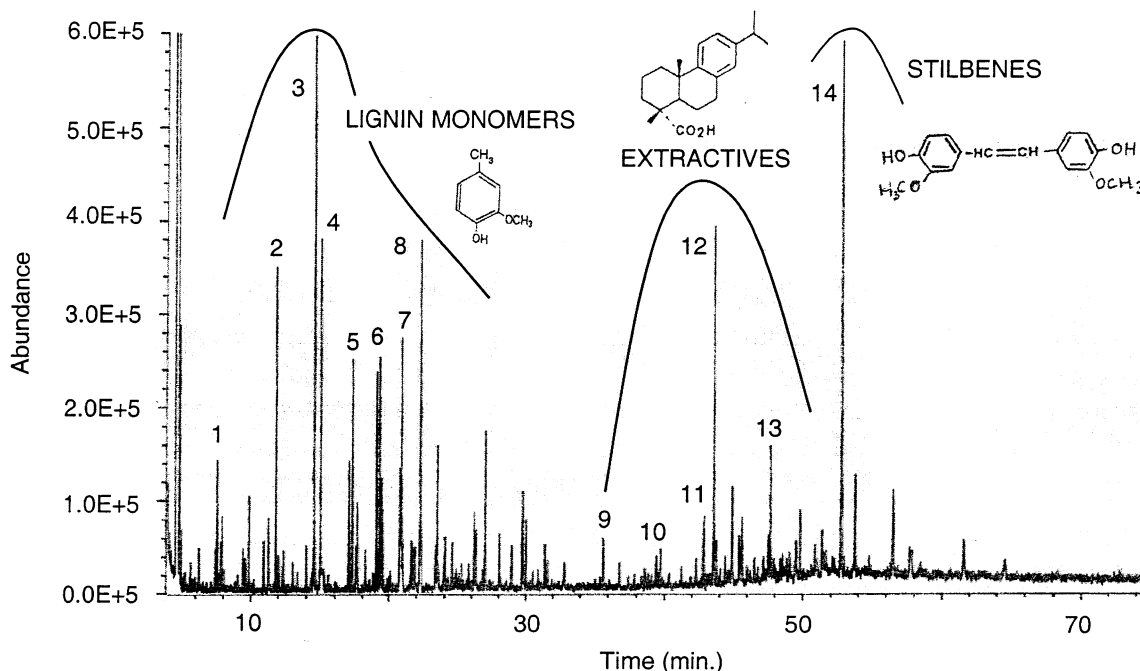


Figure 7. Total ion current chromatogram (TIC) of dichloromethane-soluble part of water-insoluble fraction in top phase, as silylated derivatives. Peak identification: (1) phenol, (2) guaiacol, (3) 4-methylguaiacol, (4) catechol, (5) methylcatechol, (6) eugenol, (7) vanillin, (8) acetovanillone, (9) hexadecanoic acid, (10) 9-octadecenoic acid, (11) isopimaric acid, (12) dehydroabietic acid, (13) 7-oxodehydroabietic acid, (14) dihydroxy-dimethoxystilbene.

soluble compounds are low. The top phase differs from the forestry residue liquid in much lower water and higher extractive content.

Water-Soluble Fraction. The top phase contained 40 wt % water-soluble compounds: water (8 wt %), "sugar"-constituent (12 wt %) and low-molecular-mass degradation products of polysaccharides and lignin (20 wt %). The GC-eluted compounds of the top phase are similar to those in the forestry residue liquid.

Water-Insoluble Fraction. The main part (60%) of the top phase is water-insoluble material (Figure 3) due to

extractives (35 wt % of the top phase). The GC-eluted compounds of the dichloromethane-soluble fraction are mainly extractives (Figures 7 and 8). Other compounds include poorly water-soluble lignin monomers (guaiacols and catechols) and lignin dimers. The dichloromethane-insoluble fraction consisted of HMM lignin material. Almost all solids (1 wt %) of the product are included in this fraction.

Comparison of Forestry Residue Liquids and Pine. The main differences of forestry residue liquids from pine liquids include: larger top phase and higher

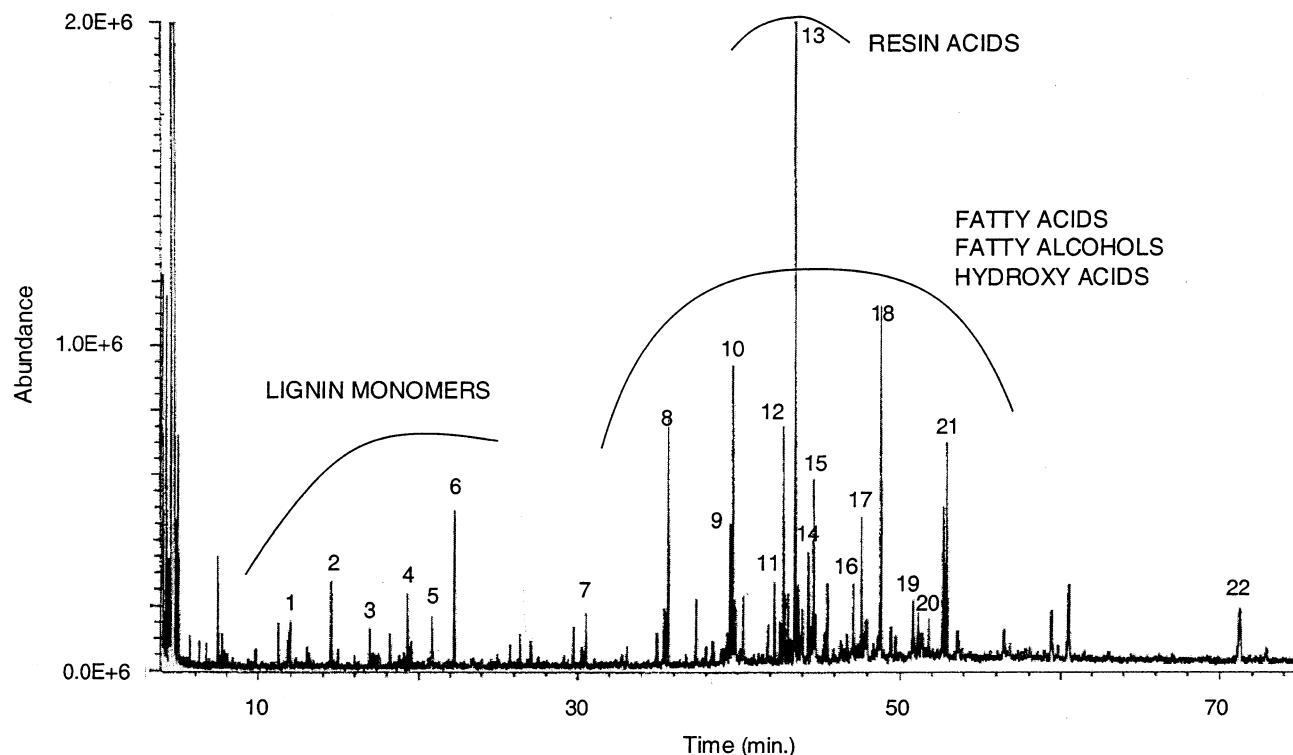


Figure 8. Total ion current chromatogram (TIC) of silylated *n*-hexane-soluble compounds in top phase of forestry residue liquid. Peak identification: (1) guaiacol, (2) 4-methyl guaiacol, (3) vanillin, (4) 4-vinylguaiacol, (5) eugenol, (6) isoeugenol, (7) tetradecanoic acid, (8) hexadecanoic acid, (9) 9,12-octadecadienoic acid, (10) 9-octadecenoic acid, (11) pimmaric acid, (12) isopimaric acid, (13) dehydroabietic acid, (14) abietic acid, (15) eicosanoic acid, (16) docosanol, (17) 7-oxodehydroabietic acid, (18) docosanoic acid, (19) tetracosanol, (20) 20-hydroxyeicosanoic acid, (21) tetracosanoic acid, (22) sitosterol.

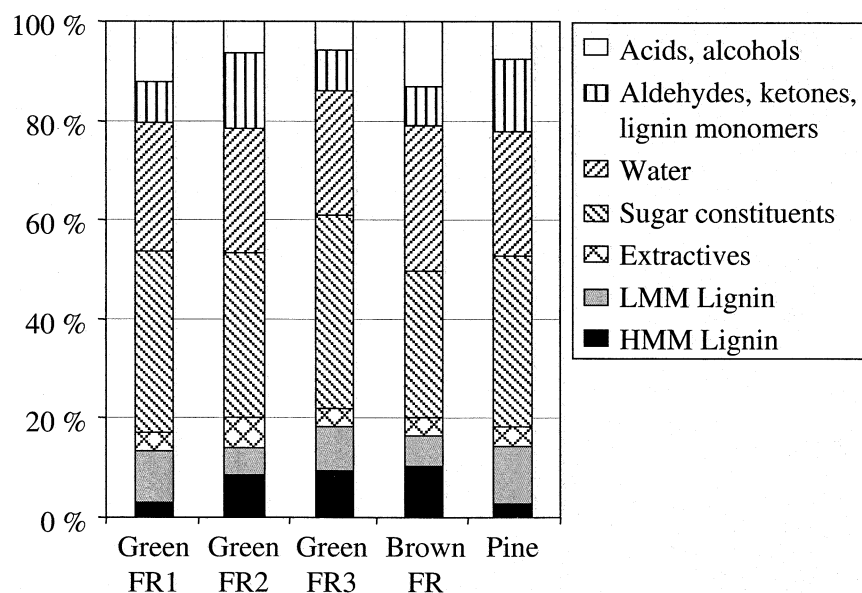


Figure 9. The composition of pyrolysis liquids produced from green and brown forestry residue and pine.

content of extractives, lower solids, and higher ash, alkali, water, and nitrogen contents.

Physical Properties. The water content of forestry residue liquids is higher than that of pine liquids. One reason for this is the rejection of water by the hydrophobic top phase. pH is higher (3–3.2) because of a higher amount of water and lower amount of formic acid (Table 8). Formic acid is a much stronger organic acid than acetic acid. The viscosity, density, and heating values of forestry residue liquids are only little higher than those for pine liquids at the same water content.

Chemical Composition. The composition of forestry residue liquid (Figure 9) is in general similar to that of pyrolysis liquid from pine sawdust. However, there are variations in chemical compositions of various forestry residue liquids due to composition and storage of feedstock, pyrolysis process, and condensation system. The amount of water insolubles is 24–29 wt % (dry basis). This is on the low side compared to the amount of water insolubles in pine pyrolysis liquids,^{9,10} but it must be borne in mind that most of the separated top phase is made up of water-insolubles. The amount of

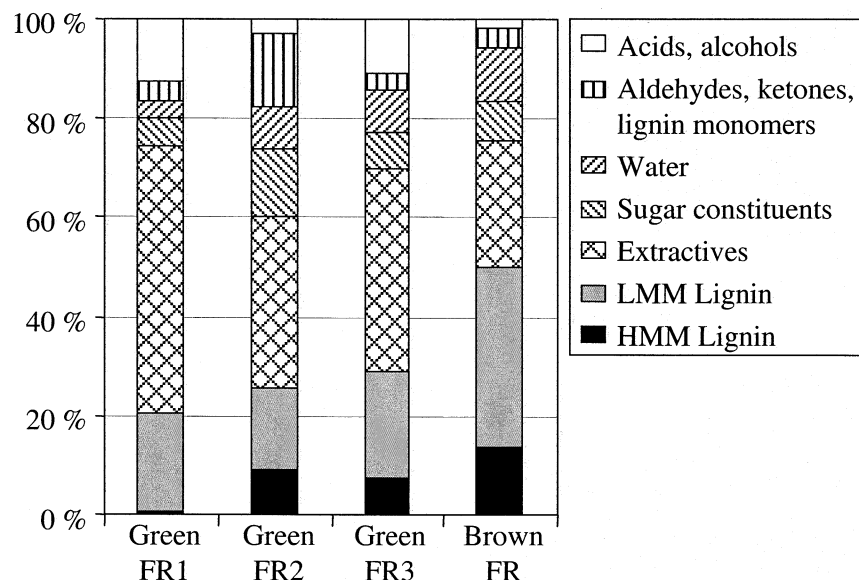


Figure 10. The composition of top phases of forestry residue pyrolysis liquid produced from green and brown feedstocks. Amount of top phase 15–20 wt % of the total liquid product.

extractives ranges 2–5 wt %. The liquids made of green forestry residue contain more syrup-like “sugar” constituents than the liquid of brown forestry residue. The water content is 24–30 wt %.

Compared to pine, the forestry residue liquids contain the same amount of volatile small-molecular-mass ($C \leq 6$) carboxylic acids (Table 7). The forestry residue liquid contains more acetic acid and less formic acid than the pine liquids. The forestry residue liquids contain more HMM lignin material than the pine liquid due to phenolic compounds in bark and needles.

Top Phase. The composition of top phases (Figure 10) depends on the efficiency of phase separation.¹⁰ The factors affecting the amount and composition of the top phase include feedstock extractives, liquid condensation conditions, and liquid yield. In good phase separation the water content of the top phase is less than 10 wt %, the amount of water-soluble compounds (water, acids, alcohols, aldehydes, ketones, and sugar constituents) less than 30 wt % of top phase, the extractive content more than 50 wt % of top phase, and high-molecular-mass HMM lignin material (and solids) less than 5 wt % of top phase. By adding water to the top phase the amount of water-soluble compounds increases. These compounds are similar to those in the forestry residue liquid. Figure 10 shows that the amount of lignin fraction (HMM lignin material + LMM lignin material) is reduced, when the water content of the top phase decreases. In efficient phase separation (water content about 5 wt %, extractives about 55 wt %) high-molecular-mass HMM lignin material separates from the top phase.

Green forestry residue contains a high amount of extractives due to the large quantity of needles and bark. The amount of needles can be as high as 37 wt % of the feedstock. Hence, the forestry residue liquids typically yield a significant phase-separation.¹⁰ Fresh feedstock can yield up to 20 wt % of hydrophobic top phase, while stored feedstock produces 8–15 wt % of top phase. The share of hexane-soluble constituents in whole green forestry residue liquids is higher (9–18 wt %) than in pine liquids (3–4 wt %).

On the other hand, brown forestry residue has dropped most of needles and degradation of extractives has already taken place. Pine produces thinner (0–5 wt %) layer on top. The amount of extractives in brown forestry residue can be similar to that of bark-free wood.

Conclusions

A 10–25 wt % top phase with a high heating value is produced from forestry residue due to the high content of extractives and low water content. The amount of the top phase of forestry residue liquids depends on feedstock (needles, freshness, moisture) and separation conditions. Polarity of the top phase (lipophilic, water-rejecting compounds) is low, which contributes to a low water content (3–15 wt %) and a low share of water-soluble compounds (5–15 wt %). Water-insoluble material (60–90 wt %) includes lignin-based constituents and extractives (35–50 wt %). The extractives consist mostly of triglycerides, resin and fatty acids, fatty alcohols and sterols. The top phase has a high heating value (30 MJ/kg dry basis) due to extractives. Its viscosity is high (200 cSt at 40 °C), but decreases rapidly by heating, when the crystalline extractives melt. Solids (>1 wt %) and ash (>0.2 wt %) contents are high.

Chemical composition of forestry residue liquid (bottom phase) is similar to that of pine pyrolysis liquid: volatile acids 8–10 wt %, aldehydes and ketones 10–15 wt %, water 25–30 wt %, “sugar constituents” 30–35 wt %, water-insoluble, mainly lignin-based constituents 15–20 wt % and extractives (2–6 wt %). Brown forestry residue produces more (35–37 wt % of d.m.) water-insoluble lignin material than pine (32–35 wt % of d.m.) and green forestry residue (17–22 wt % of d.m.). Typical physical properties of forestry residue liquid are water 28 wt %, pH 3.0, viscosity@40 °C 15 cSt, LHV 14 MJ/kg (21 MJ/kg dry basis), solids <0.05 wt %. A high amount of needles and bark in forestry residue results in high alkali metal (400–1000 mg/kg), ash (0.1–0.2 wt %), and nitrogen (0.1–0.4 wt %) contents of the liquid compared to pine (50 mg/kg, 0.02–0.03 wt %, and <0.1 wt %, respectively) liquids. This may result in higher

NO_x and particulates emissions in combustion. A high alkali metal content is detrimental in gas turbine use. For the pyrolysis of forestry residue, hot-vapor filtration would be advantageous.

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