Supporting Information for

Influence of loblolly pine anatomical fractions and tree age on oil yield and composition during fast pyrolysis

Number of Tables: 8

Number of Figures: 0

Table SI-1: Loblolly Pine Feedstock GUID for identification in Biomass Feedstock Library https://bioenergylibrary.inl.gov

Feedstock	feedstock BFL GUID
Needles (A)	7fb1ec5d-462a-4a2f-9aea-9ddaa9689993
Needles (A)	e8503c34-770b-4b91-96f2-e045f584fede
Bark (A)	72fbd035-5eaa-4136-a094-b4c8bb5c97ac
Bark (A)	72ab1304-c6e6-4e15-8ae9-818fa5dc6ef9
Stemwood (A)	cc3da623-4306-43bb-89fb-a5102bbe44e7
Stemwood (A)	9e636aa1-72ba-4609-855b-3b481bb60fd5
Stemwood (D)	ed3c91f8-be20-4177-a810-57aa46d11e02
Residues (A)	3a76859e-a064-48c7-99c3-b132d85f16b7
Residues (A) Replicate	f8cf9023-4b33-4f9d-88c0-01afbb9f82d7
Residues (A) AC 10Hz	08d8b21f-8cc8-47bd-a2bf-4b0f8311c277
Residues (A) AC 28Hz	37347643-0679-4923-802b-cd8c7ac332ca
Residues (B)	b8fd8877-13b0-4249-b6d4-ab9736b201ae
Residues (B) Replicate	3fb34f82-f4aa-40f2-8683-8b8454186293
Whole Tree (D)	80c335c3-d4c6-4fb0-81f6-6220222af89a
Bark (A) and Needles (A) 1:1 mix	cb3a8400-a04d-49aa-bb38-66bdca649575
Stemwood (A) and Needles (A) 1:1 mix	3e6de1aa-9e37-4e76-abb6-82d99393ed02
Residues (B), Bark (A), and Needles (A) 1:1:1 mix	13b752de-916a-408d-be73-09c849b93918
Residues (B), Bark (A), and Needles (A) 1:2:2 mix	b6c7947a-cbde-4e4e-b898-4ded7ca66dd9

Table SI-1b: Feedstock particle size determined by MicroTrac and based on five size bins of data

Feedstock	tree age years	volume-weighted mean		
		Mean Sauter Dia. (microsn)	Length: Width	Sphericity
Needles (A)	23	125.8	2.3	0.6
Bark (A)	23	107.7	1.9	0.7
Stemwood (A)	23	122.7	2.7	0.5
Stemwood (D)	13	150.4	2.5	0.5
Residues (A) AC 10Hz	23	147.8	2.5	0.5
Residues (A) AC 28Hz	23	159.6	2.4	0.6
Residues (B)	23	144.6	2.2	0.6
Residues (B) Replicate	23	142.0	2.2	0.6
Whole Tree (D)	13	150.8	2.3	0.6

Table SI-2: Comparison of actual and predicted (weighted average) volatile matter and fixed carbon measurement of feedstock mixtures

Feedstock	Volatile Matter	Fixed Carbon
Bark (A) and Needles (A) 1:1 mix measured	68.30	24.35

Bark (A) and Needles (A) 1:1 mix predicted	71.14	24.20
Stemwood (A) and Needles (A) 1:1 mix measured	76.31	17.16
Stemwood (A) and Needles (A) 1:1 mix predicted	76.07	19.04
Residues (B), Bark (A), and Needles (A) 1:1:1 mix measured	69.02	23.75
Residues (B), Bark (A), and Needles (A) 1:1:1 mix predicted	71.64	23.05
Residues (B), Bark (A), and Needles (A) 1:2:2 mix measured	68.57	24.12
Residues (B), Bark (A), and Needles (A) 1:2:2 mix predicted	71.44	23.51

Table SI-3: Quantification of ash species in feedstock ash fraction (subset of feedstocks analyzed)

Feedstock	Ash content, % wt/wt										
	Al as Al_2O_3	Ca as CaO	Fe as Fe_2O_3	K as K_2O	Mg as MgO	Mn as MnO	Na as Na_2O	P as P_2O_5	Si as SiO_2	Ti as TiO_2	S as SO_3
Needles (A)	4.88	8.71	1.19	10.61	3.99	0.9	0.97	4.92	53.85	0.55	2.68
Bark (A)	13.87	33.67	1.34	13.04	8	1.47	0.75	4.64	18.69	0.18	4.97
Stemwood (A)	2.57	29.32	1.8	16.34	10.87	3.18	0.94	3.14	17.82	0.24	3.5
Stemwood (D)	1.92	26.55	0.86	23.12	10.19	2.33	0.24	5.04	8.34	0.09	3.7
Residues (A) AC 10Hz	3.02	19.28	0.52	21.22	8.4	2.22	0.2	5.98	23.15	0.04	3.58
Residues (A) AC 28Hz	2.66	20.24	1.03	19.49	9.89	2.22	0.39	4.62	13.71	0.13	3.75
Residues (B)	4.42	22.58	1.28	16.92	9.14	1.6	0.42	5.63	32.7	0.09	3.95
Residues (B) Replicate	4.08	19.26	1.37	15.72	7.87	1.42	0.4	5.05	34.08	0.09	3.46
Whole Tree (D)	3.65	25.05	0.52	23.19	9.32	1.95	0.23	6.46	10.08	0.08	3.86
Bark (A) and Needles (A) 1:1 mix	6.19	11.03	1.31	9.04	4.44	0.72	1.07	4.39	50.36	0.6	2.96
Residues (B), Bark (A), and Needles (A) 1:1:1 mix	5.82	13.83	1.35	11.38	5.3	1.02	0.86	4.7	43.88	0.45	2.92
Residues (B), Bark (A), and Needles (A) 1:2:2 mix	6.4	13.34	1.4	10.89	4.96	1	0.9	4.42	43.98	0.44	3.14

Ash content measured using ICP-OES after ashing at 750C for 8 hours, ASTM D6349

Table SI-4: Compositional Analysis of subset of feedstocks

Feedstock	Water Extractable	Ethanol Extractives	Acetone Extractives	Lignin	Glucan	Xylan	Galactan	Arabinan	Mannan	Acetyl	Total %
Needles (A)	5.95	1.35	7.35	41.03	22.33	4.12	2.57	1.52	7.44	0.98	98.42
Bark (A)	4.64	0.96	6.36	50.21	20.77	4.03	2.99	1.82	5.67	0.62	98.76
Stemwood (A)	2.76	0.31	2.57	30.7	39.84	6.3	2.59	0	14.94	1.35	101.37
Residues (A) AC 10Hz	3.26	0.44	4.02	35.11	31.99	7.63	3.63	1.34	10.02	1.18	99.5
Residues (A) AC 28Hz	1.76	0.31	2.4	35.23	34.37	8.39	3.9	0	12.41	1.24	100.6
Residues (B)	6.18	0.68	7.88	35.22	26.48	6.52	3.44	2.84	6.33	0.94	97.94
Residues (B) Replicate	4.91	0.62	6.6	35.52	28.18	7.33	3.56	1.93	7.64	0.95	98.54
Bark (A) and Needles (A) 1:1 mix	4.01	0.98	5.53	45.88	22.75	4.17	3.28	2.4	5.35	0.81	97.57
Residues (B), Bark (A), and Needles (A) 1:1:1 mix	5.76	1.02	6.87	42.06	23.37	5.07	2.95	1.62	7.55	0.9	98.86
Residues (B), Bark (A), and Needles (A) 1:2:2 mix	5.53	1.04	6.51	42.9	22.92	4.64	3.03	2.23	5.91	0.85	97.68

LAP reference: J. Sluiter and A. D. Sluiter, *Summative mass closure: Laboratory analytical procedure (LAP) review and integration*, National Renewable Energy Laboratory, Golden, CO, 2011.

Table SI-5: Cost contribution of each supply chain stage to the MFSP for each feedstock. "Whole Tree + Residues" represents a case considering the harvesting, preprocessing, and conversion of both feedstocks (36% residues and 64% thinnings(whole tree), based on supply availability from a single harvest area).

	$/GGE			
Feedstock	**Supply**	**Preprocessing**	**Conversion**	**Total**
Whole Tree (D)	1.52	0.62	2.46	4.61
Residues (B)	1.06	0.62	2.66	4.34
Whole Tree + Residues	1.39	0.62	2.53	4.54

Table SI-6: LCI for 23-year-old Residues, 13-year-old whole tree (thinnings) and mixture. "Whole Tree + Residues" represents a case considering the harvesting, preprocessing, and conversion of both feedstocks (36% residues and 64% thinnings(whole tree), based on supply availability from a single harvest area).

	Flow Rate (lb/h)		
	Residues (B)	Whole Tree (D)	Whole Tree + Residues
Products			
Gasoline fuel	15602	15125	15298
Diesel fuel	12307	11612	11865
Total	27909	26737	27163
Byproducts			
Excess electricity	12682	14457	13813
MEK (2-butanone)	1165	1165	1165
Acetone	4912	4897	4902
Resource Consumption			
Blended woody biomass (wet)	204131	204131	204131
Blended woody biomass (dry)	183718	183718	183718
Sand makeup	155	155	155
Natural gas a	158	177	170
Zeolite catalyst	0	0	0
Fixed-bed VPU catalyst (0.5% Pt/TiO2)	7	7	7
Hydrotreating catalyst (sulfided CoMo)	11	11	11
Hydrocracking catalyst (crystalline Si-Al with rare-earth metals)	2	2	2
ZnO (reforming cleanup)	0.0401	0.0449	0.0432
HDS (reforming cleanup)	0.0172	0.0192	0.0185
Steam reforming catalyst	0.0887	0.0992	0.0954
Shift catalyst	0.121	0.136	0.13
PSA adsorbent	3.04	3.4	3.27
50 wt % caustic	289	289	289
Net water makeup	73713	73526	73594

Boiler feed water chemicals	2	2	2
Cooling tower chemicals	1	1	1
No. 2 diesel fuel	71	71	71
Waste Streams			
Solids purge from fluidized bed reactors	5345	5541	5470
Wastewater	23221	22921	23030
Air Emissions			
CO2 (fossil)	433	484	466
CO2 (biogenic)	217319	220833	219558
CH4	0	0	0
CO	0	0	0
NO2	11	12	12
SO2	105	105	105
H2O	144287	145995	145375
H2S	0	0	0

Table SI-7: Compounds quantified via GC-MS analysis of pyrolysis oils in cases where 75 wt.% or more of liquid yield was collected for analysis. Blank indicates below detection limit.

Feedstock	Needles (A)	Stemwood (A)	Stemwood (A)	Residues (A)	Residues (A) Replicate	Residues (A) AC 28Hz	Residues (B) Replicate	Whole Tree (D)	Residues (B), Bark (A), and Needles (A) 1:1:1 mix
Year Analyzed	2022	2021	2022	2022	2022	2021	2021	2021	2021
Compound	weight percent of liquid product								
.beta.-D-Glucopyranose, 1,6-anhydro-	3.73	3.28	3.35	2.29	2.72	2.83	2.81	1.99	2.16
1,2-Cyclopentanedione	0.04	0.82	0.72	0.17	0.12	0.63	0.14	0.61	0.09
1,2-Cyclopentanedione, 3-methyl-	0.26		0.43	0.35	0.28				
1,2-Ethanediol		0.41				0.46	0.24	0.39	0.09
1-Hydroxy-2-butanone	0.09	0.11	0.11	0.10	0.10	0.20	0.10	0.19	0.10
1-Octanol, 2,7-dimethyl-		0.25				0.19	0.12	0.15	0.07
2(3H)-Furanone, dihydro-4-hydroxy-	0.08		0.04	0.07	0.08				
2(3H)-Furanone, 5-methyl-		0.04				0.05	0.02	0.04	0.04
2(5H)-Furanone	0.38	0.55	0.66	0.48	0.43	0.62	0.40	0.57	0.34
2(5H)-Furanone, 5-methyl-		0.06				0.10	0.07	0.09	0.07
2,3-Butanedione	0.15	0.05	0.14	0.16	0.15	0.07	0.06	0.06	0.07
2-Butanone	0.13	0.08	0.14	0.15	0.03	0.10	0.06	0.12	0.06
2-Butenal		0.05				0.05	0.03	0.05	0.03
2-Cyclopenten-1-one	0.12	0.16	0.15	0.19	0.16	0.22	0.19	0.24	0.24
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-		0.30				0.36	0.29	0.38	0.33
2-Cyclopenten-1-one, 2-methyl-	0.03	0.04	0.04	0.05	0.04	0.05	0.05	0.06	0.07
2-Cyclopenten-1-one, 3-methyl-	0.03	0.12	0.04	0.05	0.04	0.14	0.12	0.15	0.14
2-Furancarboxaldehyde, 5-methyl-	0.05	0.04	0.05	0.07	0.06	0.04	0.04	0.05	0.08
2-Furanmethanol		0.05				0.05	0.05	0.06	0.04
2-Methoxy-4-vinylphenol	0.14	0.44	0.27	0.30	0.18	0.46	0.35	0.47	0.45
2-Pentanone, 4-hydroxy-4-methyl-	0.04		0.07	0.05	0.05				
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-		0.08				0.17	0.18	0.12	0.11
2-Propanone, 1-(acetyloxy)-	0.09	0.05	0.09	0.11	0.09	0.10	0.08	0.11	0.11
2-Propanone, 1-hydroxy-	1.95	1.79	2.56	1.73	2.08	2.49	1.51	2.46	1.12
3-Hexanone		0.02				0.02	0.02	0.03	0.03
3-Pentanone		0.17				0.15	0.08	0.22	0.10
4-(1-Hydroxyallyl)-2-methoxyphenol	0.02	0.08	0.06	0.04	0.04	0.09	1.25	0.06	0.04
4-Methyl-5H-furan-2-one		0.13				0.14	0.10	0.14	0.11
5-Hydroxymethylfurfural	0.24	0.49	0.58	0.29	0.27	0.32	0.22	0.24	0.16
Acetaldehyde, hydroxy-	4.80	7.11	11.14	5.32	7.08	4.14	3.19	6.14	1.64
Acetic acid	2.50	1.19	2.05	1.80	1.97	1.42	1.12	1.49	1.01
Acetic acid, (acetyloxy)-	0.65	0.72	1.00	0.63	0.70	0.52	0.38	0.63	0.26
Apocynin	0.05	0.20	0.11	0.08	0.08	0.18	0.13	0.13	0.12
Benzenepropanol, 4-hydroxy-3-methoxy-	0.02		0.06	0.05	0.06				
Benzofuran, 2,3-dihydro-		0.02				0.04	0.07	0.04	0.11
Butyrolactone	0.07		0.10	0.09	0.08				
Catechol		0.07				0.18	0.22	0.17	0.27
Coniferyl alcohol-E	0.13	0.00	0.00	0.18	0.10	0.11	0.37	0.37	0.30
Coniferyl alcohol-Z	0.03	0.02	0.04	0.05	0.05	0.15	0.12	0.13	0.09
Coniferyl aldehyde	0.05	0.19	0.13	0.12	0.11	0.49	0.36	0.34	0.31
Creosol	0.19	0.52	0.37	0.42	0.34	0.50	0.45	0.54	0.69
Cyclopent-4-ene-1,3-dione	0.02		0.05	0.05	0.03				
D-Allose		0.11				0.31	0.30	0.22	0.22
D-Limonene	0.03	0.00	0.00	0.03	0.02	0.00	0.05	0.00	0.13
d-Mannose		0.13				0.25	0.29	0.16	0.18
Eugenol	0.04	0.25	0.09	0.14	0.11	0.28	0.21	0.24	0.36
Furan, 2,5-dimethyl-	0.06		0.05	0.05	0.01				
Formaldehyde		0.02				0.02	0.01	0.02	0.00
Furfural	0.23	0.25	0.37	0.39	0.33	0.32	0.26	0.31	0.46
Glycerin		0.06				0.09	0.04	0.07	0.05
Glycolaldehyde dimer		0.41				0.53	0.21	0.23	0.09
Homovanillic acid	0.03	0.17	0.05	0.06	0.05	0.19	0.14	0.12	0.10
Hydroquinone	0.06		0.04	0.05	0.05				
Methyl Alcohol		0.68				1.08	1.03	0.99	0.77
Methyl vinyl ketone	0.05		0.02	0.04	0.03				
p-Cresol	0.07	0.07	0.04	0.09	0.07	0.10	0.16	0.13	0.32
Phenol	0.13	0.07	0.07	0.15	0.13	0.12	0.16	0.15	0.26
Phenol, 2,6-dimethyl-	0.02	0.17	0.04	0.05	0.04	0.09	0.09	0.11	0.10
Phenol, 2-methoxy-	0.22	0.40	0.35	0.35	0.30	0.49	0.37	0.51	0.51
Phenol, 2-methoxy-3-(2-propenyl)-	0.05		0.11	0.14	0.11				
Phenol, 2-methoxy-4-(1-propenyl)-	0.01		0.03	0.03	0.02				
Phenol, 2-methoxy-4-propyl-	0.00		0.12	0.05	0.05				
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-		0.48				0.51	0.41	0.47	0.57
Phenol, 2-methoxy-4-propyl-		0.15				0.11	0.04	0.08	0.02
Phenol, 4-ethyl-2-methoxy-		0.22				0.17	0.17	0.20	0.26
Phenol, 2-methyl-	0.02		0.03	0.05	0.04				
Phenol, 3-ethyl-	0.03		0.02	0.03	0.03				
Phenol, 3-methyl-	0.03		0.04	0.05	0.05				
Phenol, 4-ethyl-2-methoxy-	0.04		0.06	0.08	0.07				
Propanoic acid, 2-oxo-, methyl ester	0.23	0.35	0.47	0.30	0.20	0.16	0.19	0.20	0.12
Succindialdehyde	0.16	0.58	0.78	0.47	0.47	0.65	0.32	0.76	0.14
trans-Isoeugenol	0.28	0.11	0.38	0.52	0.40	0.12	0.11	0.12	0.15
Vanillin	0.15	0.32	0.45	0.29	0.28	0.30	0.19	0.20	0.19

GC-MS Method Details

Oils were analyzed by gas chromatography with mass spectrometry and simultaneous flame ionization detection (GC-MS-FID). Analysis was conducted using an Agilent 8890 GC equipped with an FID and post column flow splitter. Compounds were qualitatively analyzed using an Agilent 5977B mass selective detector. The column used for compound separation was a Rtx-50 (Restek, 50% phenyl polydimethylsiloxane) of dimensions 30 m x 250 µm, 0.25 µm. Oil samples were diluted 1:10 in acetone for GC analysis. An autosampler (Agilent 7693A) was used to inject 1 µL of diluted sample into a split/splitless inlet held at 275 °C and a split ratio of 100:1. The GC oven was held at 40 °C for 2 min followed by a ramp to 140 °C at 7 °C/min, then to a final temperature of 290 °C at a rate of 12 °C/min. The final temperature was held for 10 min. Inert capillary flow restrictors were selected such that the difference in retention times between the FID and MS were within 0.1 minutes. Both FID and the MS transfer line were held at 350 °C. The MS was set to scan from m/z 29 to 300. Compounds were identified by spectral matching with the NIST library, and quantification was conducted using the calibrated FID signal. The detector was calibrated with a mixture of 36 compounds representative compound classes found in fast pyrolysis oils. All compounds had an $R2 \geq 0.99$ in the calibration range. For compounds detected that were not in the standard mixture the response factors (RF) were calculated using effective carbon number of the compound identified by M