UV Extinction Coefficient determination for GVL Lignin

GVL lignin was precipitated from the spent liquor after fractionation of *Eucalyptus* chips in 50 wt% GVL, at 180 °C for 180 minutes with a L:W ratio of 10 L/kg. The ratio of water-to-spent liquor for precipitation was 3 g/g. The dry-matter content of lignin was 94.12% and the lignin content (sum of AIL and ASL) was 92.97%. Two lignin stock solutions were prepared in 50 wt% GVL solution, and different amounts of stock solution were diluted with 35 wt% ethanol. The UV absorbance of each diluted solution at 205nm was measured with a Shimadzu UV-2550 spectrophotometer. The extinction coefficient of GVL lignin was calculated by the formula:

$$\varepsilon = \frac{Abs_{205}}{l \times [Lignin]}$$

Where:

ε [L/(g.cm)] is the extinction coefficient
Abs₂₀₅ is the UV absorption at 205 nm
l [cm] is the width of the quartz cuvette used in the measurement
[Lignin] [g/L] is the lignin concentration in 35 wt% ethanol

The determination was repeated 20 times. The results are shown in Table 1.

In Table 1:

 $m_{L-solution}$: amount of stock solution being diluted in 35 wt% ethanol m_L : amount of lignin in the diluted solution (35 wt% ethanol) $V_{diluted}$: volume of the diluted solution (35 wt% ethanol) [Lignin]: concentration of lignin in the diluted solution (35 wt% ethanol)

Table 1. UV Extinction coefficient determination for GVL lignin.

		Sample	m _{L-solution}	m _L	V _{diluted}	[Lignin]	Abs. 205 nm	3
			g	g	L	g/L		L/(g.cm)
1 st Lignin stock solution:		1	0.0201	0.00050	0.05	0.0101	1.397	138.85
Lignin sample	0.2935 g	2	0.0203	0.00051	0.05	0.0102	1.434	141.12
Lignin (pure)	0.2568 g	3	0.0155	0.00039	0.05	0.0078	1.207	155.57
GVL 50%	10.0046 g	4	0.0190	0.00048	0.05	0.0095	1.521	159.92
		5	0.0182	0.00045	0.05	0.0091	1.346	148.15
		6	0.0349	0.00087	0.10	0.0087	1.269	145.28
		7	0.0337	0.00084	0.10	0.0084	1.226	145.36
		8	0.0382	0.00096	0.10	0.0096	1.393	145.70
		9	0.0370	0.00093	0.10	0.0093	1.335	144.16
		10	0.0359	0.00090	0.10	0.0090	1.368	152.25
2 nd Lignin stock solution:		11	0.0197	0.00049	0.05	0.0098	1.379	141.07
Lignin sample	0.2905 g	12	0.0204	0.00051	0.05	0.0101	1.486	146.80
Lignin (pure)	0.2542 g	13	0.0205	0.00051	0.05	0.0101	1.484	146.24
GVL 50%	9.9925 g	14	0.0205	0.00051	0.05	0.0102	1.482	145.69
		15	0.0150	0.00037	0.05	0.0074	1.194	160.95
		16	0.0342	0.00085	0.10	0.0085	1.273	150.03
		17	0.0332	0.00082	0.10	0.0082	1.205	146.29
		18	0.0337	0.00084	0.10	0.0084	1.257	150.34
		19	0.0346	0.00086	0.10	0.0086	1.271	148.27
		20	0.0363	0.00090	0.10	0.0090	1.321	146.68
							AVERAGE	147.94
							deviation	5.58

Pulp properties and identified chemical composition after GVL/H₂O fractionation of *Eucalyptus* wood chips at 180°C

Comm la(a)	Yield	Intrinsic viscosity	Vanna	ISO Brightness Pulp composition [% oven-dried pulp]						
Sample	%	mL/g	Карра	%	Others ^(b)	Glucose	Xylose	Mannose	Lignin	
50-60	52.7	833	26.0	31.7	0.0	77.1	5.5	0.9	4.7	
50-90	47.8	818	17.6	34.5	0.0	88.9	5.7	0.9	3.6	
50-120	46.8	630	12.7	37.0	0.0	86.3	4.5	0.8	2.4	
50-150	45.0	551	10.6	39.8	0.0	89.2	4.1	0.6	2.4	
50-180	44.6	456	10.3	38.9	0.0	91.4	3.9	0.6	2.1	
60-60	51.9	936	27.5	32.9	0.0	83.1	6.1	1.2	4.8	
60-90	48.6	862	19.6	33.7	0.2	84.9	5.6	1.2	4.3	
60-120	47.3	737	13.5	37.8	0.0	85.6	4.9	1.0	2.6	
60-150	45.8	710	14.0	36.2	0.0	84.4	4.9	0.9	3.1	
60-180	44.8	592	11.5	39.9	0.0	88.1	4.8	0.7	2.6	

(a) The sample is named as: GVL content in fractionation liquor (in wt%)-Fractionation time (in minutes)

(b) Other carbohydrates: arabinose, rhamnose, galactose

Detailed composition of spent liquor (SL) after GVL/H₂O fractionation of *Eucalyptus* wood chips at 180°C

C arran 1a(3)	Free SL	L Composition of spent liquor ^(b) [% oven-dried wood]									Mono/Total ^(d)			
Sample	g	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose	HMF	Furfural	FA ^(c)	AA ^(c)	LA ^(c)	Lignin	%
50-60	282.7	0.2	0.2	0.9	0.8	7.6	0.3	0.1	1.5	5.5	2.5	0.5	26.8	49.1
50-90	285.7	0.1	0.2	0.7	0.4	6.4	0.4	0.2	2.5	6.0	3.1	0.4	26.9	67.2
50-120	283.8	0.1	0.1	0.6	0.5	5.2	0.4	0.3	3.7	5.0	3.2	0.3	27.8	80.7
50-150	289.4	0.1	0.1	0.6	0.5	4.0	0.3	0.4	4.8	4.3	3.4	0.3	28.0	91.3
50-180	290.8	0.1	0.1	0.5	0.6	3.1	0.3	0.5	5.6	3.8	3.7	0.3	28.1	93.8
60-60	282.8	0.2	0.2	0.7	0.4	6.9	0.3	0.1	1.0	6.3	1.8	0.3	24.7	39.6
60-90	272.0	0.1	0.2	0.7	0.4	6.4	0.3	0.1	1.9	6.8	3.1	0.3	26.3	55.8
60-120	286.3	0.1	0.1	0.6	0.3	4.7	0.2	0.2	3.0	6.3	3.6	0.4	28.2	75.0
60-150	278.5	0.1	0.1	0.5	0.4	3.9	0.2	0.3	3.2	5.9	2.8	0.2	27.6	73.5
60-180	286.9	0.1	0.1	0.5	0.5	3.5	0.3	0.4	4.5	5.8	3.7	0.3	28.1	85.9

(a) The sample is named as: GVL content in fractionation liquor (in wt%)-Fractionation time (in minutes)

(b) Component content in SL is the sum of that in free SL and washing liquids

(c) FA, AA, LA: formic, acetic and levulinic acids, respectively
(d) Ratio of the amount of monomeric carbohydrate and the total amount of carbohydrate in the spent liquor

Furfural conversion yield during fractionation of *Eucalyptus* wood chips at 180°C

Sample ^(a)	Pulp xylose ^(b)	Furfural conversion ^(d)			
	%odw	Xylose	Degraded xylose(c)	Furfural	mol %
Wood	18.0	0.0	0.0	0.0	0.0
50-60	3.5	7.6	6.9	1.5	21.7
50-90	2.9	6.4	8.7	2.5	28.7
50-120	2.4	5.2	10.4	3.7	35.6
50-150	2.1	4.0	12.0	4.8	40.0
50-180	1.9	3.1	13.0	5.6	43.1
60-60	3.5	6.9	7.6	1.0	13.2
60-90	3.0	6.4	8.6	1.9	22.1
60-120	2.6	4.7	10.7	3.0	28.0
60-150	2.6	3.9	11.5	3.2	27.8
60-180	2.4	3.5	12.1	4.5	37.2

(a) The sample is named as: GVL content in fractionation liquor (in wt%)-Fractionation time (in minutes)

(b) The components are express as polymeric xylan equivalent (anhydroxylose)(c) Difference between initial xylose and the sum of xylose in pulp and spent liquor

(d) Conversion is the ratio of furfural to degraded xylose

Conversion of spent liquor xylose to furfural catalyzed by sulfuric acid

Spent liquor (SL) obtained from the fractionation of wood chips with 50 wt% GVL, L:W = 10 L/kg, at 180°C for 150 minutes were mixed with pure GVL to increase the GVL concentration to 90 wt%. The diluted spent liquor samples were treated with 0.1M sulfuric acid at 200°C .

Xylose was quantitatively converted to furfural after 5 minutes. Beyond that point, significant degradation of furfural and organic acids occurred. In the mass balance below, the amount of organic acids and other degradation products from xylan are not considered.

Time	Xylose in pulp	Xylose in treated SL		Furfural in treated SL ^(a)		Degraded xylose ^(c)	Furfural conversio	n (mol %)
min	% odw ^(b)	%odw	mmol/L	%odw	mmol/L	%odw	H ₂ SO ₄ treatment	Overall ^(d)
wood	18.0	0.0	0.00	0.0	0.00	0.0	0.0	0.0
0	2.1	4.0	5.83	4.8	7.14	11.9	0.0	40.3
5	2.1	0.0	0.00	8.1	12.03	15.9	83.9	50.9
15	2.1	0.0	0.00	7.2	10.69	15.9	60.9	45.3
30	2.1	0.0	0.00	6.5	9.72	15.9	44.3	40.9
60	2.1	0.0	0.00	4.4	6.51	15.9	-10.8	27.7
90	2.1	0.0	0.00	3.1	4.66	15.9	-42.5	19.5
120	2.1	0.0	0.00	2.2	3.32	15.9	-65.5	13.8

(a) Furfural is expressed as xylan in original wood

(b) Percent on oven-dried wood

(c) Difference between initial xylose and the sum of xylose in pulp and spent liquor

(d) Combined conversion yield by fractionation and sulfuric acid treatment, equals to the ratio of furfural to degraded xylose.