

Are Lignin-Derived Monomers and Polymers truly sustainable? An In-Depth Green Metrics Calculations Approach

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Table S1. Monomers syntheses

Table S2. Polymerizations

57			c	48	1,0	306	-	0,005	42	1,304	90				78	5,64		9,41	36			
				Epichlorohydrin	20	93	7,858	0,085	-	-	-											
				TEBAC	0,1	228	0,092	0,000	-	-	-											
				NaOH solution 10 M	16	40	2,717	0,068	-	-	-											
				Water (for NaOH)	89	18	6,795	0,378	-	-	-											
	1,0	531	-	0,004	49	1,802	80															
58		52	e	Methylated diVanillin	1,0	330	2,000	0,006	-	-	-	60	100	2	90	1,72	3,21	12,5	80	57,5	93	125
				Hydroxylamine hydrochlor	1,2	69	1,000	0,007	-	-	-											
				Sodium acetate	2,0	82	2,000	0,012	-	-	-											
				Ethanol	57	46	15,78	0,343	-	-	-											
				Water	37	18	4,000	0,222	-	-	-											
	1,0	360	-	0,006	51	1,838	85															
59			f	51	1,0	360	1,840	0,005	-	-	-	60	70	15	92	0,55		38,2	96			
				nickel Raney	nd	nd	nd	nd	-	-	-											
				Ethanol	190	46	44,76	0,972	-	-	-											
	1,0	332	-	0,005	52	1,188	70															
60		56	g	Methylated divanillic acid	1,0	362	1,087	0,003	-	-	-	5	0	2	77	7,18	146	42,0	81	1068	86	125
				THF	78	72	16,87	0,234	-	-	-											
				Water	167	18	9,002	0,500	-	-	-											
				Triethylamine	5,7	101	1,730	0,017	-	-	-											
				Ethylchloroformate	6,3	109	2,051	0,019	-	-	-											
	1,0	412	-	0,003	54	0,742	60															
61			h	54	1,0	412	0,740	0,002	-	-	-	5	80	8	86	0,45		18,7	93			
				Toluene	57	92	9,342	0,101	-	-	-											
					1,0	356	-	0,002	55	0,512	80											
62			i	55	1,0	356	0,510	0,001	-	-	-	5	80	12	85	18,1		132	86			
				Toluene	38	92	4,959	0,054	-	-	-											
				KOH	4,0	56	0,321	0,006	-	-	-											
	1,0	304	-	0,001	56	0,044	10															
63	9	58	a	Vanillin	1,0	152	1,913	0,013	-	-	-	76	110	2	67	27,6	30,3	27,6	0	169	82	127
				Acetic acid	53	60	39,63	0,660	-	-	-											
				NH ₂ OH.HCl	1,5	69	1,310	0,019	-	-	-											
					1,0	149	-	0,013	57	1,500	80											
				57	1,0	149	1,500	0,010	-	-	-											
64			b	Acetone	27	58	15,65	0,270	-	-	-	76			99	1,11		139	98			
				NaOAc	1,8	82	1,480	0,018	-	-	-											
				Water	994	18	180,0	10,00	-	-	-											
				Laccase	-	-	0,012	-	-	-	-											
					0,5	296	-	0,005	58	1,415	95											
65		59	c	Vanillin	1,0	152	1,500	0,010	-	-	-	77	80	1,5-2	99	1,09	1,85	138	98	107	97	123
				Acetone	27	58	15,69	0,270	-	-	-											
				NaOAc	1,8	82	1,480	0,018	-	-	-											
				Water	1014	18	180,0	10,00	-	-	-											
				Laccase	-	-	0,012	-	-	-	-											
	0,5	302	-	0,005	41	1,430	96															
66			d	41	1,0	302	1,430	0,005	-	-	-	77	80	2 to 12	77	1,08		8,93	79		129	
				DMSO	43	78	15,78	0,202	-	-	-											
				KOH	2,4	56	0,637	0,011	-	-	-											
				2-ethylhexyl bromide	2,3	193	2,101	0,011	-	-	-											
					1,0	531	-	0,005	59	2,009	80 (assumed)											
67		60	e	Diacid	1,0	362	2,890	0,008	-	-	-		room temperature	72	94	3,01	3,01	36,2	89	36,2	89	128
				Undecenol	3,0	172	4,130	0,024	-	-	-											
				N,N'-diisopropylcarbodiimi	5,7	126	5,800	0,046	-	-	-											
				p-Toluene sulfonic acid/4 d	nd	-	nd	nd	-	-	-											
				DCM	157	85	106,4	1,253	-	-	-											
	-	667	-	0,008	60	3,200	60															
68	10	65	a	Guaiacol	2,5	124	93,10	0,750	-	-	-	56	60	2 to 24	94	1,80	5,15	1,80	0	6,34	16	136
				Vanillyl alcohol	1,0	154	46,25	0,300	-	-	-											
				Dowex DR2030 10 wt%	nd	nd	13,94	nd	-	-	-											
					1,0	260	-	0,300	61	54,66	70											
				61	1,0	260	54,66	0,210	-	-	-											
69			c	Epichlorohydrin	10	93	196,2	2,121	-	-	-	56			84	3,57		4,77	21			
				Tetrabutylammonium brom	0,1	228	4,783	0,021	-	-	-											
				NaOH 40 wt% solution	3,6	40	30,23	0,756	-	-	-											
				Water	20	18	74,84	4,158	-	-	-											
					1,0	372	-	0,210	65	62,57	80 (assumed)											
70		64	b	Vanillyl alcohol	1,0	154	10,00	0,065	-	-	-	50	15	94	2,53		2,53	0			133	
				Guaiacol	3,6	124	28,99	0,234	-	-	-											

102	85	b	Ferulic acid	1,0	194	250,5	1,290	-	-	-	81	reflux, room temperature	48, 18 (in H ₂)	93	2,94	5,64	2,94	74	5,64	69	168
			Pd/C	0,0	106	4,500	0,042	-	-	-											
			Ethanol (few drops HCl)	12	46	710,1	15,41	-	-	-											
103	85	f	Ethyl dihydroferulate	1,0	224	245,0	0,049	-	-	-	61	75	4	83	0,98	7,00	0,98	0	13,6	79	168
			1,4-butanediol	0,3	90	32,82	0,016	-	-	-											
			CAL-B	-	-	27,78	-	-	-	-											
104	86	b	Ferulic acid	1,0	194	250,5	1,290	-	-	-	57	reflux, room temperature	48, 18 (in H ₂)	93	2,94	8,86	2,94	74	14,6	73	168
			Pd/C	0,0	106	4,500	0,042	-	-	-											
			Ethanol (few drops HCl)	12	46	710,1	15,41	-	-	-											
105	86	f	Ethyl dihydroferulate	1,0	224	245,0	0,049	-	-	-	78	75	4	82	1,07	6,05	1,07	0	6,05	70	168
			1,4-butanediol	0,3	90	32,82	0,016	-	-	-											
			CAL-B	-	-	27,78	-	-	-	-											
106	86	g	85	1,0	447	154,4	0,002	-	-	-	70	room temperature	18	88	1,01	6,09	7,60	77	12,0	79	168
			Acryloyl chloride	2,2	91	66,18	0,005	-	-	-											
			Triethylamine	2,2	101	72,19	0,005	-	-	-											
107	87	b	Ferulic acid	1,0	194	250,5	1,290	-	-	-	62	reflux, room temperature	48, 18 (in H ₂)	93	2,94	8,20	2,94	74	12,6	71	168
			Pd/C	0,0	106	4,500	0,042	-	-	-											
			Ethanol (few drops HCl)	12	46	710,1	15,41	-	-	-											
108	87	f	Ethyl dihydroferulate	1,0	224	245,0	0,049	-	-	-	81	75	4	82	1,07	6,03	1,07	0	6,03	69	177
			1,4-butanediol	0,3	90	32,82	0,016	-	-	-											
			CAL-B	-	-	27,78	-	-	-	-											
109	87	h	85	1,0	447	154,4	0,009	-	-	-	81	room temperature	18	76	2,02	6,03	7,74	65	14,6	73	168
			Allyl bromide	2,1	121	86,47	0,019	-	-	-											
			K ₂ CO ₃	3,0	138	143,5	0,027	-	-	-											
110	88	b	Ferulic acid	1,0	194	250,5	1,290	-	-	-	62	reflux, room temperature	48, 18 (in H ₂)	93	2,94	8,20	2,94	74	12,6	71	168
			Pd/C	0,0	106	4,500	0,042	-	-	-											
			Ethanol (few drops HCl)	12	46	710,1	15,41	-	-	-											
111	88	i	Ethyl dihydroferulate	1,0	224	245,0	0,045	-	-	-	78	75	4	82	1,07	6,05	1,07	0	6,05	70	168
			1,3-propanediol	0,3	76	27,65	0,015	-	-	-											
			CAL-B	-	-	27,27	-	-	-	-											
112	89	b	Ferulic acid	1,0	194	250,5	1,290	-	-	-	70	reflux, room temperature	48, 18 (in H ₂)	93	2,94	6,09	2,94	74	12,0	79	168
			Pd/C	0,0	106	4,500	0,042	-	-	-											
			Ethanol (few drops HCl)	12	46	710,1	15,41	-	-	-											
113	89	i	Ethyl dihydroferulate	1,0	224	245,0	0,045	-	-	-	78	75	4	82	1,07	6,09	1,07	0	12,0	79	168
			1,3-propanediol	0,3	76	27,65	0,015	-	-	-											
			CAL-B	-	-	27,27	-	-	-	-											
114	89	j	88	1,0	432	144,6	0,009	-	-	-	78	room temperature	18	88	0,70	6,57	78	12,0	79	168	
			Acryloyl chloride	2,1	91	64,30	0,020	-	-	-											
			Triethylamine	2,1	101	67,73	0,020	-	-	-											
115	90	b	Ferulic acid	1,0	194	250,5	1,290	-	-	-	62	reflux, room temperature	48, 18 (in H ₂)	93	2,94	8,20	2,94	74	12,6	71	168
			Pd/C	0,0	106	4,500	0,042	-	-	-											
			Ethanol (few drops HCl)	12	46	710,1	15,41	-	-	-											
116	90	i	Ethyl dihydroferulate	1,0	224	245,0	0,045	-	-	-	78	75	4	82	1,07	6,09	1,07	0	12,0	79	168
			1,3-propanediol	0,3	76	27,65	0,015	-	-	-											
			CAL-B	-	-	27,27	-	-	-	-											
117	90	k	88	1,0	432	144,6	0,006	-	-	-	78	room temperature	18	76	1,74	6,15	62	12,6	71	168	
			Allyl bromide	2,2	121	88,61	0,014	-	-	-											
			K ₂ CO ₃	3,0	138	138,5	0,019	-	-	-											
118	91	l	Ferulic acid	1,0	194	250,5	1,290	-	-	-	81	reflux, room temperature	48, 48 (in H ₂)	93	2,47	6,03	2,47	73	6,03	69	177
			Hydrochloric acid (37.5%)	0,0	36	0,941	0,026	-	-	-											
			Pd/C	0,1	106	12,53	0,118	-	-	-											
119	91	m	Ethyl dihydroferulate	1,0	224	280,6	0,036	-	-	-	81	75	72	82	1,30	6,03	1,30	0	6,03	69	177
			Glycerol	0,2	92	25,64	0,008	-	-	-											
			CAL-B	-	-	30,63	-	-	-	-											
120	92	b	Ferulic acid	1,0	194	250,5	1,290	-	-	-	81	reflux, room temperature	48, 18 (in H ₂)	93	2,94	5,64	2,94	74	5,64	69	168
			Pd/C	0,0	106	4,500	0,042	-	-	-											
			Ethanol (few drops HCl)	12	46	710,1	15,41	-	-	-											

Table S2. Green metric calculations of selected polymerizations

Entry No.	Input Material	Initiator/ Catalyst Conc. %	Equivalent Ratios (Eq)	Molar Mass (g/mol)	Input Weight (mg)	Molar Amount (mmol)	Output Material	Output Weight (g)	% Yield	sEF	E factor	Solvent Contribution to E factor %	Ref
1	26			207	400	1,9							94
	AIBN	1 wt%		164	1	0,0							
	Toluene			92	1734	18,8							
	DMF			73	1888	25,8							
							Poly(26)	40	10	9,0	99,6	90	
2	26			207	400	1,9							94
	AIBN	4 wt%		164	16	0,1							
	Toluene			92	1734	18,8							
	DMF			73	1888	25,8							
							Poly(26)	384	96	0,08	41,1	90	
3	82		1,0	503	503	1,0							170
	Succinyl chloride		1,0	155	155	1,0							
							Poly[succinic-alt-(IDF)] (PSIDF)	618	94	0,06	0,06	0	
4	82		1,0	503	503	1,0							170
	Azelaoyl chloride		1,0	225	225	1,0							
							Poly[azelaic-alt-(IDF)] (PAIDF)	691	95	0,05	0,05	0	
5	85		1,0	447	447	1,0							170
	Succinyl chloride		1,0	155	155	1,0							
							Poly[succinic-alt-(BDF)] (PSBDF)	577	96	0,04	0,04	0	
6	85		1,0	447	447	1,0							170
	Azelaoyl chloride		1,0	225	225	1,0							
							Poly[azelaic-alt-(BDF)] (PABDF)	638	95	0,05	0,05	0	
7	88		1,0	432	432	1,0							171
	1,6-hexamethylene diisocyanate (HDI)		1,0	168	168	1,0							
							Poly[1,6-hexamethylene diisocyanate-alt-PDF]] (P	595	99	0,01	0,01	0	
8	88		1,0	432	432	1,0							171
	1,4-toluene diisocyanate (TDI)		1,0	174	174	1,0							
							Poly[1,4-toluene diisocyanate-alt-PDF]] (PTDI-PDF	595	98	0,02	0,02	0	
9	85		1,0	447	447	1,0							171
	1,6-hexamethylene diisocyanate (HDI)		1,0	168	168	1,0							
							Poly[1,6-hexamethylene diisocyanate-alt-BDF]] (P	572	93	0,08	0,08	0	
10	85		1,0	447	447	1,0							171
	1,4-toluene diisocyanate (TDI)		1,0	174	174	1,0							
							Poly[1,4-toluene diisocyanate-alt-BDF]] (PTDI-BDF	614	99	0,01	0,01	0	
11	82		1,0	503	503	1,0							171
	1,6-hexamethylene diisocyanate (HDI)		1,0	168	168	1,0							
							Poly[1,6-hexamethylene diisocyanate-alt-IDF]] (P	497	99	0,35	0,35	0	
12	82		1,0	503	503	1,0							171
	1,4-toluene diisocyanate (TDI)		1,0	174	174	1,0							
							Poly[1,4-toluene diisocyanate-alt-IDF]] (PTDI-IDF)	497	99	0,36	0,36	0	
13	88		1,0	432	432	1,0							171
	1,6-hexamethylene diisocyanate (HDI)		1,0	168	168	1,0							
	Methyl ethyl ketone (1000 g/L)		6,7	72	484	6,7							
							Poly[1,6-hexamethylene diisocyanate-alt-PDF]] (P	571	95	0,05	0,90	45	
14	88		1,0	432	432	1,0							171
	1,4-toluene diisocyanate (TDI)		1,0	174	174	1,0							
	Methyl ethyl ketone (1000 g/L)		6,8	72	488	6,8							
							Poly[1,4-toluene diisocyanate-alt-PDF]] (PTDI-PDF	510	84	0,19	1,15	45	

15	85		1,0	447	447	1,0							171
	1,6-hexamethylene diisocyanate (HDI)		1,0	168	168	1,0							
	Methyl ethyl ketone (1000 g/L)		6,9	72	495	6,9							
							Poly[1,6-hexamethylene diisocyanate-alt-BDF]] (P	559	91	0,10	0,98	45	
16	85		1,0	447	447	1,0							171
	1,4-toluene diisocyanate (TDI)		1,0	174	174	1,0							
	Methyl ethyl ketone (1000 g/L)		6,9	72	500	6,9							
							Poly[1,4-toluene diisocyanate-alt-BDF]] (PTDI-BDF	577	93	0,08	0,94	45	
17	82		1,0	503	503	1,0							171
	1,6-hexamethylene diisocyanate (HDI)		1,0	168	168	1,0							
	Methyl ethyl ketone (1000 g/L)		7,5	72	540	7,5							
							Poly[1,6-hexamethylene diisocyanate-alt-IDF]] (P	624	93	0,08	0,94	45	
18	82		1,0	503	503	1,0							171
	1,4-toluene diisocyanate (TDI)		1,0	174	174	1,0							
	Methyl ethyl ketone (1000 g/L)		7,6	72	545	7,6							
							Poly[1,4-toluene diisocyanate-alt-IDF]] (PTDI-IDF)	643	95	0,05	0,90	45	
19	99		1,0	238	1000	4,2							179
	Antimony trioxide	1 mol%	0,01	292	12	0,04							
							Polyethylene ferulate (PEF)	896	90	0,13	0,13	0	
20	100		1,0	240	1009	4,2							179
	Antimony trioxide	1 mol%	0,01	292	12	0,04							
							Polyethylene dihydroferulate	879	87	0,16	0,16	0	
21	101		1,0	252	1488	5,9							179
	Antimony trioxide	1 mol%	0,01	292	17	0,06							
							Polypropylene ferulate	1386	93	0,09	0,09	0	
22	102		1,0	294	1501	5,1							179
	Antimony trioxide	1 mol%	1,0	292	15	0,05							
							Polyhexalene ferulate	1392	93	0,09	0,09	0	
23	118		1,0	208	1499	7,2							179
	Antimony trioxide	1 mol%	0,01	292	21	0,07							
							Polyethylene coumarate (PEC)	1288	86	0,18	0,18	0	
24	119		1,0	210	1493	7,1							179
	Antimony trioxide	1 mol%	0,01	292	21	0,07							
							Polyethylene dihydrocoumarate	1351	91	0,12	0,12	0	
25	121		1,0	180	4324	24,0							185
	Sodium acetate	1 mol%	0,01	174	42	0,24							
	Anhydride acetic acid		6,2	72	10800	149,8							
							Poly(3,4-dihydroxycinnamic acid) (PDHCA)	2983	69	4,08	4,08	0	
26	114		1,0	164	3937	24,0							185
	Sodium acetate	1 mol%	0,01	174	42	0,24							
	Anhydride acetic acid		6,2	72	10800	149,8							
							Poly(4-hydroxycinnamic acid) (P4HCA)	3543	90	3,17	3,17	0	
27	81		1,0	194	4660	24,0							185
	Sodium acetate	1 mol%	0,01	174	42	0,24							
	Anhydride acetic acid		6,2	72	10800	149,8							
							Poly(3-methoxy-4-hydroxycinnamic acid) (PMHCA)	4101	88	2,78	2,78	0	
28	127		1,0	283	4212	14,9							200
	PLLA50		0,2	3570	13209	3,7							
	Pyridine		1,67	79,10	1964	24,8							
	DCM		42,0	84,93	53200	626,4							
							3,4-diacetoxycinnamic acid (DACA)-terminally con	16376	94	0,06	3,43	24	
29	137		1,0	212	1528	7,2							214

	Antimony trioxide		0,01	292	20	0,07							
							Poly(4-(2-hydroxyethoxy)-3-methoxybenzoic acid)	1100	79	0,41	0,41	0	
30	138		1,0	226	2104	9,3							214
	Antimony trioxide		0,01	292	35	0,12							
							Poly(4-(3-hydroxypropoxy)-3-methoxybenzoic acid)	1199	57	0,78	0,78	0	
31	141		1,0	242	1969	8,1							214
	Antimony trioxide		0,01	292	20	0,07							
							Poly(4-(2-hydroxyethoxy)-3,5-dimethoxybenzoic acid)	1398	71	0,42	0,42	0	
32	142		1,0	256	1699	6,6							214
	Antimony trioxide		0,01	292	17	0,06							
							Poly(4-(3-hydroxypropoxy)-3,5-dimethoxybenzoic acid)	1393	82	0,23	0,23	0	