Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information for

From waste to resource: advancements in sustainable lignin modification

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General information

The E-factor calculations presented herein consider the synthetic E-factors, without considering any pretreatment/solubilization done to the lignin prior to the synthesis. E_{simple} is defined as the simple E-factor, where no solvents are included in the calculation; $E_{complex}$ on the other hand also includes the solvent contribution to the E-factor.

If no final, isolated weight of lignin was reported in the respective manuscripts, a theoretical yield was calculated assuming 100% conversion of the reactive sites towards the main reaction, thus assuming the lowest possible E-Factor for the respective literature described reaction, following Equation S1:

$$m_f = m_i \ (1 + \Delta M_{graft} \ (reactive \ sites \ in \ \frac{mol}{g})) \qquad \text{Eq. S1}$$

where:

m_f = final mass of the modified lignin (g)

m_i = initial mass of pristine lignin (g)

ΔM_{graft}= increase in the molecular weight caused by the modification (g/mol)

Reactive sites = number of moieties participating in the reaction (depending on the reaction type) in mol/g.

This assumption represents a deliberate simplification that assumes 100% recovery of the modified lignin from the synthetic process, quantitative conversion, and considers only the main reaction. Despite its inherent simplifying nature, this assumption serves as a practical means to derive an estimate for the minimal attainable E-factor.

Abbreviation list

AlOH: aliphatic hydroxyl groups

ArOH: aromatic hydroxyl groups

COOH: carboxylic acid groups

Amino group functionalized lignin

Calculated E-factors for amination procedures are summarized in Table S1. Below the table, all calculations are listed to ensure reproducibility.

Table S1 - E factors for amination procedures.

Work	Modification	Functionalizing agent	E_{simple}	$E_{complex}$	$E_{solvent}$ / %
She[1]	Amination (Mannich)	dimethylamine, ethylenediamine and diethylenetriamine	4.15[a]	12.66[a]	67
Li[2]	Amination (Mannich)	dimethylamine	5.51[a]	20.62[a]	73
Jameel[3]	Amination (Mannich)	dimethylamine, diethylamine	2.98	13.74	78
Biesalski[4]	Amination (Mannich)	diethylenetriamine, 1,3-propylenediamine, ethylenediamine, ammonia	1.91-5.04	12.93-26.59	81-90
Kim[5]	Amination	2-chloroethylamine hydrochloride	12.27	142	91
Renneckar[6]	Amination	2-oxazolidinone	3.10	–	–

[a]: no final weight of isolated product was reported, therefore final weight of the product was calculated based on theoretical yield.

Jiao, G.-J.; Peng, P.; Sun, S.-L.; Geng, Z.-C.; She, D. Amination of Biorefinery Technical Lignin by Mannich Reaction for Preparing Highly Efficient Nitrogen Fertilizer. Int. J. Biol. Macromol. ***2019****, 127, 544–554*

Starting materials: 5 g phenolated lignin (**7.79 mmol per g lignin reactive sites**, 0.13 mmol per g lignin AlOH, 5.84 mmol per g lignin ArOH), 20 g formaldehyde (666 mmol in 37% aq. solution, 54 g total weight considering water), 15 g ethylenediamine (250 mmol, in 40% aq. solution, 37.5 g total weight considering water), 0.16 g sodium hydroxide (4 mmol, 0.4 mol/L, 10.02 g total weight considering water).

Desired product: 7.81 g (theoretical yield)

$$m_f = m_i \left(1 + \Delta M_{graft} \left(reactive\ sites\ in \frac{mol}{g}\right)\right) = 5\ g \left(1 + 72.1\ \frac{g}{mol} \left(7.79 \times 10^{-3} \frac{mol}{g}\right) = 7.81\ g$$

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{40.16 - 7.81}{7.81} = \ 4.14$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{106.52 - 7.81}{7.81} = \ 12.64$$

Solvent contribution to the E-factor:

$$Solvent\ contribution = \frac{weight\ \ of\ \ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{66.36}{98.72} = 0.672 = \ \mathbf{67.2}\%$$

Du, X.; Li, J.; Lindström, M. E. Modification of Industrial Softwood Kraft Lignin Using Mannich Reaction with and without Phenolation Pretreatment. Ind. Crops Prod. ***2014****, 52, 729–735*

Starting materials: 0.1 g LignoBoost lignin from spruce kraft black liquor (**1.96 mmol per g lignin reactive sites**, 1.60 mmol per g lignin AlOH, 0.45 mmol per g lignin COOH, 3.59 mmol per g lignin ArOH), 0.165 g formaldehyde (5.5 mmol, in 37% aq. solution, 0.446 g total weight considering water), 0.248 g dimethylamine (5.5 mmol, in 40% aq. solution, 0.62 g total weight considering water), 0.21 g acetic acid (3.5 mmol), 1.024 g (80% solution of 1,4-dioxane in water).

Desired product: 0.111 g (theoretical yield)

$$m_f = m_i \,(1 + \Delta M_{graft} \,(reactive\ sites\ in \frac{mol}{g})) = 0.1\ g\ (1 + 57.06\ \frac{g}{mol}\,(1.96 \times 10^{-3} \frac{mol}{g}) = 0.111\ g$$

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{0.723 - 0.111}{0.111} = 5.51$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{2.4 - 0.111}{0.111} = 20.62$$

Solvent contribution to the E-factor:

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{1.677}{2.29} = 0.732 = \mathbf{73.2}\%$$

Kollman, M.; Jiang, X.; Thompson, S. J.; Mante, O.; Dayton, D. C.; Chang, H.; Jameel, H. Improved Understanding of Technical Lignin Functionalization through Comprehensive Structural Characterization of Fractionated Pine Kraft Lignins Modified by the Mannich Reaction. Green Chem. ***2021****, 23 (18), 7122–7136*

Starting materials: 0.1 g BioChoice® lignin, 0.150 g formaldehyde (5 mmol in 37% aq. solution, 0.406 g total weight considering water), 0.2254 g dimethylamine (5 mmol), 1.03 g 1,4-dioxane.

Volume of 0.5M NaOH solution used to adjust the pH is not reported.

Desired product: 0.1192 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{0.475 - 0.1192}{0.1192} = 2.98$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{1.76 - 0.1192}{0.1192} = 13.78$$

Solvent contribution to the E-factor:

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{1.286}{1.64} = 0.783 = \mathbf{78.3}\%$$

*Ott, M. W.; Dietz, C.; Trosien, S.; Mehlhase, S.; Bitsch, M. J.; Nau, M.; Meckel, T.; Geissler, A.; Siegert, G.; Huong, J.; Hertel, B.; Stark, R. W.; Biesalski, M. Co-Curing of Epoxy Resins with Aminated Lignins: Insights into the Role of Lignin Homo Crosslinking during Lignin Amination on the Elastic Properties. Holzforschung **2021**, 75 (4), 390–398*

Starting materials: 40 g Softwood kraft lignin, 3.2 g sodium hydroxide (80 mmol, 404 g of total solution considering water), 18.62 g formaldehyde (620 mmol, in 35% aq. solution, 53.2 g total weight considering water), 64 g diethylene triamine (DETA, 620 mmol); or 45.9 g of 1,3-propylenediamine (PDA, 619 mmol); or 60.1 g of ethylenediamine (EDA, 1000 mmol); or 17.5 g of ammonia (1028 mmol, in 25% aq. solution, 70 g total weight considering water).

Desired product(s):

diethylenetriamine-functionalized lignin KL-DETA: 40.3 g (isolated yield)

1,3-propylenediamine-functionalized lignin KL-PDA: 37 g (isolated yield)

ethylenediamine-functionalized lignin KL-EDA: 20.2 g (isolated yield)

ammonia-functionalized lignin KL-NH3: 25.0 g (isolated yield)

Desired product	Raw materials (total weight in g without solvent)	Raw materials (total weight in g with solvent)	Desired product (g)	E_{simple}	$E_{complex}$	Solvent contribution to the E-factor
KL-DETA	125.82	561.2	40.3	2.12	12.93	84%
KL-PDA	107.72	543.1	37.0	1.91	13.68	86%
KL-EDA	121.92	557.3	20.2	5.04	26.59	81%
KL-NH3	79.32	567.2	25.0	2.17	21.69	90%

*Chen, J.; An, L.; Bae, J. H.; Heo, J. W.; Han, S. Y.; Kim, Y. S. Green and Facile Synthesis of Aminated Lignin-Silver Complex and Its Antibacterial Activity. Ind. Crops Prod. **2021**, 173, 114102*

Starting materials: 1 g kraft lignin, 3.22 g 2-chloroethylamine hydrochloride (27.76 mmol), 6 g sodium hydroxide (150 mmol, 106 g of total solution considering water).

Desired product: 0.77 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{10.22 - 0.77}{0.77} = 12.27$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{110.22 - 0.77}{0.77} = 142.14$$

Solvent contribution to the E-factor:

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{100}{109.45} = 0.914 = \mathbf{91.4\%}$$

Liu, L.; Wan, X.; Chen, S.; Boonthamrongkit, P.; Sipponen, M.; Renneckar, S. Solventless Amination of Lignin and Natural Phenolics Using 2-Oxazolidinone. ChemSusChem ***2023****, 16 (15), e202300276.*

Starting materials: 2 g softwood kraft lignin (5.9 mmol reactive sites per g lignin, total sum of ArOH and COOH groups), 6.16 g 2-oxazolidinone (70.8 mmol, 6 equiv. in respect to the sum of ArOH and COOH groups), 0.12 g sodium hydroxide (2.95 mmol, 0.25 equiv.)

Desired product: 2.02 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{8.28 - 2.02}{2.02} = 3.10$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Epoxide functionalized lignin

Calculated E-factors for epoxidation procedures are summarized below. Table S2 prvovides an overview and all calculations are listed below to ensure reproducibility.

Table S2 - E-factors for epoxidation procedures.

Work	**Modification**	**Functionalizing agent**	**E_{simple}**	**$E_{complex}$**	**$E_{solvent}$ / %**	**$E_{sequence}$**
Meier[7]	Glycidylation	epichlorohydrin	6.35	–	–	–
Zhang[8]	Glycidylation	epichlorohydrin	4.24[a]	4.50[a]	5.7	–
Sun[9]	Glycidylation	epichlorohydrin	0.73[a]	57.0[a]	99	–
Sasaki[10]	Glycidylation	epichlorohydrin	14.0	16.2	14	–
Zhang[11]	Glycidylation	epichlorohydrin	6.23	16.2	62	–
Daugaard[12]	1. Epoxidation	hydrogen peroxide	1.05	4.78	78	38.0
	2. Esterification	epoxidized fatty acids	4.29	22.7	81	
Avérous[13]	1. Chlorination	oxalyl chloride	0.78[a]	7.13[a]	89	14.2
	2. Esterification	oleyl chloride	0.57	–	–	
	3. Epoxidation	peracetic acid	0.21[a]	7.39[a]	97	
Renneckar[14]	1. Hydroxyethylation	ethylene carsonate	2.19	–	–	5.80
	2. Esterification	oleic Acid	2.15	–	–	
Vásquez-Garay[15]	1. Allylation	allyl bromide	2.58[a]	31.4[a]	92	82.8
	2. Epoxidation	hydrogen peroxide, enzyme	1.45	51.5	97	

[a]: no final weight of isolated product was reported, therefore final weight of the product was calculated based on theoretical yield.

Over, L. C.; Grau, E.; Grelier, S.; Meier, M. A. R.; Cramail, H. Synthesis and Characterization of Epoxy Thermosetting Polymers from Glycidylated Organosolv Lignin and Bisphenol A. Macromol. Chem. Phys. ***2017****, 218, 1600411.*

Starting materials: 25.0 g organosolv lignin (6.08 mmol OH per g lignin), 118 g epichlorohydrin (1.28 mol, 8.41 equiv.), 9.5 g tetrabutylammonium bromide (19.7 mmol, 13.0 mol%), 29.9 g potassium hydroxide (533 mmol, 3.51 equiv.).

Desired product: 24.8 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{182.4 - 24.8}{24.8} = 6.35$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Wang, X.; Leng, W.; Nayanathara, R. M. O.; Caldona, E. B.; Liu, L.; Chen, L.; Advincula, R. C.; Zhang, Z.; Zhang, X. Anticorrosive epoxy coatings from direct epoxidation of bioethanol fractionated lignin. Int. J. Biol. Macromol. ***2022****, 221, 268-277.*

Starting materials: 10.0 g bioethanol fractionated lignin (**6.20 mmol reactive sites per g lignin**: 1.59 mmol AlOH per g lignin, 3.24 mmol ArOH per g lignin, 1.37 mmol COOH per g lignin), 59.7 g epichlorohydrin (645 mmol, 10.4 equiv.), 0.1 g tetramethylammonium chloride (91.0 µmol, 1.47 mol%), 4.30 g sodium hydroxide (20 wt% aqueous NaOH solution, 21.5 mmol, 0.347 equiv.).

Desired product: 13.48 g (theoretical yield)

$$m_f = m_i\ (1 + \Delta M_{graft}\,(reactive\ sites\ in\ \frac{mol}{g}))$$

$$m_f = 10.0\ \text{g}\ (1 + 56.064\,\frac{g}{mol}\ \ (6.20 \times 10^{-3}\ \frac{mol}{g})) = 13.48\ \text{g}$$

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{70.66 - 13.48}{13.48} = 4.24$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{74.1 - 13.48}{13.48} = 4.50$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{3.44}{60.62} = 0.057 = \mathbf{5.7}\%$$

Li, X.-Y.; Xiao, L.-P.; Zou, S.-L.; Xu, Q.; Wang, Q.; Lv, Y.-H.; Sun, R.-C. Preparation and Characterization of Bisphenol A-Based Thermosetting Epoxies Based on Modified Lignin. ACS Appl. Polym. Mater. ***2023****, 5, 3611-3621.*

Starting materials: 2.00 g lignin (**0.94 mmol reactive sites per g lignin**: 0.36 mmol AlOH per g lignin, 0.42 mmol ArOH per g lignin, 0.16 mmol COOH per g lignin), 1.55 g epichlorohydrin (16. 8 mmol, 8.91 equiv.), 0.10 g sodium hydroxide (2.50 mmol ,1.33 equiv.), 118.65 g acetone (150 ml).

Desired product: 2.11 g (theoretical yield)

$$m_f = m_i\ (1 + \Delta M_{graft}\,(reactive\ sites\ in\ \frac{mol}{g}))$$

$$m_f\ = 2.00\ \mathrm{g}\ (1 + 56.064\ \frac{g}{mol}(0.94 \times 10^{-3}\frac{mol}{g}))\ =\ 2.11\ \mathrm{g}$$

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{3.65 - 2.11}{2.11} = 0.73$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{122.3 - 2.11}{2.11} = 56.96$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{118.65}{120.19} = 0.987 = \mathbf{98.7}\%$$

Sasaki, C.; Wanaka, M.; Takagi, H.; Tamura, S.; Asada, C.; Nakamura, Y. Evaluation of epoxy resins synthesized from steam-exploded bamboo lignin. Ind. Crops Prod. ***2013****, 43, 757-761.*

Starting materials: 10.0 g bamboo lignin (8.30 mmol OH per g lignin), 160 g epichlorohydrin (1.73 mol, 20.8 equiv.), 7.00 g tetrabutylammonium bromide (14.5 mmol, 17.5 mol%), 50.0 g sodium hydroxide (50 wt% aqueous NaOH solution, 625 mmol, 7.53 equiv.), 5.5 g dimethyl sulfoxide (5 ml).

Desired product: 13.5 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{202 - 13.5}{13.5} = 13.96$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{232.5 - 13.5}{13.5} = 16.22$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{30.5}{219} = 0.139 = \mathbf{13.9}\%$$

Xin, J.; Li, M.; Li, R.; Wolcott, M. P.; Zhang, J. Green Epoxy Resin System Based on Lignin and Tung Oil and Its Application in Epoxy Asphalt. ACS Sustainable Chem. Eng. ***2016****, 4, 2754-2761.*

Starting materials: 5.00 g partially depolymerized lignin (**4.70 mmol reactive sites per g lignin**: 0.700 mmol AlOH per g lignin, 3.70 mmol ArOH per g lignin, 0.3 mmol COOH per g lignin), 30.0 g epichlorohydrin (314 mmol, 13.4 equiv.), 75 mg benzyltriethylammonium chloride (329 µmol, 1.40 mol%), 1.23 g sodium hydroxide (30.8 mmol, 1.31 equiv.), 50 g dimethyl sulfoxide.

Desired product: 5.02 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{36.31 - 5.02}{5.02} = 6.23$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{86.31 - 5.02}{5.02} = 16.19$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{50}{81.29} = 0.615 = \mathbf{61.5}\%$$

Silau, H.; Garcia, A. G.; Woodley, J. M.; Dam-Johansen, K.; Daugaard, A. E. Bio-Based Epoxy Binders from Lignin Derivatized with Epoxidized Rapeseed Fatty Acids in Bimodal Coating Systems. ACS Appl. Polym. Mater. ***2022****, 4, 444-451.*

Epoxidation of rapeseed oil fatty acid mixture

Starting materials: 50 g biodiesel fatty acids (238 mmol vinyl groups), 27.33 g formic acid (594 mmol, 2.00 equiv.), 67.34 g hydrogen peroxide (30 wt%, 594 mmol, 2.00 equiv.), 129.75 g toluene (150 ml).

Desired product: 47.5 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{97.532 - 47.5}{47.5} = 1.05$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{274.42 - 47.5}{47.5} = 4.78$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{176.89}{226.92} = 0.780 = \mathbf{78.0}\%$$

Steglich esterification

Starting materials: 10.0 g kraft lignin (6.40 mmol OH per g lignin), 0.78 g 4-dimethylaminopyridine (6.40 mmol, 10 mol%), 38.5 g epoxidized fatty acid (128 mmol, 2.00 equiv.), 14.52 g dicyclohexylcarbodiimide (70.4 mmol, 1.10 equiv.), 222.25 g tetrahydrofuran (250 ml).

Desired product: 12.05 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{63.8 - 12.05}{12.05} = 4.29$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{286.05 - 12.05}{12.05} = 22.74$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{222.25}{274} = 0.811 = \mathbf{81.1}\%$$

E-factor of complete sequence

Reaction 1: A (fatty acids) + Reagents → B (epoxidized Fatty Acids(eFA))

Reaction 2: B (eFA) + C (lignin) + Reagents → D (lignin epoxide)

Reaction 1: $E_{complex}$: 4.78 $\frac{\text{kg waste}}{\text{kg eFA}}$

Reaction 2: $E_{complex}$: 22.74 $\frac{\text{kg waste}}{\text{kg lignin epoxide}}$; **Multiplier Reaction 1:** $\frac{\text{kg eFA}}{\text{kg lignin epoxide}} = \frac{38.5}{12.05} = 3.20$

$E_{sequence}$: 22.74 $\frac{\text{kg waste}}{\text{kg lignin epoxide}}$ (**Reaction 2**)

+ 4.78 $\frac{\text{kg waste}}{\text{kg eFA}} \times 3.20 \frac{\text{kg eFA}}{\text{kg lignin epoxide}}$ (**Reaction 1**)

= 38.00 $\frac{\text{kg waste}}{\text{kg lignin epoxide}}$

Laurichesse, S.; Huillet, C.; Avérous, L. Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethane synthesis. Green Chem. ***2014****, 16, 3958-3970.*

Chlorination of oleic acid

Starting materials: 40.0 g oleic acid (142 mmol), 35.95 g oxalyl chloride (283 mmol, 2.00 equiv.), 270.6 g ethyl acetate (300 ml)

Desired product: 42.6 g (142 mmol, theoretical yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{75.95 - 42.6}{42.6} = 0.78$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{346.55 - 42.6}{42.6} = 7.13$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{270.6}{304.02} = 0.890 = \mathbf{89.0}\%$$

Esterification of organosolv lignin with oleyl chloride

Starting materials: 30 g organosolv lignin (2.26 mmol OH per g lignin), 40.7 g oleyl chloride (135 mmol, 2.00 equiv.).

Desired product: 45.0 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{70.7 - 45.0}{45.0} = 0.57$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Epoxidation of oleic acid lignin ester

Starting materials: 45 g esterified lignin (1.6 mmol double bonds per g lignin), 10.95 g peracetic acid (144 mmol, 2.00 equiv.), 331.25 g dichloromethane (250 ml).

Desired product: 46.15 g (theoretical yield)

$$m_f = m_i\ (1 + \Delta M_{graft}\,(reactive\ sites\ in\ \frac{mol}{g}))$$

$$m_f\ = 45.0\text{ g}\ (1 + 15.999\ \frac{g}{mol}(1.60 \times 10^{-3}\ \frac{mol}{g}))\ = 46.15\text{ g}$$

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{55.95 - 46.15}{46.15} = 0.21$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{387.2 - 46.15}{46.15} = 7.39$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{331.25}{341.05} = 0.971 = \mathbf{97.1}\%$$

E-factor of complete sequence

Reaction 1:	**A (oleic acid)**		**+ Reagents**	**→ B (oleyl chloride)**
Reaction 2:	**B (oleyl Chloride)**	**+ C (lignin)**	**+ Reagents**	**→ D (lignin ester)**
Reaction 3:	**D (lignin ester)**		**+ Reagents**	**→ E (lignin epoxide)**

Reaction 1: $E_{complex}$: $7.13\ \frac{\text{kg waste}}{\text{kg oleyl chloride}}$

Reaction 2: $E_{complex}$: $0.57\ \frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg oleyl chloride}}{\text{kg lignin ester}} = \frac{40.7}{45.0} = 0.904$**Reaction 3:** $E_{complex}$: $7.39\ \frac{\text{kg waste}}{\text{kg lignin epoxide}}$; **Multiplier Reaction 2:** $\frac{\text{kg lignin ester}}{\text{kg lignin epoxide}} = \frac{45.0}{46.15} = 0.975$

$\mathbf{E_{sequence}}$**:** $7.39\ \frac{\text{kg waste}}{\text{kg lignin epoxide}}$ (**Reaction 3**)

$+\ 0.57\ \frac{\text{kg waste}}{\text{kg lignin ester}} \times 0.975\ \frac{\text{kg lignin ester}}{\text{kg lignin epoxide}}$ (**Reaction 2**)

$+\ 7.13\ \frac{\text{kg waste}}{\text{kg oleyl chloride}} \times 0.904\ \frac{\text{kg oleyl chloride}}{\text{kg lignin ester}} \times 0.975\ \frac{\text{kg lignin ester}}{\text{kg lignin epoxide}}$ (**Reaction 1**)

= 14.24

Liu, L.-Y.; Hua, Q.; Renneckar, S. A simple route to synthesize esterified lignin derivatives. Green Chem. ***2019****, 21, 3682-3692.*

Hydroxyethylation of organosolv lignin

Starting materials: 30 g organosolv lignin (**6.36 mmol reactive sites per g lignin**: 1.97 mmol AlOH per g lignin, 4.07 mmol ArOH per g lignin, 0.32 mmol COOH per g lignin), 64.51 g ethylene carbonate (733 mmol, 6.00 equiv. of ArOH), 1.29 g sodium carbonate (12.2 mmol, 0.100 equiv. of ArOH).

Desired product: 30 g (isolated yield; 4.30 mmol AlOH and 0.41 mmol ArOH per g lignin, 0.02 mmol COOH per g lignin**, 91% AlOH**)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{95.80 - 30.0}{30.0} = 2.19$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Esterification of hydroxyethylated lignin with oleic acid

Starting materials: 5 g hydroxyethylated lignin (**4.71 mmol reactive sites per g lignin**: 4.30 mmol AlOH per g lignin, 0.41 mmol ArOH per g lignin, 0.02 COOH per g lignin), 44.5 g oleic acid (50 ml, 158 mmol, 6.66 equiv.).

Recycled starting materials: 40.05 g oleic acid (90%)

Desired product: 3 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product - recycled\ oleic\ acid}{desired\ product} = \frac{49.5 - 3.0 - 40.05}{3.0}$$

$$E_{simple} = \frac{49.5 - 3.00 - 40.05}{3.00} = 2.15$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

E-factor of complete sequence

Reaction 1: **A (lignin)** **+ Reagents** **→ B (hydroxyethylated lignin (HEL))**

Reaction 2: **B (HEL)** **+ Reagents** **→ C (lignin ester)**

Reaction 1: $E_{complex}$: 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$

Reaction 2: $E_{complex}$: 2.15 $\frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg HEL}}{\text{kg lignin ester}} = \frac{5}{3} = 1.667$

$E_{sequence}$:

$$2.15 \frac{\text{kg waste}}{\text{kg lignin ester}} \text{ (Reaction 2)}$$

$$+ 2.19 \frac{\text{kg waste}}{\text{kg HEL}} \times 1.667 \frac{\text{kg HEL}}{\text{kg lignin ester}} \text{ (Reaction 1)}$$

$$= 5.80$$

Vásquez-Garay, F.; Teixeira Mendonça, R.; Peretti, S. W. Chemoenzymatic lignin valorization: Production of epoxidized pre-polymers using Candida antarctica lipase B. Enzyme Microb. Technol. ***2018****, 112, 6-13.*

Allylation of organosolv lignin

Starting materials: 3.0 g organosolv lignin (2.29 mmol OH per g lignin), 4.7 g potassium carbonate (34.0 mmol, 4.95 equiv.), 4.05 g allyl bromide (97 wt%, 32.5 mmol, 4.73 equiv.), 94.4 g dimethylformamide (100 ml).

Desired product: 3.28 g (theoretical yield)

$$m_f = m_i\ (1 + \Delta M_{graft}\,(reactive\ sites\ in\ \frac{mol}{g}))$$

$$m_f = 3.0\ \text{g}\ (1 + 40.065\ \frac{g}{mol}(2.29 \times 10^{-3}\ \frac{mol}{g}))\ = 3.28\ \text{g}$$

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{11.75 - 3.28}{3.28} = 2.58$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{106.15 - 3.28}{3.28} = 31.36$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{94.4}{102.87} = 0.918 = \mathbf{91.8}\%$$

Epoxidation of allylated lignin

Starting materials: 3 g allylated lignin (2.09 mmol double bonds per g lignin), 2.46 g caprylic acid (17.1 mmol, 2.72 equiv.), 0.6 g immobilized lipase, 4.27 g hydrogen peroxide (30 wt%, 37.7 mmol, 6.00 equiv.), 147.05 g toluene (170 ml).

Desired product: 3.0 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{7.34 - 3.0}{3.0} = 1.45$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{157.38 - 3.0}{3.0} = 51.46$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{147.05}{154.38} = 0.972 = \mathbf{97.2}\%$$

E-factor of complete sequence

Reaction 1: **A (lignin)** **+ Reagents** **→ B (allylated lignin)**

Reaction 2: **B (allylated lignin)** **+ Reagents** **→ C (lignin epoxide)**

Reaction 1: $E_{complex}$: $31.36\ \frac{\text{kg waste}}{\text{kg allylated lignin}}$

Reaction 2: $E_{complex}$: $51.46\ \frac{\text{kg waste}}{\text{kg lignin epoxide}}$; **Multiplier Reaction 1:** $\frac{\text{kg allylated lignin}}{\text{kg lignin epoxide}} = 1.0$

$E_{sequence}$: $51.46\ \frac{\text{kg waste}}{\text{kg lignin epoxide}}$ (**Reaction 2**)

$+\ 31.36\ \frac{\text{kg waste}}{\text{kg allylated lignin}} \times 1.0\ \frac{\text{kg allylated lignin}}{\text{kg lignin epoxide}}$ (**Reaction 1**)

$= 82.82$

Carboxylic acid functionalized lignin

Hirose, S.; Hatakeyama, T.; Hatakeyama, H. Synthesis and thermal properties of epoxy resins from ester-carboxylic acid derivative of alcoholysis lignin. Macromolecular Symposia. ***2003****, 197, 157-170.*

Starting materials: 50 g alcoholysis lignin, 50 g ethylene glycol (806 mmol), 196 g succinic anhydride (1.96 mol), 2.69 g dimethylbenzylamine (19.9 mmol).

Desired product: 298.69 g (“ALEGPA”, theoretical yield)

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{298.69 - 289.69}{298.69} = 0$$

$$Lignin\ \mathrm{wt\%\ in\ ALEGPA} = \frac{50}{298.69} = 0.167 = \mathbf{16.7}\%$$

Exemplary wt% calculation of lignin in epoxy resin with 100% and 80% ALEGPA (acid/epoxy = 1.0)

Carboxylic acid content (ALEGPA) = 6.62 mmol × g^{-1}

Carboxylic acid content (ethylene glycol polyacid, EGPA) = 7.63 mmol × g^{-1}

Epoxy content (EGDGE) = 7.70 mmol × g^{-1}

$$\mathrm{Lignin\ wt\%\ in\ 100\%\ ALEGPA\ Resin} = \frac{\mathrm{m(ALEGPA)}}{\mathrm{m(ALEGPA) + m(EGDGE)}} \times \mathrm{wt\%\ lignin\ in\ ALEGPA}$$

$$= \frac{\frac{1}{6.62}}{\frac{1}{6.62} + \frac{1}{7.70}} \times 16.7\ \mathrm{wt\%} = 8.98\ \mathrm{wt\%}$$

$$\mathrm{Lignin\ wt\%\ in\ 80\%\ ALEGPA, 20\%\ EGPA\ Resin} =$$

$$\frac{\mathrm{m(ALEGPA)}}{\mathrm{m(ALEGPA) + m(EGPA) + m(EGDGE)}} \times \mathrm{wt\%\ lignin\ in\ ALEGPA}$$

$$\frac{0.8}{0.8 + 0.2 + \frac{(0.8 \times 6.62 + 0.2 \times 7.63)}{7.70}} \times 16.7\ \mathrm{wt\%}$$

$$= 7.08\ \mathrm{wt\%}$$

Ester group functionalized lignin

Calculated E-factors for esterification procedures are summarized in Table S3. Below the table, all calculations are listed to ensure reproducibility.

Table S3 - E-factors for esterification procedures.

Work	Modification	Functionalizing agent	E_{simple}	$E_{complex}$	$E_{solvent}$ / %	$E_{sequence}$
Koivu[16]	Esterification	1. acetyl chloride	1.02	6.65	85	–
		2. octanoyl chloride	1.63	7.25	78	–
		3. lauroyl chloride	2.03	7.66	73	–
		4. palmitoyl chloride	2.44	8.07	70	–
Dubois[17]	Esterification	oleyl chloride	0.08[a]	–	–	–
	1. Chlorination	oxalyl chloride	0.86	2.01	57	
	2. Esterification	10-undecenoyl chloride	0.10[a]	–	–	1.25
Avérous[13]	Chlorination	oxalyl chloride	0.78[a]	7.13[a]	89	–
Wool[18]	Esterification	1. acetic anhydride	2.05	–	–	–
		2. propionic anhydride	2.05	–	–	–
		3. butyric anhydride	2.05	–	–	–
		4. methacrylic anhydride	6.36	10.5	39	10.5
Luo[19]	Esterification	1. crotonic anhydride	1.75	–	–	–
		2. butyric anhydride	1.59	–	–	–
Renneckar[14,20]	1. Hydroxyethylation	ethylene carbonate[14]	2.19	–	–	–
	2. Esterification	1a. propionic acid[20]	9.93	–	–	12.1
		1b. propionic acid with recycling[14]	0.99	–	–	3.18
		2. valeric acid[14]	0.94	–	–	3.13
		3. octanoic acid[14]	0.91	–	–	3.10
		4. oleic acid[14]	2.15	–	–	5.80
Verge[21]	Esterification	3-(4-hydroxyphenyl) propanoic acid	1.19	–	–	–

[a]: no final weight of isolated product was reported, therefore final weight of the product was calculated based on theoretical yield.

Koivu, K. A. Y.; Sadeghifar, H.; Nousiainen, P. A.; Argyropoulos, D. S.; Sipilä, J. Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin. ACS Sustainable Chem. Eng. ***2016****, 4, 5238-5247.*

Starting materials: 5.0 g softwood kraft lignin (**6.70 mmol reactive groups per g lignin**: 2.30 mmol AlOH per g lignin, 4.40 mmol ArOH per g lignin), 3.72 g pyridine (47.0 mmol, 1.40 equiv.), 26.67 g tetrahydrofuran (30 ml), 7.08 g dimethylformamide (7.5 ml), and 3.40 g acetyl chloride (43.4 mmol, 1.30 equiv.); or 7.05 g octanoyl chloride (43.4 mmol, 1.30 equiv.); or 9.48 g lauroyl chloride (43.4 mmol, 1.30 equiv.); or 11.92 g palmitoyl chloride (43.4 mmol, 1.30 equiv.).

Desired product: 6 g for all modifications (isolated yield)

Desired product	Raw materials (total weight in g without solvent)	Raw materials (total weight in g with solvent)	Desired product (g)	E_{simple}	$E_{complex}$	$E_{solvent}$ / %
lignin acetate	12.12	45.87	6	1.02	6.65	84.7
lignin octanoate	15.77	49.52	6	1.63	7.25	77.6
lignin laurate	18.20	51.95	6	2.03	7.66	73.4
lignin palmitate	20.64	54.39	6	2.44	8.07	69.7

Xing, Q.; Ruch, D.; Dubois, P.; Wu, L.; Wang, W.-J. Biodegradable and High-Performance Poly(butylene adipate-co-terephthalate)–Lignin UV-Blocking Films. ACS Sustainable Chem. Eng. ***2017****, 5, 10342-10351.*

Chlorination of 10-undecenoic acid

Starting materials: 25 g 10-undecenoic acid (136 mmol), 26.25 g oxalyl chloride (204 mmol, 1.50 equiv.), 31.57 g ethyl acetate.

Desired product: 27.5 g (isolated yield, 95%)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{51.25 - 27.5}{27.5} = 0.86$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{82.82 - 27.5}{27.5} = 2.01$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{31.57}{55.32} = 0.571 = \mathbf{57.1}\%$$

Esterification of soda lignin with 10-undecenoyl chloride and oleyl chloride

Starting materials: 40 g soda lignin (5.20 mmol OH per g lignin), and 62.59 g oleyl chloride (208 mmol, 1.00 equiv.) or 42.17 g 10-undecenoyl chloride (208 mmol, 1.00 equiv.).

Desired products:

Oleyl lignin: 95.0 g (theoretical yield, $\Delta M_{graft} = 264.453 \text{ g mol}^{-1}$)

10-Undecenoyl lignin: 74.58 g (theoretical yield, $\Delta M_{graft} = 166.264 \text{ g mol}^{-1}$)

Desired product	Raw materials (total weight in g without solvent)	Raw materials (total weight in g with solvent)	Desired product (g)	E_{simple}	$E_{complex}$	$E_{solvent}$ / %
Oleyl lignin	102.59	102.59	95.0	0.08	–	–
10-Undecenoyl lignin	82.17	82.17	74.58	0.10	–	–

E-factor of esterification sequence

Reaction 1: **A (10-undecenoic acid)** **+ Reagents** **→ B (10-undecenoyl chloride)**

Reaction 2: **B (10-undecenoyl chloride)** **+ Reagents** **→ C (lignin ester)**

Reaction 1: $E_{complex}$: $2.01 \ \frac{\text{kg waste}}{\text{kg undecenoyl chloride}}$

Reaction 2: $E_{complex}$: $0.10 \ \frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg undecenoyl chloride}}{\text{kg lignin ester}} = \frac{42.17}{74.58} = 0.57$

E

$E_{sequence}$**:**

$$0.10 \ \frac{\text{kg waste}}{\text{kg lignin ester}} \ \textbf{(Reaction 2)}$$

$$+ \ 2.01 \ \frac{\text{kg waste}}{\text{kg undecenoyl chloride}} \times 0.57 \ \frac{\text{kg undecenoyl chloride}}{\text{kg lignin ester}} \ \textbf{(Reaction 1)}$$

$$= 1.25$$

Laurichesse, S.; Huillet, C.; Avérous, L. Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethane synthesis. Green Chem. ***2014****, 16, 3958-3970.*

Chlorination of oleic acid

Starting materials: 40.0 g oleic acid (142 mmol), 35.95 g oxalyl chloride (283 mmol, 2.00 equiv.), 270.6 g ethyl acetate (300 ml)

Desired product: 42.6 g (142 mmol, theoretical yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{75.95 - 42.6}{42.6} = 0.78$$

$$E_{complex} = \frac{\sum starting\ materials\ (+solvents) - desired\ product}{desired\ product} = \frac{346.55 - 42.6}{42.6} = 7.13$$

$$Solvent\ contribution = \frac{weight\ of\ solvent}{\sum starting\ materials\ (+solvent) - desired\ product} = \frac{270.6}{304.02} = 0.890 = \mathbf{89.0}\%$$

Thielemans, W.; Wool, R. P. Lignin Esters for Use in Unsaturated Thermosets: Lignin Modification and Solubility Modeling. Biomacromolecules. ***2005****, 6, 1895-1905.*

Starting materials: 1 g kraft lignin, 50.0 mg 1-methylimidazole (609 µmol), and 2.00 g acetic anhydride (19.6 mmol) or 2.00 g propionic anhydride (15.4 mmol) or 2.00 g butyric anhydride (12.6 mmol) or 6.31 g methacrylic anhydride (40.9 mmol) and 4.14 g dioxane (4 ml).

Desired product: 1 g for all modifications (isolated yield)

Desired product	Raw materials (total weight in g without solvent)	Raw materials (total weight in g with solvent)	Desired product (g)	E_{simple}	$E_{complex}$	$E_{solvent}$ / %
lignin acetate	3.05	3.05	1	2.05	–	–
lignin propionate	3.05	3.05	1	2.05	–	–
lignin butyrate	3.05	3.05	1	2.05	–	–
lignin methacrylate	7.36	11.5	1	6.36	10.5	39.4

Luo, S.; Cao, J.; McDonald, A. G. Cross-linking of technical lignin via esterification and thermally initiated free radical reaction. Ind. Crops Prod. ***2018****, 121, 169-179.*

Starting materials: 10 g kraft lignin (5.10 mmol OH per g lignin), 1.03 g 1-methylimidazole (12.5 mmol, 25.0 mol%), and 26.0 g crotonic anhydride (167 mmol, 3.31 equiv.) or 24.18 g butyric anhydride (153 mmol, 3.00 equiv.).

Desired products:

Lignin crotonate: 13.47 g (theoretical yield, $\Delta M_{graft} = 68.075$ g mol^{-1})

Lignin butyrate: 13.57 g (theoretical yield, $\Delta M_{graft} = 70.091$ g mol^{-1})

Desired product	Raw materials (total weight in g without solvent)	Raw materials (total weight in g with solvent)	Desired product (g)	E_{simple}	$E_{complex}$	$E_{solvent}$ / %
Lignin crotonate	37.03	37.03	13.47	1.75	–	–
Lignin butyrate	35.21	35.21	13.57	1.59	–	–

Liu, L.-Y.; Cho, M.; Sathitsuksanoh, N.; Chowdhury, S.; Renneckar, S. Uniform Chemical Functionality of Technical Lignin Using Ethylene Carbonate for Hydroxyethylation and Subsequent Greener Esterification. ACS Sustainable Chem. Eng. ***2018****, 6, 12251-12260.*

Hydroxyethylation of organosolv lignin

***Note:* Calculation is performed from other reference of same authors to allow sequence calculation[7]**

Starting materials: 30 g organosolv lignin (**6.36 mmol reactive sites per g lignin**: 1.97 mmol AlOH per g lignin, 4.07 mmol ArOH per g lignin, 0.32 mmol COOH per g lignin), 64.51 g ethylene carbonate (733 mmol, 6.00 equiv. of ArOH), 1.29 g sodium carbonate (12.2 mmol, 0.100 equiv. of ArOH).

Desired product: 30 g (isolated yield; 4.30 mmol AlOH and 0.41 mmol ArOH per g lignin, 0.02 mmol COOH per g lignin**, 91% AlOH**)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{95.80 - 30.0}{30.0} = 2.19$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Esterification of hydroxyethylated lignin with propionic acid (no recycling)

Starting materials: 1 g hydroxyethylated lignin, 9.93 g propionic acid (10 ml).

Desired product: 1 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{10.93 - 1.0}{1.0} = 9.93$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

E-factor of sequence: hydroxyethylation and esterification with propionic acid (no recycling)

Reaction 1: **A (lignin)** **+ Reagents** **→ B (hydroxyethylated lignin (HEL))**

Reaction 2: **B (HEL) +** **+ Reagents** **→ C (lignin ester)**

Reaction 1: $E_{complex}$: 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$

Reaction 2: $E_{complex}$: 9.93 $\frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg HEL}}{\text{kg lignin ester}} = \frac{1}{1} = 1.0$

$E_{sequence}$: 9.93 $\frac{\text{kg waste}}{\text{kg lignin ester}}$ (**Reaction 2**)

+ 2.19 $\frac{\text{kg waste}}{\text{kg HEL}} \times 1.0 \frac{\text{kg HEL}}{\text{kg lignin ester}}$ (**Reaction 1**)

= 12.12

Liu, L.-Y.; Hua, Q.; Renneckar, S. A simple route to synthesize esterified lignin derivatives. Green Chem. ***2019****, 21, 3682-3692.*

Hydroxyethylation of organosolv lignin

Starting materials: 30 g organosolv lignin (**6.36 mmol reactive sites per g lignin**: 1.97 mmol AlOH per g lignin, 4.07 mmol ArOH per g lignin, 0.32 mmol CO_2H per g lignin), 64.51 g ethylene carbonate (733 mmol, 6.00 equiv. of ArOH), 1.29 g sodium carbonate (12.2 mmol, 0.100 equiv. of ArOH).

Desired product: 30 g (isolated yield; 4.30 mmol AlOH and 0.41 mmol ArOH per g lignin, 0.02 mmol CO_2H per g lignin, **91% AlOH**)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{95.80 - 30.0}{30.0} = 2.19$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Esterification of hydroxyethylated lignin with propionic acid (recycling)

Starting materials: 5 g hydroxyethylated lignin (**4.71 mmol reactive sites per g lignin**: 4.30 mmol AlOH per g lignin, 0.41 mmol ArOH per g lignin, 0.02 mmol COOH per g lignin), 49.65 g propionic acid (50 ml, 670 mmol, 28.5 equiv.).

Recycled starting materials: 44.69 g propionic acid (90%)

Desired product: 5 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product - recycled\ propionic\ acid}{desired\ product}$$

$$E_{simple} = \frac{54.65 - 5.00 - 44.69}{5.00} = 0.99$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

E-factor of sequence: hydroxyethylation and esterification with propionic acid (recycling)

Reaction 1:	**A (lignin)**	**+ Reagents**	**→ B (hydroxyethylated lignin (HEL))**
Reaction 2:	**B (HEL) +**	**+ Reagents**	**→ C (lignin ester)**

Reaction 1: $E_{complex}$: 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$

Reaction 2: $E_{complex}$: 0.99 $\frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg HEL}}{\text{kg lignin ester}} = \frac{5}{5} = 1.00$

$E_{sequence}$: 0.99 $\frac{\text{kg waste}}{\text{kg lignin ester}}$ (**Reaction 2**)

+ 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$ × 1.00 $\frac{\text{kg HEL}}{\text{kg lignin ester}}$ (**Reaction 1**)

= 3.18

Esterification of hydroxyethylated lignin with valeric acid (recycling)

Starting materials: 5 g hydroxyethylated lignin (**4.71 mmol reactive sites per g lignin**: 4.30 mmol AlOH per g lignin, 0.41 mmol ArOH per g lignin, 0.02 mmol COOH per g lignin), 46.95 g valeric acid (50 ml, 460 mmol, 19.5 equiv.).

Recycled starting materials: 42.26 g valeric acid (90%)

Desired product: 5 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product - recycled\ valeric\ acid}{desired\ product}$$

$$E_{simple} = \frac{51.95 - 5.00 - 42.26}{5.00} = 0.94$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

E-factor of sequence: hydroxyethylation and esterification with valeric acid (recycling)

Reaction 1: **A (lignin)** **+ Reagents** **→ B (hydroxyethylated lignin (HEL))**

Reaction 2: **B (HEL) +** **+ Reagents** **→ C (lignin ester)**

Reaction 1: $E_{complex}$: $2.19\ \frac{\text{kg waste}}{\text{kg HEL}}$

Reaction 2: $E_{complex}$: $0.94\ \frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg HEL}}{\text{kg lignin ester}} = \frac{5}{5} = 1.00$

$E_{sequence}$: $0.94\ \frac{\text{kg waste}}{\text{kg lignin ester}}$ (**Reaction 2**)

$+\ 2.19\ \frac{\text{kg waste}}{\text{kg HEL}} \times 1.00\ \frac{\text{kg HEL}}{\text{kg lignin ester}}$ (**Reaction 1**)

= 3.13

Esterification of hydroxyethylated lignin with octanoic acid (recycling)

Starting materials: 5 g hydroxyethylated lignin (**4.71 mmol reactive sites per g lignin**: 4.30 mmol AlOH per g lignin, 0.41 mmol ArOH per g lignin, 0.02 mmol COOH per g lignin), 45.5 g octanoic acid (50 ml, 316 mmol, 13.4 equiv.).

Recycled starting materials: 40.95 g octanoic acid (90%)

Desired product: 5 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product - recycled\ octanoic\ acid}{desired\ product}$$

$$E_{simple} = \frac{50.5 - 5.00 - 40.95}{5.00} = 0.91$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

E-factor of sequence: hydroxyethylation and esterification with octanoic acid (recycling)

Reaction 1:	**A (lignin)**	**+ Reagents**	**→ B (hydroxyethylated lignin (HEL))**
Reaction 2:	**B (HEL) +**	**+ Reagents**	**→ C (lignin ester)**

Reaction 1: $E_{complex}$: 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$

Reaction 2: $E_{complex}$: 0.91 $\frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg HEL}}{\text{kg lignin ester}} = \frac{5}{5} = 1.00$

E

$\mathbf{E_{sequence}}$: 0.91 $\frac{\text{kg waste}}{\text{kg lignin ester}}$ (**Reaction 2**)

+ 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$ × 1.00 $\frac{\text{kg HEL}}{\text{kg lignin ester}}$ (**Reaction 1**)

= 3.10

Esterification of hydroxyethylated lignin with oleic acid (recycling)

Starting materials: 5 g hydroxyethylated lignin (**4.73 mmol reactive sites per g lignin**: 4.30 mmol AlOH per g lignin, 0.41 mmol ArOH per g lignin, 0.02 COOH per g lignin), 44.5 g oleic acid (50 ml, 158 mmol, 6.66 equiv.).

Recycled starting materials: 40.05 g oleic acid (90%)

Desired product: 3 g (isolated yield)

$$E_{simple} = \frac{\sum starting\ materials - desired\ product - recycled\ oleic\ acid}{desired\ product} = \frac{49.5 - 3.0 - 40.05}{3.0}$$

$$E_{simple} = \frac{49.5 - 3.00 - 40.05}{3.00} = 2.15$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

E-factor of sequence: hydroxyethylation and esterification with oleic acid (recycling)

Reaction 1: **A (lignin)** **+ Reagents** **→ B (hydroxyethylated lignin (HEL))**

Reaction 2: **B (HEL) +** **+ Reagents** **→ C (lignin ester)**

Reaction 1: $E_{complex}$: 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$

Reaction 2: $E_{complex}$: 2.15 $\frac{\text{kg waste}}{\text{kg lignin ester}}$; **Multiplier Reaction 1:** $\frac{\text{kg HEL}}{\text{kg lignin ester}} = \frac{5}{3} = 1.667$

E$_{\text{sequence}}$: 2.15 $\frac{\text{kg waste}}{\text{kg lignin ester}}$ (**Reaction 2**)

+ 2.19 $\frac{\text{kg waste}}{\text{kg HEL}}$ × 1.667 $\frac{\text{kg HEL}}{\text{kg lignin ester}}$ (**Reaction 1**)

= 5.80

Adjaoud, A.; Dieden, R.; Verge, P. Sustainable Esterification of a Soda Lignin with Phloretic Acid. Polymers. ***2021****, 13, 637.*

Starting materials: 2 g soda lignin (**2.00 mmol reactive sites per g lignin**: 2.00 mmol AlOH per g lignin, 3.94 mmol ArOH per g lignin, 0.78 mmol CO_2H per g lignin), 3.32 g phloretic acid (20.0 mmol, 5.00 equiv.), 500 mg *para*-toluene sulfonic acid (2.90 mmol, 72.6 mol%).

Desired product: 2.66 g (theoretical yield)

$$m_f = m_i\ (1 + \Delta M_{graft}\,(reactive\ sites\ in\ \frac{mol}{g}))$$

$$m_f = 2.0\ \mathrm{g}\ (1 + 165.168\ \frac{g}{mol}(2.00 \times 10^{-3}\ \frac{mol}{g})) = 2.66\ \mathrm{g}$$

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{5.82 - 2.66}{2.66} = 1.19$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Multiple bond functionalized lignin

Calculated E-factors for multiple bond insertion procedures are summarized in Table S4, all calculations are listed to ensure reproducibility.

Table S4 - Calculated E-factors for multiple bond insertion.

Work	Modification	Functionalizing agent	E_{simple}	$E_{complex}$	$E_{sequence}$
Renneckar[22]	Hydroxyethylation	Ethylene carbonate	4.80	–	7.76
	Esterification	Acrylic acid	3.07		
Meier and Over[23]	Allylation	Diallyl carbonate	5.42 -9.43	–	–
Meier et al.[24]	Allylation	Diallylcarbonate	1.87[a]	–	–
Johansson[25]	Allylation	Diallyl carbonate	2.09[a]	–	–
Avérous[26]	Vinylation	Vinyl ethylene carbonate	6.01	–	–

[a]: no final weight of isolated product was reported, therefore final weight of the product was calculated based on theoretical yield.

Functional Lignin Building Blocks: Reactive Vinyl Esters with Acrylic Acid, Qi Hua, Li-Yang Liu, Mijung Cho, Muzaffer A. Karaaslan, Huaiyu Zhang, Chang Soo Kim, and Scott Renneckar; Biomacromolecules 2023, 24, 2, 592–603.

Hydroxyethylation of softwood kraft lignin

10 g softwood kraft lignin (3.9 mmol ArOH per g lignin), 50 g ethylene carbonate (568 mmol, 14.5 equiv. in respect of the total of ArOH), 0.8 g Na_2CO_3 (7.55 mmol, 0.2 equiv.).

Desired product: 10.5 g (isolated yield)

$$E_{simple}\ hydroxyethylation = \frac{\sum starting\ materials\ step\ 1 - desired\ product\ 1}{desired\ product\ 1} = \frac{60.8-10.5}{10.5} = 4.8$$

Esterification of hydroxyethylated lignin with acrylic acid

1 g hydroxyethylated lignin (4.3 mmol AlOH per g lignin, 0.38 mmol per g lignin ArOH, 0.11 mmol per g lignin COOH), 3.15 g acrylic acid (43.7 mmol, 3 ml, d=1.05 g/ml)

Desired product: 1.02 g (isolated yield)

$$E_{simple}\ esterification = \frac{\sum starting\ materials\ step\ 2 - desired\ product\ 2}{desired\ product\ 2} = \frac{4.15-1.02}{1.02} = 3.07$$

E-factor of whole sequence

Reaction 1:	**A (lignin)**	**+ Reagents**	**→ B (hydroxyethylated lignin(HEL))**
Reaction 2:	**B (hydroxyethylated lignin)**	**+ Reagents**	**→ C (final product)**

Reaction 1: E_{complex}: $4.8\ \frac{\text{kg waste}}{\text{kg HEL}}$

Reaction 2: E_{complex}: $3.07\ \frac{\text{kg waste}}{\text{kg final product}}$; **Multiplier Reaction 1:** $\frac{\text{kg HEL}}{\text{kg final product}} = \frac{1}{1.02} = 0.978$

E_{sequence}: $3.07\ \frac{\text{kg waste}}{\text{kg final product}}$ (**Reaction 2**)

$+ 4.8\ \frac{\text{kg waste}}{\text{kg HEL}} \times 0.978\ \frac{\text{kg HEL}}{\text{kg final prouct}}$ (**Reaction 1**)

$= 7.76\ \frac{\text{kg waste}}{\text{kg final product}}$

Over, L. C.; Meier, M. A. R. Sustainable Allylation of Organosolv Lignin with Diallyl Carbonate and Detailed Structural Characterization of Modified Lignin. Green Chem. ***2016****, 18 (1), 197–207.*

Starting materials: 0.15 g organosolv lignin (6.1 mmol OH per g lignin), 1.30 g diallyl carbonate (9.15 mmol DAC, 10 equiv.), 0.295 g tetrabutylammonium bromide (0.915 mmol TBAB, 1 equiv.)

Procedure for recovery of TBAB: obtained allylated lignin 0.140 g, recovered TBAB: 0.285 g (97%)

Procedure for recovery of DAC: obtained allylated lignin 0.146 g, DAC recovered: 0.807 g (62%)

$$E_{simple}(TBAB\ recov.) = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{1.46 - 0.14}{0.14} = 9.43$$

$$E_{simple}(DAC\ recov.) = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{0.938 - 0.146}{0.146} = 5.42$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Over, L. C.; Hergert, M.; Meier, M. A. R. Metathesis Curing of Allylated Lignin and Different Plant Oils for the Preparation of Thermosetting Polymer Films with Tunable Mechanical Properties. Macromol. Chem. Phys. ***2017****, 218 (16), 1700177.*

Starting materials: 30 g organosolv lignin (**6.1 mmol g^{-1} reactive sites**), 76 g diallyl carbonate (535 mmol DAC, 3 equiv.), 11.9 g tetrabutylammonium bromide (37 mmol TBAB, 0.2 equiv.)

Recovery of TBAB: 10.9 g (92%)

Desired product: 37.33 g (theoretical yield)

$$m_f = m_i\ (1 + \Delta M_{graft}\ (reactive\ sites\ in\ \frac{mol}{g})) = 30\ g\ (1 + 40.032\ \frac{g}{mol}\ (6.1\ \times 10^{-3}\ \frac{mol}{g}) = 37.33\ g$$

$$E_{simple}(TBAB\ recov.) = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{107 - 37.33}{37.33} = 1.87$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Ribca, I.; Sochor, B.; Betker, M.; Roth, S. V.; Lawoko, M.; Sevastyanova, O.; Meier, M. A. R.; Johansson, M. Impact of Lignin Source on the Performance of Thermoset Resins. Eur. Polym. J. ***2023****, 194, 112141.*

Starting materials: 1 g hardwood lignin (**6 mmol g^{-1} reactive sites**, ~6 mmol per g lignin of various OH groups), 2.6 g diallyl carbonate (18.3 mmol DAC, 3.00 equiv.), 1.9 g tetrabutylammonium bromide (5.9 mmol TBAB, 1 equiv.)

Recovery of TBAB: 1.672 g (88%)

Desired product: 1.24 g (theoretical yield)

$$m_f = m_i\ (1 + \Delta M_{graft}\ (reactive\ sites\ in\ \frac{mol}{g})) = 1\ g\ (1 + 40.032\ \frac{g}{mol}\ (6 \times 10^{-3}\ \frac{mol}{g}) = 1.24\ g$$

$$E_{simple}(TBAB\ recov.) = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{3.828 - 1.24}{1.24} = 2.09$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Duval, A.; Avérous, L. Cyclic Carbonates as Safe and Versatile Etherifying Reagents for the Functionalization of Lignins and Tannins. ACS Sustain. Chem. Eng. 2017, 5 (8), 7334–7343.

Starting materials: 10 g Soda lignin (**5.8 mmol g^{-1} reactive sites**, 1.76 mmol AlOH per g lignin, 4.04 mmol COOH groups per g lignin), 66.17 g vinyl ethylene carbonate (580 mmol VEC, 10 equiv.), 0.8 g potassium carbonate (5.8 mmol K_2CO_3, 0.1 equiv.).

Desired product: 10.97 g (isolated yield, 78% of theoretical yield)

Theoretical yield:

$$m_f = m_i\ (1 + \Delta M_{graft}\ (reactive\ sites\ in\ \frac{mol}{g})) = 10\ g\ (1 + 70\ \frac{g}{mol}\ (5.8 \times 10^{-3}\ \frac{mol}{g}) = 14.06\ g$$

Isolated yield = 78%, 10.97 g

$$E_{simple} = \frac{\sum starting\ materials - desired\ product}{desired\ product} = \frac{76.97 - 10.97}{10.97} = 6.01$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Hydroxyl group functionalized lignin

Table S5 - Summary of E-factor for hydroxyalkylation procedures.

Work	Modification	Functionalizing agent	E_{simple}	$E_{complex}$	$E_{sequence}$
Lehnen et al.[27]	Hydroxyalkylation	ethylene carbonate	3.59[a]	–	–
		propylene carbonate	3.89[a]		
		butylene carbonate	4.16[a]		
		glycerol carbonate	4.19[a]		
Avérous et al.[28]	Hydroxyalkylation	ethylene carbonate	4.94	–	–
		propylene carbonate	6.17		
		vinyl ethylene carbonate	6.02		
		glycerol carbonate	6.02		
Avérous et al.[29]	Hydroxyalkylation	ethylene carbonate (PEG)	0	–	–
Lehnen et al.[30]	Hydroxyalkylation	glycerol carbonate	4.19[a]	–	9.06
	Transesterification	dimethyl carbonate	5.04[a]		

- : no solvents have been used, therefore $E_{complex}$ is not reported; [a]: no final weight of isolated product was reported, therefore final weight of the product was calculated based on theoretical yield.

Kühnel, I.; Saake, B.; Lehnen, R. Comparison of Different Cyclic Organic Carbonates in the Oxyalkylation of Various Types of Lignin. React. Funct. Polym. 2017, 120, 83–91.

Starting materials: 1 g organosolv lignin (5.17 mmol OH per g lignin), 4.55 g ethylene carbonate (51.7 mmol, 10 equiv.), or 5.28 g propylene carbonate (51.7 mmol, 10 equiv.), or 6.00 g butylene carbonate (51.7 mmol, 10 equiv.), or 6.10 g glycerol carbonate (51.7 mmol, 10 equiv.), 79 mg DBU (0.517 mmol, 0.1 equiv.).

Desired product: (theoretical yield, calculated for 5.17 x 10^{-3} mol g^{-1} reactive sites)

$$m_f = m_i\ (1 + \Delta M_{graft}\,(reactive\ sites\ in\ \frac{mol}{g}))$$

Functionalizing agent	Raw materials (Total weight in g)	Desired product (Theoretical yield, g)	E_{simple}	$E_{complex}$	$E_{solvent}$ / %
EC	5.63	1.23	3.59	–	–
PC	6.36	1.30	3.89	–	–
BC	7.08	1.37	4.16	–	–
GC	7.18	1.38	4.19	–	–

EC:

$$m_f = 1.00\ \mathrm{g}\ (1 + 44.032\ \mathrm{g\ mol^{-1}} \times 5.17\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 1.23\ \mathrm{g}$$

PC:

$$m_f = 1.00\ \mathrm{g}\ (1 + 58.048\ \mathrm{g\ mol^{-1}} \times 5.17\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 1.30\ \mathrm{g}$$

BC:

$$m_f = 1.00\ \mathrm{g}\ (1 + 72.064\ \mathrm{g\ mol^{-1}} \times 5.17\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 1.37\ \mathrm{g}$$

GC:

$$m_f = 1.00\ \mathrm{g}\ (1 + 74.048\ \mathrm{g\ mol^{-1}} \times 5.17\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 1.38\ \mathrm{g}$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Duval, A.; Avérous, L. Cyclic Carbonates as Safe and Versatile Etherifying Reagents for the Functionalization of Lignins and Tannins. ACS Sustain. Chem. Eng. ***2017****, 5 (8), 7334–7343.*

Starting materials: 10 g soda lignin (5.80 mmol OH per g lignin), 51.07 g ethylene carbonate (58.0 mmol, 10.0 equiv.), or 59.21 g propylene carbonate (58.0 mmol, 10.0 equiv.), or 66.18 g vinyl ethylene carbonate (58.0 mmol, 10.0 equiv.), or 68.44 g glycerol carbonate (58.0 mmol, 10.0 equiv.), 0.8 g potassium carbonate (5.8 mmol, 0.1 equiv.).

$$m_f = m_i\ (1 + \Delta M_{graft}(reactive\ sites\ in\ \frac{mol}{g}))$$

Functionalizing agent	Raw materials (Total weight in g)	Theoretical yield, (g)[a]	Desired product Yield /%, (g)	E_{simple}	$E_{complex}$	$E_{solvent}$ / %
EC	61.87	12.55	83%, 10.42	4.94	–	–
PC	70.01	13.37	73%, 9.76	6.17	–	–
VEC	76.98	14.06	78%, 10.97	6.02	–	–
GC	79.24	14.30	79%, 11.29	6.02	–	–

[a]: theoretical yield calculated for 5.8 x 10^{-3} mol g^{-1} reactive sites

EC:

$$m_f = 10.00\ \mathrm{g}\ (1 + 44.032\ \mathrm{g\ mol^{-1}} \times 5.8\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 12.55\ \mathrm{g}$$

PC:

$$m_f = 10.00\ \mathrm{g}\ (1 + 58.048\ \mathrm{g\ mol^{-1}} \times 5.8\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 13.37\ \mathrm{g}$$

VEC:

$$m_f = 10.00\ \mathrm{g}\ (1 + 70.056\ \mathrm{g\ mol^{-1}} \times 5.8\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 14.06\ \mathrm{g}$$

GC:

$$m_f = 10.00\ \mathrm{g}\ (1 + 74.048\ \mathrm{g\ mol^{-1}} \times 5.8\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 14.30\ \mathrm{g}$$

$E_{complex} = E_{simple}$ because no additional solvents are used.

Duval, A.; Vidal, D.; Sarbu, A.; René, W.; Avérous, L. Scalable Single-Step Synthesis of Lignin-Based Liquid Polyols with Ethylene Carbonate for Polyurethane Foams. Mater. Today Chem. 2022, 24, 100793.

Starting materials: 40-60 g organosolv lignin (1.89 AlOH, 3.58 ArOH, and 0.06 COOH groups, mmol per g lignin), 160 – 140 g PEG (of average molar mass 200, 300 and 400 g/mol; 3.62, 2.41, 1.81 equiv. with respect to total OH groups in lignin, considering 40 g of lignin), EC 38.96 g (0.44 mol, 2 equiv. with respect to total OH groups in lignin, considering 40 g of lignin), 6.114 g K_2CO_3 (0.044 mol, 0.1 equiv. to EC).

The obtained homogeneous liquid polyols were used without further purification for the foam preparation, therefore no waste is generated.

$$E_{simple} = 0$$

Kühnel, I.; Saake, B.; Lehnen, R. A New Environmentally Friendly Approach to Lignin-Based Cyclic Carbonates. Macromol. Chem. Phys. ***2018****, 219 (7), 1700613.*

Oxyalkylation of organosolv lignin with glycerol carbonate

1 g organosolv lignin (5.17 mmol OH per g lignin), 6.10 g glycerol carbonate (51.7 mmol, 10 equiv. in respect of the total of OH in lignin), 79 mg DBU (0.517 mmol, 0.1 equiv. in respect of the total of OH in lignin).

Desired product 1: 1.38 g (theoretical yield)

$$m_f = 1.00\ \mathrm{g}\ \left(1 + 74.048\ \frac{g}{mol}\left(5.17 \times 10^{-3}\ \frac{mol}{g}\right)\right) = 1.38\ \mathrm{g}$$

$$E_{simple}\ oxyalkylation = \frac{\sum starting\ materials\ step\ 1 - desired\ product\ 1}{desired\ product\ 1} = \frac{7.18 - 1.38}{1.38} = 4.19$$

Transesterification of organosolv lignin with dimethyl carbonate

0.2 g oxyalkylated lignin (5.05 mmol AlOH per g lignin), 0.455 g dimethyl carbonate (5.05 mmol, 5 equiv. in respect of the total of OH in lignin), 0.55 g DMSO (0.5 ml), 0.056 g K_2CO_3 (0.404 mmol, 0.4 equiv. in respect of the total of OH in lignin).

Desired product 2: 0.2087 g (98% theoretical yield)

$$m_f = 0.200\ \mathrm{g}\ (1 + 25.984\ \mathrm{g\ mol^{-1}} \times 2.525\ \times 10^{-3}\ \mathrm{mol\ g^{-1}}) = 0.213\ \mathrm{g}$$

$$E_{simple}\ transesterification = \frac{\sum starting\ materials\ step\ 2 - desired\ product\ 2}{desired\ product\ 2} = \frac{1.26 - 0.209}{0.209} = 5.04$$

E-factor of whole sequence

Reaction 1: **A (lignin)** **+ Reagents** **→ B (oxyalkylated lignin(OL))**

Reaction 2: **B (oxyalkylated lignin)** **+ Reagents** **→ C (final product)**

Reaction 1: E_{complex}: $4.19\,\frac{\text{kg waste}}{\text{kg OL}}$

Reaction 2: E_{complex}: $5.04\,\frac{\text{kg waste}}{\text{kg final product}}$; **Multiplier Reaction 1:** $\frac{\text{kg OL}}{\text{kg final product}} = \frac{0.2}{0.2087} = 0.958$

E_{sequence}:

$$5.04\,\frac{\text{kg waste}}{\text{kg final product}}\ (\textbf{Reaction 2})$$

$$+\ 4.19\,\frac{\text{kg waste}}{\text{kg OL}} \times 0.958\,\frac{\text{kg OL}}{\text{kg final prouct}}\ (\textbf{Reaction 1})$$

$$=\ 9.055\,\frac{\text{kg waste}}{\text{kg final product}}$$

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