DigiLignin: ab-initio modelling of sustainable polymers

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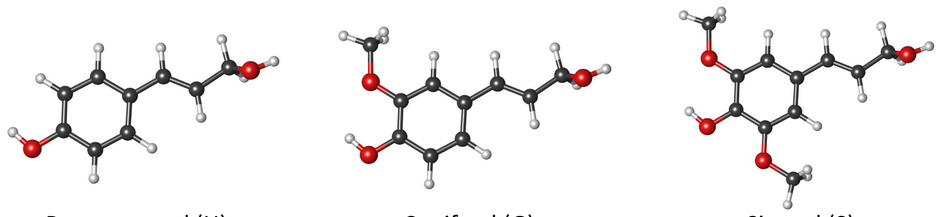
Abstract

The design and creation of bio-inspired materials is an active research area with thrilling potential applications in sustainable production. Particularly, lignin polymers—which are molecules mostly responsible for the structural support of plants—have potential as renewable source of biofuels, aromatic chemicals and value-added products in polymer chemistry. Lignin polymers are composed of three building blocks (paracoumaryl, coniferyl and sinapyl alcohols) which can form long branched chains through different linkages, making the exact large scale atomic structure an unknown.

Building blocks

There are three constitutive monomers (*monolignols)* in lignin polymers: the paracoumaryl (H), coniferyl (G) and sinapyl (S) alcohols.



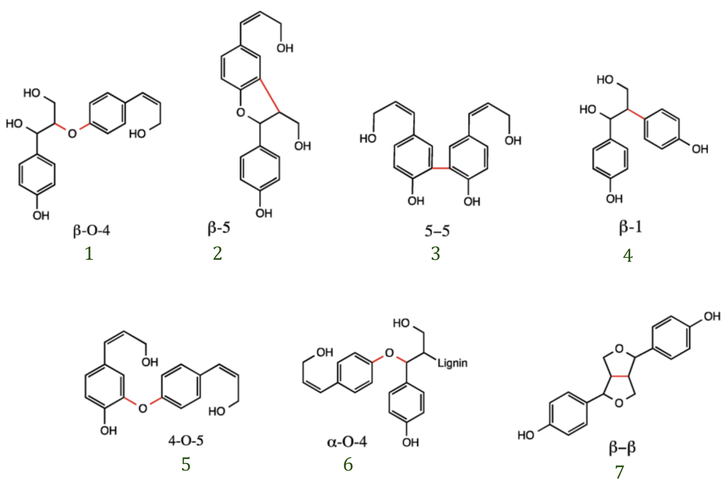
Paracoumaryl (H) Coniferyl (G) Sinapyl (S)

The difference between the monomers is the number of methoxy groups on the aromatic ring: 0, 1 or 2 for the H, G, and S monolignols, respectively

Monolignols crosslinking

Monolignols assemble into polymer by means of different linkages, seven of which constitute the vast majority of crosslinks in lignin.

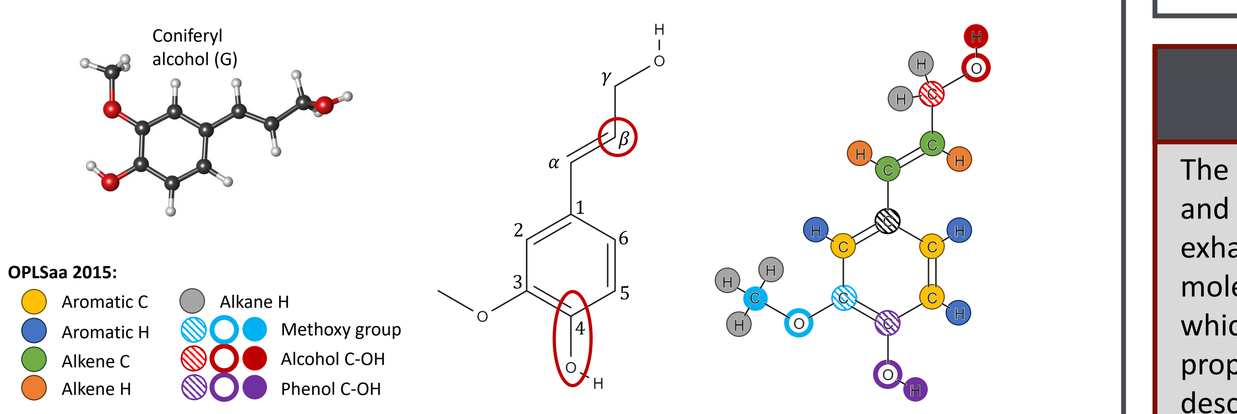
1	β-O-4	Fwd	-	-
		Bwd	-	-
2	β-3	Fwd	-	~~G, S~~
		Bwd	~~G, S~~	-
	β-5	Fwd	-	~~S~~
		Bwd	~~S~~	-
3	β-1	Fwd	-	-
		Bwd	-	-
4	4-O-3	Fwd	-	~~G, S~~
		Bwd	~~G, S~~	-
	4-O-5	Fwd	-	~~S~~
		Bwd	~~S~~	-
5	3-3	Sym.	~~G, S~~	~~G, S~~
	3-5	Fwd	-	~~S~~
		Bwd	~~S~~	-
	5-5	Sym.	~~S~~	~~S~~
6	α-O-3	Fwd		~~G, S~~
		Bwd	~~G, S~~	-
	α-O-5	Fwd	-	~~S~~
		Bwd	~~S~~	-
7	β-β	Sym.	-	-



The characteristic linkage distribution of a polymer with known fraction of H, G or S monolignols allows to compare its molecular composition with the emerging mechanical properties of the plant it is extracted from and the bio-inspired materials it can potentially form.

Coniferyl alcohol: a case study for molecular dynamics calculations

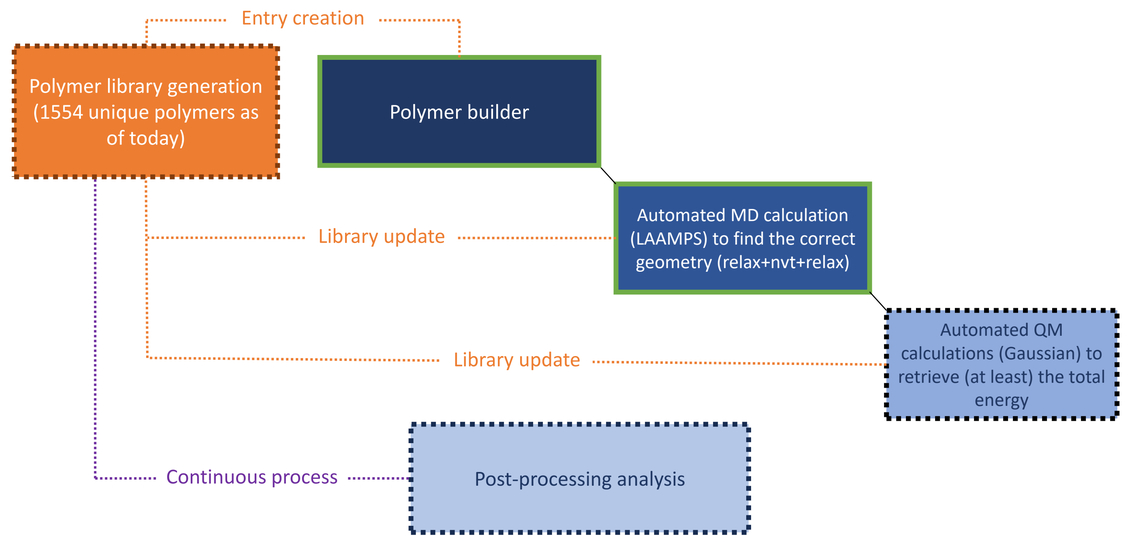
Part of this project consists of finding the atomic-scale geometry configuration of different monomer. To alleviate possible biases from which the theoretical polymer suffers upon generation, a molecular dynamic simulation at T=300 K is performed for each molecule.



The force-fields used in this example are adequate to study molecular crystal, but some of the bonds encountered in lignin may not be properly described by the OPLSAA library.

Polymer library generation workflow

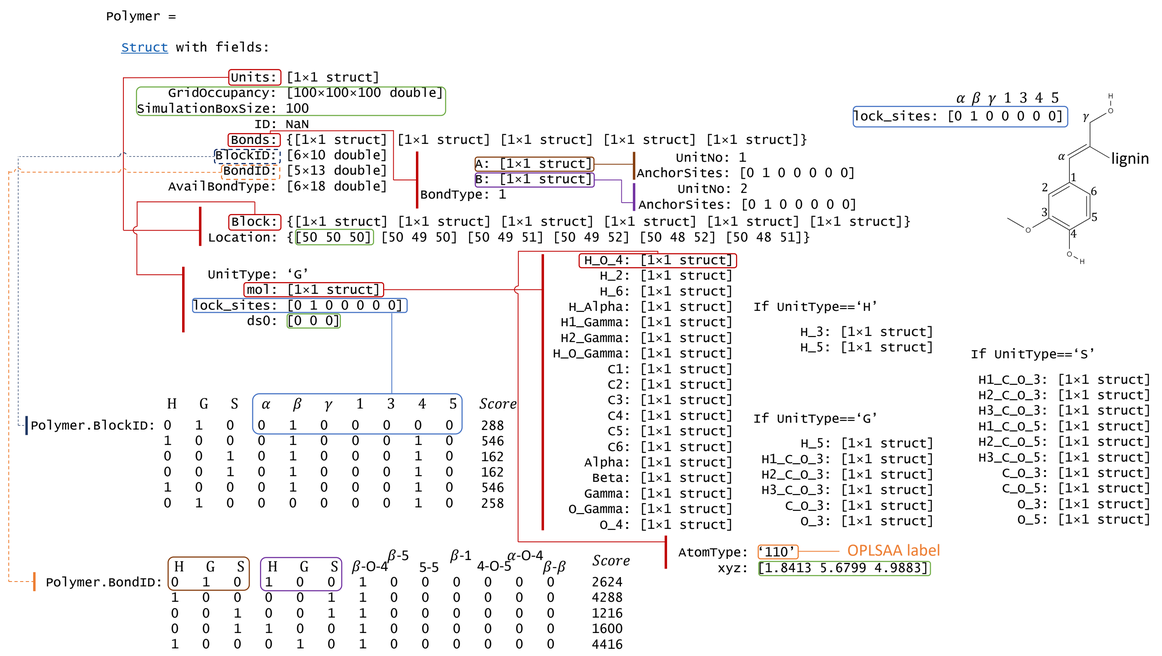
The numerical side of the DigiLignin project revolves around the creation of a library of polymers, which properties are computed at the MD and QM level.



Since the number of polymers that can be made with three different units and numerous crosslinks is massive, the generated polymers will sample the configurational space as evenly as possible. In addition, a ML-based refinement of the sampling is currently under consideration to identify low density sampling areas.

Polymer library entry

The format of each entry is structured in a way that allows for fast comparison between polymers. However, there may be duplicated polymer in the library, which are symmetrical equivalent of one another. The determination of a truly unique polymer identifier would not only solve this conundrum, but also provide a unique structure-based ID to refer to each individual polymer.



Outlook & Acknowledgment

The precise influence of lignin polymer structure at the atomic level on their physical and chemical properties remains unknown. In this work, we aim at providing the most exhaustive description of lignin. For this purpose, we plan on generating a library of molecules using molecular dynamics, to discriminate the most relevant lignin polymer, which will be investigated in depth by means of DFT calculations to predict their properties. We believe the insights our work will provide could lead to a more accurate description of these materials, potentially paving the way for sustainable production of high-quality alternatives to plastics for many applications. The resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Research Foundation - Flanders (FWO) and the Flemish Government. This project was funded by FWO and the European Union—NextGenerationEU grant n°G0E0223N .

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[2] Yanez, Abraham J., et al. "A stochastic method to generate libraries of structural representations of lignin." Energy & Fuels 30.7 (2016): 5835-5845.