

Identification and characterisation of the reaction path of β -O-4 dimerisation of monolignols by means of first-principles calculations

P. Castenetto^{1,2,3}, E. Guillaume^{1,2,3,4}, M.-T. Bui^{1,2,3} and D. E. P. Vanpoucke^{1,2,3}

¹Hasselt University, Institute for Materials Research (IMO-IMOMEC), Diepenbeek, 3590, Belgium

²Hasselt University, Quantum and Artificial Intelligence design Of Materials (QuATOMs), Diepenbeek, 3590, Belgium

³IMOMEC, IMEC vzw, Diepenbeek, 3590, Belgium

⁴University of Namur, Namur Institute of Structured Matter (NISM), Namur, 5000, Belgium

Lignin is a naturally occurring substance found in plant cells, which confer their rigidity and therefore, their structural support. It is primarily composed of three monolignol units: p-coumaryl alcohol (H), coniferol alcohol (G) and sinapyl alcohol (S). In the paper industry, lignin is a by-product often regarded as low-value and incinerated for energy production. However, with increasing interest in sustainable materials, this by-product has emerged as a promising candidate for the development of bio-based plastics due to its potential to form durable and robust products [1].

Although early industrial processes have been established, the molecular details of lignin polymerisation remain unclear. This study uses first principles methods to investigate the dimerisation of monolignols. Focusing on the formation of the β -O-4 linkage, the most prevalent in native lignin, the energy profile of the reaction is investigated in detail to gain fundamental understanding of the physics behind the dimerformation.

Contrary to earlier studies [2, 3, 4], we find that monolignol dimerization is not a straightforward process but possess a small barrier. Additionally, the role of solvents, both including and excluding van der Waals interactions, is examined. These results shed new light on the dimerisation of monolignols, thus unravelling part of the (de)polymerisation process of lignin.

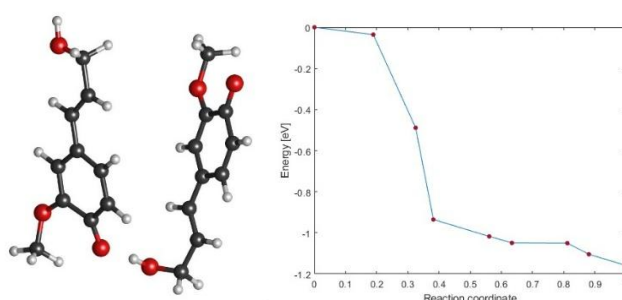


Figure 1: Representation of two G monolignols forming a β -O-4 linkage and energy profile along the reaction pathway.

- [1] M. N. Collins M. N. *et al* 2019 *International Journal of Biological Macro-molecules* **131**, 828
- [2] Gani T. Z. H. *et al* 2019 *ACS Sustainable Chem. Eng.* **7**, 15, 13270–13277
- [3] Bickelhaupt F. M. and Houk K. N. 2017 *Angewandte Chemie International Edition* **56**, 10070
- [4] C. H. Lee, J. Kim, J. Ryu, W. Won, C. G. Yoo, and J. S.-I. Kwon 2024 *Chemical Engineering Journal* **487**, 150680