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A Well-defined Diamine from Lignin Depolymerization Mixtures for Constructing Bio-based Polybenzoxazines

AUTHORS

Xianyuan WU / UNIVERSITY OF GRONINGEN, NIJENBORGH 4, GRONINGEN
Corresponding author : Katalin BARTA WEISSERT / k.barta@rug.nl

PURPOSE OF THE ABSTRACT

The demand for high performance materials in many industries (such as aviation, automobile, and construction) is expected to markedly increase in the coming decades; however, the vast majority of these materials are still petroleum-derived. There is high demand for renewable alternatives, preferably sourced from biomass waste-streams. [1,2,3] The paper and pulp industry produce approximately 50 Mt lignin annually as side-product, but there is still a large gap between such depolymerization efforts of waste lignin and accessing well-defined industrially relevant products, and consequently, important applications.

The alkaline oxidation of softwood lignosulfonate to vanillin, industrially implemented by Borregaard, gives a product mixture consisting of predominately phenolic vanillin and smaller amounts of syringaldehyde, 4-hydroxybenzaldehyde, ketones, and carboxylic acids. When hardwood lignosulfonate is used instead of softwood, for example Eucalyptus (manufactured by Borregaard and Sappi), the aldehyde yield increases at the expense of vanillin selectivity, and a more complex mixture of phenolic aldehydes (predominately syringaldehyde, vanillin and small amount of 4 hydroxybenzaldehyde), is obtained. These aldehyde mixtures can be isolated from the crude lignin depolymerization oil by bisulfitation with NaHSO3 and subsequent precipitation. However, further separation of the individual components would be very tedious and economically unfeasible, due to similar chemical-physical properties. Nonetheless, either vanillin or aldehyde mixtures should serve as excellent starting material for the production of value-added industrially relevant chemicals, especially for input into the fine chemicals and polymer sectors.

Here we describe a robust catalytic strategy suitable to transform crude, pre-purified lignin depolymerization mixtures typically produced by the paper and pulp industry, into 4,4'-methylenebiscyclohexanamine (MBCA) in high overall yield. [4] The approach described here allows for converting mixture of aldehydes into a single aliphatic diol 4,4'-methylenebiscyclohexanol (MBC), and subsequently diamine MBCA, using commercially available catalysts and widely accessible and/or potentially bio-derived reagents such as phenol and ammonia, without the need for extensive purification procedures (See attached Figure). The developed sequence consists of 1.) Hydrogenation using Pd/Al2O3 as catalyst; 2.) Electrophilic aromatic substitution promoted by Amberlyst 15; 3.) Selective Raney nickel catalysed funneling via demethoxylation/hydrogenation to MBC; and 4.) The direct amination of MBC with ammonia via the hydrogen borrowing strategy, in near perfect MBCA selectivity. 5.) The renewable polybenzoxazines were prepared from MBCA and phenolic lignin platform chemicals. The most promising, cured poly (S-MBCA) shows high glass transition temperature Tg of 315 °C, outstanding thermal stability (T10% = 400 °C) and good storage modulus (E'25 °C = 3.8 GPa), which is competitive with commercial resins.

The novel catalytic upgrading method described here that is capable of converting industrially relevant waste streams to single compounds with minimal purification effort, will contribute to broadening the scope of future bio-refinery methods. Moreover, given their waste- and solvent free manner of preparation, excellent thermal and mechanical properties and industrial relevance, the polybenzoxazines obtained here are attractive examples for emerging bio-based polymers.

FIGURES

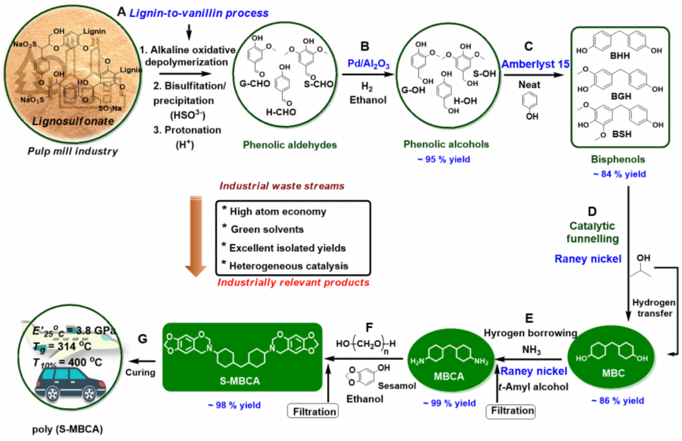

FIGURE 1

From lignin oxidation mixtures to industrially relevant diamine and high-performance polybenzoxazine resin.

(A-F). A proposed sustainable multi-catalytic protocol towards the production of industrially relevant MBCA diamine from lignin oxidation mixtures to construct high-performance polybenzoxazines over commercially available catalysts and green solvents.

FIGURE 2

KEYWORDS

catalytic funneling | amination of alcohols to diamines | benzoxazines | waste to materials

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