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Insight into structure–reactivity relationships for the iron-catalyzed hydrotreatment of technical lignins

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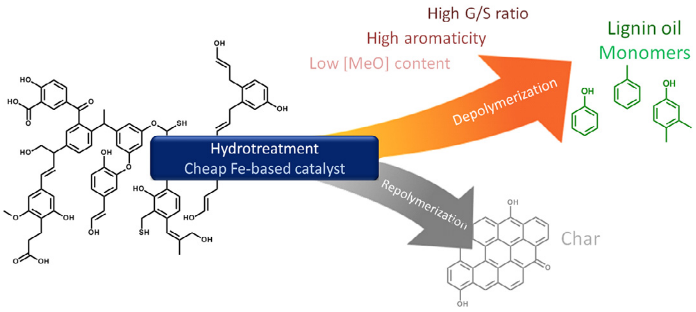
GRAPHICAL ABSTRACT



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ABSTRACT

The viability of several technical lignins as a source for biobased platform chemicals was investigated via hydrotreatment using a cheap Fe-based limonite catalyst and without using a solvent. In general, high-quality oils (up to 29 wt% total monomers) with an average relative composition of 55% alkylphenolics and 27% aromatics were obtained. Detailed structural investigations showed that the S-G aromatic unit content of the lignins was the most important factor positively affecting overall oil yields. A second parameter was the lignocellulose processing method. Even though alkaline lignin isolation provides more recalcitrant lignins, their lower aliphaticity and methoxy group content partially limit char and gas formation. Finally, enhanced monomer yields could be obtained irrespective of the ether linkage content, and a high amount of β-O-4 linkages actually showed a slightly negative effect on monomer yields. Overall, the results demonstrate that this route is particularly suitable for processing residual lignin streams.

1. Introduction

In the current world energetic scenario, where important challenges are being faced regarding an increasing energetic world demand and depletion of fossil resources, the potential of lignocellulosic biomass as an alternative and sustainable resource for energy, fuels and chemicals acquires an outstanding relevance for future biorefinery schemes (Özdenkçi et al., 2017; Wettstein et al., 2012). In contrast with the other two main biopolymers in lignocellulose (cellulose and hemicellulose), lignin conversion towards added-value products is lagging behind (Rinaldi et al., 2016). Even though it is the most abundant source for renewable aromatics, lignin is still mostly utilized solely for heat and power production through combustion (Calvo-Flores and Dobado, 2010). This underutilization is related to the complexity of the

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lignin structure, consisting of three main aromatic units, which differ on their methoxylation degree: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, connected through a variety of (mostly ether-type) linkages that can occur depending on the biomass source and processing conditions (Constant et al., 2016; Sun et al., 2018).

Technical lignins are cheap and commercially available in large quantities, which make them attractive feedstock for valorization towards chemicals (Zakzeski et al., 2010). However, their structural heterogeneity demands advanced insight into their reactivity in order to optimize high-value applications (Pang et al., 2017; Park et al., 2018), but detailed structural analysis in combination with reactivity studies are generally lacking in literature, even though this information is crucial for developing more efficient lignin applications (Deuss et al., 2017; Naseem et al., 2016). Due to their higher quality and purity, organosolv (sulfur-free) lignins are in principle preferred for biorefinery processing, and have attracted the largest share of research attention over the past years (Hashmi et al., 2017; Kuznetsov et al., 2017). However, most of the available commercial lignin is derived from Kraft pulping, mainly generated in the paper industry (Azadi et al., 2013). To date, several works have reported the performance of different types of lignins (either different biomass sources or originated from different isolation processes), but the dependence of their reactivity on their structure and composition is still not quite understood.

From all the lignin conversion techniques available for the production of chemicals, reductive methods like hydrotreatment stand out due to their capacity to produce relatively stable products with a lower oxygen content, simultaneously performing the last two stages of the traditional fractionation-depolymerization-upgrading sequence for lignin valorization (Schutyser et al., 2018). Traditionally, lignin hydrotreatment has been carried out in the presence of a solvent, mostly to avoid recondensation of intermediate radicals (Agarwal et al., 2017; Narani et al., 2015). However, it is known that solvents are not bystanders in the catalytic conversion of lignin, and solvent recycling can be challenging and costly (Wang and Rinaldi, 2012). One method that circumvents this issue is the development of solvent-free strategies. Nevertheless, examples of solvent-free hydrotreatment studies are still scarce in literature. Meier et al. (1992) performed a solvent-free hydropyrolysis of different lignins and reported lignin oil yields of 61.6 wt% using a NiMo/SiO_2-Al_2O_3 catalyst with a monomer yield of 21.8 wt% when processing organocell lignin. Our group recently reported a solvent-free hydrotreatment approach using supported Ru, Pd and Cu catalysts for Alcell® lignin obtaining lignin oil yields of 78 wt%, with a monomer yield of 22.1 wt% using a Ru/TiO_2 catalyst (Kloekhorst and Heeres, 2015). Furthermore, sulfided NiMo and CoMo catalysts were studied by Kumar et al. (2015) for the solvent-free hydrotreatment of Kraft lignin achieving a lignin conversion of 65–87% and a monomer yield of 55 wt% using a NiMo/AC catalyst.

The conversion of low-value feedstock requires cheap and sturdy catalysts from an economic perspective. In this context, Fe-based catalysts like limonite iron ore, which have traditionally been applied for direct coal liquefaction (Kaneko et al., 2002), have also recently shown promising features for the catalytic conversion of bio-derived feedstock in reforming (Zhao et al., 2017) and cracking (He et al., 2018) processes. Specifically for lignin conversion through hydrotreatment, Agarwal et al. (2017) recently explored the possibilities of a limonite catalyst for solvent-free lignin hydrotreatment obtaining a lignin oil yield of 33.7 wt% with a total 30.9 wt% monomer yield at 450 °C. Furthermore, in a work by Breunig et al. (2017), Fe-based catalysts also proved to be beneficial in order to prevent the formation of char in favor of higher oil yields, in comparison with Mo-based catalysts in the hydrogenolysis of different technical lignins in a solvent-free environment. This type of catalysts also present the advantage of being activated in their sulfided form, which makes them more robust when dealing with sulfur containing feedstock, like lignins derived from popular sulfur-based isolation methods (like lignosulfonate and Kraft techniques).

Table 1
Designation, biomass source and isolation procedure for all the lignins used in this study.

Code	Biomass source[a]	Extraction
Kraft AT	SW	Kraft (alkaline)
Kraft M	SW	Kraft (alkaline)
Soda	G/S (wheat straw and Sarkanda grass)	Soda (alkaline)
Alcell	Mixed HW (maple, birch and poplar)	Organosolv (ethanol–water)
Org BW	HW (beech)	Organosolv (60% ethanol- 40% water, 190 °C, 20 mM H_2SO_4)
Org WS	G/S (wheat)	Organosolv (60% ethanol- 40% water, 190 °C, 20 mM H_2SO_4)
Org P	SW (pine)	Organosolv (60% ethanol- 40% water, 190 °C, 11 mM H_2SO_4)
Org PLC	SW (pine)	Organosolv (60% ethanol- 40% water, 140 °C, 40 mM H_2SO_4)
PL	SW (pine)	Pyrolysis (water-insoluble fraction)

[a] Softwood, SW; hardwood, HW; grass/straw, G/S.

This work explores the potential of several technical lignins as a source for renewable platform chemicals through hydrotreatment in solvent-free conditions, using a cheap and readily available Fe-based limonite catalyst. Extensive lignin characterization studies (EA, GPC, FTIR, TGA, HSQC NMR, ^{13}C NMR) have allowed for gathering important information on the lignin composition and structure, which has been applied to lay relationships between the lignin structure and product distributions. This aided identification of specific desirable lignin features that link to optimal amounts of obtained high quality lignin oils, with a high content of desired monomers, specifically alkylphenolic and aromatic components.

2. Materials and methods

2.1. Lignins and catalyst

A total of nine lignins were studied, three of which were obtained from alkaline extraction processes (see Table 1 for details): two commercial softwood Kraft lignins (Kraft AT and Kraft M), and a commercial mixed grass/straw Soda Protobind 1000 lignin (Abacherli and Deppenberg, 1998) (see Constant et al., 2016, Deuss et al., 2017; Hu et al., 2016 for more information). Beech wood (Org BW), wheat straw (Org WS), and two pine lignins (Org P and Org PLC) were obtained from an acid-catalyzed ethanol-based organosolv procedure and provided by the Energy research Center of the Netherlands (ECN). Org WS and Org BW were isolated using a 60/40 wt% ethanol/water mixture at 190 °C and a catalyst concentration of 20 mM H_2SO_4, while Org P and Org PLC have been were extracted using the same ethanol/water mixture at 190 °C with a catalyst concentration of 11 mM H_2SO_4 (Org P) and 140 °C and 40 mM H_2SO_4 as a catalyst (Org PLC), respectively (Constant et al., 2016; de Wild et al., 2012; Wildschut et al., 2013). Organosolv Alcell lignin (from mixed maple, birch and poplar hardwoods) was produced by Repap (Canada) and provided by Wageningen University and Research Center (WUR, The Netherlands) (Constant et al., 2016). Pyrolytic lignin (PL) was supplied by Biomass Technology Group (BTG, Enschede, The Netherlands) and was obtained from the water fractionation of pine wood-derived pyrolysis liquids. The limonite ore catalyst was used as obtained from the nickel mine of PT Inco in Soroako (Sulawesi Island, Indonesia).

2.2. Catalytic hydrotreatment of the lignins

The catalytic hydrotreatment runs were carried out in a stainless steel 100 ml Parr Instruments Co. batch reactor equipped with a Rushton type turbine mechanical stirrer, and surrounded by a metal block containing an electrical resistance for heating purposes and