



Research article

Biobased chemicals from the catalytic depolymerization of Kraft lignin using supported noble metal-based catalysts

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ABSTRACT

Kraft lignin, a side-product of the paper industry, is considered an attractive feedstock for the production of biorenewable chemicals. However, its recalcitrant nature and sulfur content render catalytic conversions challenging. This study demonstrates the efficacy of noble metal-based catalysts for the production of a lignin oil enriched in alkylphenolic and aromatic compounds, by a catalytic hydrotreatment of Kraft lignin without the use of an external solvent. Eight commercially available catalysts were evaluated using four different metals (Ru, Pt, Pd, Rh) on two supports (activated carbon and Al₂O₃). The product oils were extensively analyzed by means of GPC, GCxGC-FID, GC-MS-FID, and elemental analysis. The catalysts were characterized by various techniques (N₂ physisorption, NH₃-TPD, XRD and TEM) before and after reaction, and their physico-chemical properties were correlated with catalytic performance. Al₂O₃ as support gave better results than carbon as support in terms of lignin oil yield and composition, due to a combination of higher total acidity, mildly acidic sites and a mesoporous structure. The metallic phase also significantly affected product distribution. The best results were obtained using a Rh/Al₂O₃ catalyst, resulting in a lignin oil yield of 36.3 wt% on a lignin intake and a total monomer yield of 30.0 wt% on lignin intake including 15.3 wt% of alkylphenolic and 7.9 wt% of aromatic compounds, and with a sulfur content < 0.01 wt%.

1. Introduction

The International Lignin Institute (ILI) recently reported that between 40 and 50 mT of lignin are produced annually, mainly from the pulp and paper industry [1–3]. Lignins are typically regarded as waste products and almost exclusively used in industry for onsite energy (steam) production. Lignin depolymerization processes have attracted increasing research interest, and are particularly aiming for the production of biofuels and value-added chemicals [4]. Several approaches have been reported for the valorization of lignin, examples are enzymatic processes [5, 6], thermal or catalytic pyrolysis [7, 8], depolymerization using basic catalysts [9], or oxidative processes [4, 10]. These studies so far have mainly focused towards the use of sulfur-free (organosolv) lignins as the lignin source. However, the most commercially employed pulping technique is the Kraft process, which leads to the formation of a lignin which contains significant amounts of sulfur [11].

Among the catalytic transformations studied so far, reductive processes like catalytic hydrotreatment have shown potential for lignin valorization [3]. Abundant research is available regarding the catalytic

hydrotreatment of lignins in the presence of a solvent [12–14]. However, this approach has some major drawbacks such as partial incorporation of the solvent or solvent fragments into the products and, when considering industrial feasibility, the need for an efficient solvent recycling strategy. For this reason, a catalytic hydrotreatment without the use of an external solvent may have considerable advantages [15, 16].

Our group has reported on the catalytic hydrotreatment of Kraft lignin using sulfided NiMo and CoMo catalysts over basic and acidic supports at 350 °C and 100 bar of initial H₂ pressure, obtaining lignin oils in yields of up to 48 wt% with a high concentration of alkylphenolics (> 15 wt% on lignin intake) [14]. Recently Agarwal et al., showed that when using more severe conditions (450 °C), sulfided iron-based catalysts also proved suitable to obtain lignin oils (> 34 wt% on lignin intake) with even higher concentrations of alkylphenolics and aromatics (> 17 wt% and > 8 wt%, respectively) [17]. Up to now, only the use of sulfided catalysts has been reported to be effective, but their major disadvantage is the necessity to use an external sulfur source for in-situ activation of the catalysts and to maintain catalyst activity. This inevitably leads to products which contain significant amounts of

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sulfur. In this context, noble-metal based catalysts could offer potential advantages, as a sulfur source is not required for catalytic activation [18]. Nevertheless, noble metal based catalysts have shown to be prone to deactivation due to catalyst poisoning in the presence of significant amounts of sulfur [19, 20].

So far, noble metals have been widely applied for the catalytic hydrotreatment of pyrolysis oils aiming for high-quality fuel production [21–25]. However, in comparison, limited research has been reported on the catalytic hydrotreatment of lignins using such catalysts. To date, the hydrotreatment of model compounds and particularly monomeric using noble metals has been reported extensively and shown the potential of these catalysts for lignin valorization [18, 26, 27], but exploratory studies on real lignin feedstock are limited.

Concerning the use of sulfur-free technical lignins, Bengoechea et al. recently explored the use of Rh, Ru and Pd catalysts supported on Al_2O_3 for the hydrotreatment of such lignins in water/formic acid, achieving oil yields of up to 91.2 wt% with a high concentration of hydrodeoxygenated compounds [28]. Kloekhorst et al. reported good performance of Ru and Pd supported catalysts for the hydrotreatment of a sulfur free organosolv Alcell lignin to obtain lignin oil yields up to 78 wt % and total monomer yields of 22 wt% (on lignin oil basis) [29]. Another example is the use of Ru/C for the hydrotreatment of pyrolytic lignins, the lignin (water insoluble) fraction from pyrolysis oil, which has reported to give lignin oils enriched in alkylphenolics and aromatics [30–32].

When considering sulfur-containing lignins, Yang et al. proposed a one-pot catalytic hydrocracking strategy for Kraft lignin over noble metal based catalysts (Ru, Pt, Pd, Rh) using isopropanol as a solvent. They found that temperature was the most important process variable considering lignin oil yields of up to 47 wt% could be obtained at 330 °C [33]. The product oil was rich in oxygen-containing cyclic and acyclic saturated compounds, indicating excessive hydrogenation of the lignin oil, which represents a drawback when the main goal is to obtain aromatic building blocks.

To the best of our knowledge, research on the valorization of Kraft lignin via hydrotreatment using noble metal based catalysts without the use of an external solvent has not been reported to date, evidencing the novelty of this work. As such, the molten lignin and the products (in a later stage of the batch reaction), are used to dissolve/disperse the lignin source.

In the research reported here, the use of eight noble metal based catalysts (5 wt% metal loading) for the catalytic hydrotreatment of Kraft lignin aiming for the production of valuable platform chemicals is discussed. The focus has been mainly on the optimization of the lignin oil yield and the content of alkylphenolics and aromatic compounds like substituted benzenes. Four different metallic phases were used (Ru, Pt, Pd, and Rh) over two commercially available and economically viable supports with different physico-chemical properties (activated carbon and Al_2O_3). Catalytic activity was evaluated in terms of lignin oil yield and composition. Extensive characterization and analysis of the lignin oils has been carried out by means of a wide variety of techniques (GCxGC-FID, GC-MS-FID, GPC, HSQC NMR, among others). The catalysts before and after reaction have been characterized in detail using a variety of techniques to correlate their physico-chemical properties with catalyst performance. In addition, the regenerability of the spent Rh/ Al_2O_3 catalyst has been explored using an oxidation protocol.

2. Experimental

2.1. Chemicals and feed

All the chemicals used in this study were of analytical grade and used without further purification. Indulin-AT (Kraft lignin) was from Meadwestvaco Specialty Chemical, USA. Indulin-AT is a purified form of Kraft pine lignin and does not contain hemicellulose. All noble metal catalysts (Ru/C, Ru/ Al_2O_3 , Pt/C, Pt/ Al_2O_3 , Pd/C, Pd/ Al_2O_3 , Rh/C and

Rh/ Al_2O_3) were acquired from Sigma Aldrich with a 5 wt% metal loading. Dichloromethane (DCM) and acetone (both purchased from Boom B.V.) were used as solvents for recovering the different product fractions. Hydrogen (> 99.99%, purchased at Hoek Loos) was used as the reaction gas. The reference gas used for identification of the permanent gases in the gas product was supplied by Westfalen Gassen Nederland B.V.

2.2. Catalyst characterization

The surface area, pore volume and pore distribution of the fresh and regenerated catalyst samples were measured by means of N_2 physisorption at 77 K and using a Micromeritics 2020 apparatus. Prior to analysis, samples (~100 mg) were degassed for 4 h at 180 °C in vacuum conditions for desorbing impurities.

Surface concentration of acidic sites was determined by using a linear quartz micro-reactor (*l*, 200 mm; *i.d.*, 4 mm) in a conventional flow apparatus operating both in continuous and pulse mode. Before TPD experiments, the catalyst samples (~100 mg) were reduced under hydrogen atmosphere at 500 °C for 30 min and then saturated for 30 min at 150 °C in a gas mixture containing 5 vol% NH_3/He (flow rate of 25 mL min^{-1}). Then, the samples were purged in helium flow until a constant baseline level was attained. TPD measurements were performed in the temperature range of 150–600 °C at a rate of 10 °C min^{-1} using helium (25 STP mL min^{-1}) as carrier flow. The evolved ammonia was detected by an online thermal-conductivity detector, calibrated by the peak area of known pulses of NH_3 .

Transmission Electron Microscopy (TEM) images were acquired using a Philips CM12 microscope operated at an acceleration voltage of 120 kV. Prior to analysis, the samples were ultrasonically dispersed in ethanol and subsequently placed on a carbon coated copper grid.

X-Ray diffraction (XRD) was used to gain information about the crystallinity of the samples, using a Bruker D8 Advance diffractometer, operating at 40 kV and 40 mA using $\text{CuK}\alpha$ radiation ($\lambda = 1,5544 \text{ \AA}$). Data were collected using a coupled Theta-2Theta configuration in the 2–80° 2 θ range with a step size of 0.02 and a scan time of 1 s.

2.3. Catalytic hydrotreatment of Kraft lignin and product analysis

The catalytic hydrotreatment of Kraft lignin was carried out in a stainless steel batch reactor (100 mL, Parr Instruments Co.) equipped with a Rushton-type turbine and surrounded by a metal block containing an electrical resistance for heating purposes and channels allowing the flow of cooling water, as described in a previous publication from our group [15]. The unit is provided with both temperature and pressure sensors which, during the experiments, allow for these variables to be monitored online and logged on a PC. The temperature of the liquid in the reactor is measured by a thermocouple placed in the center of the reactor close to the mechanical stirrer. Lignins typically start to melt at approximately 200 °C which, together with the heavy stirring used in the process (1200 rpm), ensures that the temperature of the reactive liquid phase at reaction conditions is essentially uniform.

In all the experiments, the reactor was loaded with 15 g of Kraft lignin and 0.75 g of catalyst. After loading the reactor, it was flushed 3–4 times with H_2 to expel air, and then pressurized to 180 bar for a leak test at room temperature. Subsequently, the H_2 pressure was set at 100 bar and stirring was started at 1200 rpm. After that, the reactor was heated up to 450 °C (catalyst reduction occurs in-situ) at an approximate rate of 10 °C min^{-1} , and time zero was set once the desired reaction temperature was reached. After 4 h, the reactor was cooled to room temperature (setpoint 25 °C) and the pressure at room temperature was recorded allowing determination of the total amount of H_2 consumed during the reaction. Gas products were collected in a 3 L Tedlar gas bag to determine its composition. Fig. 1 depicts the lignin hydrotreatment workup procedure. After reaction, an aqueous phase and an organic phase (lignin oil) were obtained. The lignin oil and

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