



Controlled depolymerization of lignin in an electrochemical membrane reactor



Serafin Stiefel^{a,b}, Jonas Lölsberg^{a,b}, Lukas Kipshagen^a, Robin Möller-Gulland^a, Matthias Wessling^{a,b,*}

^a RWTH Aachen University, Aachener Verfahrenstechnik-Chemical Process Engineering, Turmstr. 46, 52064 Aachen, Germany

^b DWI – Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52056 Aachen, Germany

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ABSTRACT

The electrochemical oxidative cleavage of lignin is a promising approach to valorize lignin's monomeric subunits as bulk and fine chemicals. It is attractive since it does not require toxic solvents or expensive catalysts. However, due to the rather unselective nature of the electrochemical depolymerization, overoxidation of the generated products occurs. In order to prevent the degradation of the aromatic monomeric compounds into acids and CO₂, a selective product removal strategy from the reaction environment is necessary. We report the use of an electrochemical membrane reactor for the continuous electrochemical cleavage of lignin integrated with an in-situ nanoporous filtration process. The generated cleavage products are removed through the nanofiltration membrane from the oxidative environment and product degradation is prevented. The reaction/separation unit comprises an unprecedented electrode configuration: electrode rods integrated into a 3D-printed turbulence-promoting mixer minimizing fouling and polarization phenomena at membrane and electrodes.

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1. Introduction

The valorization of lignin into value-added compounds, such as fuel additives or fine chemicals, is a prerequisite for a positive energy balance of biorefinery concepts [1]. Especially when targeting the fuel sector, the processing cost of lignocellulosic biomass must be extremely low in order to be competitive on the current fuel market [2]. Many lignin valorization techniques use expensive catalysts as well as high temperatures and pressures in order to effect the intermolecular bond cleavage that leads to the desired low-molecular compounds [3]. Even though the organic chemistry community strongly focuses on catalysts based on cheaper materials [4], most lignin utilization processes will continue to be rather elaborate and expensive. Yet another issue in heterogeneous catalysis is catalyst deactivation by impurities, which especially occurs when technical lignin is processed [5]. In contrast, the cleavage of lignin by electrochemical oxidation can be done at room temperature and ambient pressure with the use of dimensionally stable nickel electrodes without the need for toxic solvents or additives [6–11]. If one uses excess green electricity in order to drive the process, lignin can be cleaved at potentially low costs. In addition, the electrochemical oxidation is very robust in terms of impurities. However, electrooxidation of lignin in fact is a process with little selectivity when compared to heterogeneous catalysis that usually targets specific binding types in the lignin molecule. A major issue of the electrochemical

lignin valorization is the overoxidation of desired products, for example to organic acids and CO₂ [12–17]. Another challenge in the valorization of lignin is the separation of unreacted lignin and lignin fractions from the desired products, which can be achieved by different technologies [11,18,19]. Membrane processes are especially promising due to the possibility of truly continuous operation, freedom of used solvents and the large window of module and process conditions that can be employed [20].

1.1. Electrochemical membrane reactor concept

In the presented work, we suggest to closely integrate the electrochemical depolymerization of lignin and the product/lignin separation by designing an electrochemical membrane reactor (ECMR), where the anodic lignin cleavage takes place inside a tubular ceramic membrane. The formed products are directly separated from the reaction environment by a slight overpressure on the anode side: the nanofiltration membrane (NFM) permeates some solvent carrying the low molecular weight degradation products, but retains the high molecular weight lignin. Some lignin types are only soluble in alkaline solution, so the utilized membranes need to be able to withstand high pH values for a prolonged duration. Ceramic membranes, consisting of an aluminum-oxide support structure and an active layer of titanium dioxide, have pores in the 1 nm range with a narrow pore size distribution and thus have proved suitable to this task. A membrane similar to the one used in this work, albeit with slightly smaller pore sizes, was characterized by [21].

In order to answer the almost omnipresent challenge of membrane fouling in membrane applications, the reported reactor is composed of

* Corresponding author at: Turmstraße e 46, 52064 Aachen, Germany. Tel.: +49 241 8095470; fax: +49 241 8092252.

E-mail address: Manuscripts.cvt@avt.rwth-aachen.de (M. Wessling).

a novel composite electrode mixer that combines a rod electrode with a 3D-printed static mixer. This integration of anode and mixing device further amplifies the mass transport of reaction products from the electrodes to the membrane surface. Fig. 1a shows the reactor unit of the ECMR.

2. Materials and methods

2.1. Module design

In order to realize the simultaneous formation and separation of low-molecular compounds, two nickel rod anodes with a diameter of 3.2 mm (Alfa Aesar, 39705) have been inserted into a tubular ceramic membrane (Fraunhofer IKTS) with an inner diameter of 15.4 mm and a length of 99.35 mm. The membrane consists of an α - Al_2O_3 support structure with an average pore diameter of 3 μm and an active layer of TiO_2 with an average pore diameter of 1 nm. In order to increase mixing and thus membrane performance, a static mixer has been 3D-printed (Stratasys Objet Eden 260 V, VeroClear RGD810) with the characteristic dimensions shown in Fig. 1b. This unit is where the lignin degradation and product separation take place and both nickel rods will be utilized as anodes. The tubular nanofiltration membrane is then placed in a Polymethylmetacrylate (PMMA) casing, separating the inside of the membrane (lumen) from the outside where the permeate will be gathered. In order to close the electrical circuit a counter electrode (Ni felt, fiber diameter: 14 μm , porosity: 40%, thickness: 0.1 mm, Bekaert) has been positioned in a second PMMA casing, that is separated from the permeate volume by an ion exchange membrane (fumasep FAB,

Fumatech). Thus, three distinct volumes are created: The lumen of the tubular membrane, where the electrooxidation of lignin takes place (anode compartment), the outside of the ceramic membrane where the permeate with the products are gathered (permeate compartment) and the cathodic compartment where the cathode is placed as a counter electrode. Fig. 1d shows a cross section of the module.

2.2. Kraft lignin

The lignin used was purchased from Sigma Aldrich (370959) and used as received. It was extracted by the Kraft process [5] from beech wood and mainly consists of high-molecular-weight compounds, however it is not free of low-molecular-weight species. Data on the low-molecular-weight species composition, molecular weight, ash content and elemental composition can be found in [6].

2.3. Electrochemical depolymerization of lignin

2.5 g of Kraft lignin was dissolved in 500 ml of 1 M aqueous NaOH and was delivered from a reservoir to the anode compartment via a gear pump at a flow rate of 125 ml/min. The cathode and the permeate compartment were each filled with 1 M aqueous NaOH. Nitrogen was used to pressurize the anode compartment, resulting in a trans-membrane pressure difference of 1.4 bars (pressure transducer: WIKA P-31). The permeate flow was measured via a balance (Sartorius AX6202). The system was used in a semicontinuous mode so that the flow exiting from the anodic compartment was fed back to the reservoir. The system was run until 150 ml of the original solution permeated

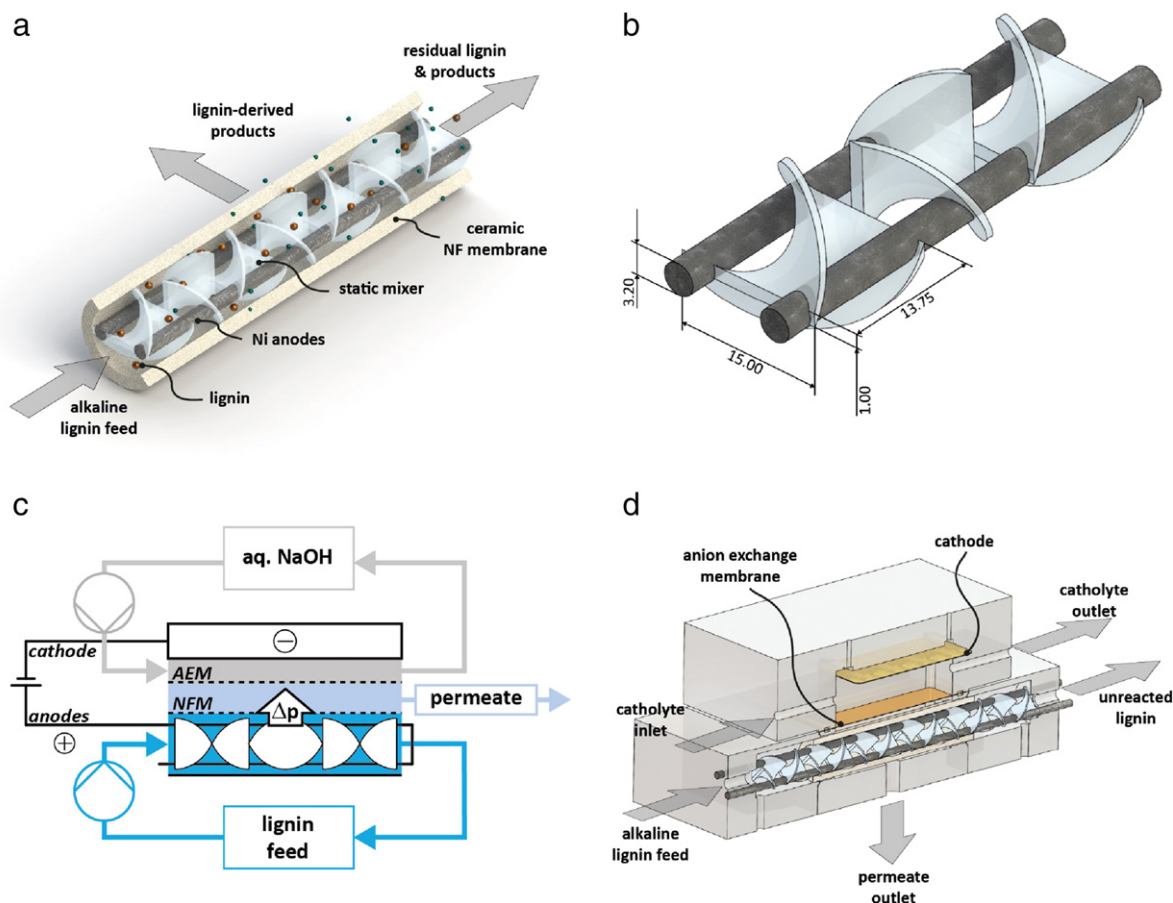


Fig. 1. (a) Scheme of the electrochemical membrane reactor with in-situ product removal for the electrooxidative cleavage of lignin (b) Detailed scheme of the electrode/mixer-unit, dimension are given in mm (c) Process scheme of the complete experimental setup. (AEM: Anion Exchange Membrane, NFM: Nanofiltration Membrane) (d) Cross section of the module. The inside of the ceramic membrane is used as the reactor, the volume between the ceramic and the ion-exchange membrane is used for the collection of the permeate and the cathodic volume is only used to close the electrical circuit.

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