β-Zeolite Assisted Lignin-First Fractionation in a Flow-Through Reactor

Alexei Kramarenko, Deniz Etit, G. Laudadio, Fernanda Neira Dangelo

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Lignin is one of the main constituents of lignocellulosic biomass, whose valorization is essential for an economically feasible biorefinery process scheme. In the present work, a hydrogen-free one step catalytic fractionation of woody biomass using commercial b-zeolite as catalyst in a flow-through reactor was carried out, leading to a maximum aromatic monomer yield of 20.5 wt.%. Birch, spruce and walnut shells were used and compared as lignocellulosic feedstocks. Relevant insights in the reaction mechanism were obtained through 2D HSQC NMR analysis, revealing that b-O-4 cleavage is catalyzed by the zeolite. To optimize system operation, a rate limiting step analysis was performed by using different reactor configurations. It was found that the system operated in a mixed regime where the rates of both solvolytic delignification and zeolite-based depolymerization/dehydration affect the net rate of aromatic monomer production. Oxalic acid addition was found to enhance monomer production at moderate concentrations by improving solvolysis; however, it caused structural changes to the zeolite leading to lower monomer yields at higher concentrations. Zeolite stability was assessed through catalyst recycling and characterization using NH₃-TPD, XRD, N₂ physisorption and TGA. Main catalyst deactivation mechanisms were found to be coking and leaching, respectively leading to larger pore size and lower concentration of acid sites.
β-zeolite assisted lignin-first fractionation in a flow-through reactor

A. Kramarenko\textsuperscript{a}, D. Etit\textsuperscript{a}, G. Laudadio\textsuperscript{a,b}, F. Neira D'Angelo\textsuperscript{a*}

\textsuperscript{a}Department of Chemical Engineering and Chemistry. Sustainable Process Engineering Group. Eindhoven University of Technology, Het Kranenveld 14 5612 AZ Eindhoven, Nederlands

\textsuperscript{b} (current affiliation) Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA,92037, United States.

Abstract

The valorization of lignin, one of the main constituents of lignocellulosic biomass, is essential for an economically feasible biorefinery. In the present work, a hydrogen-free one step catalytic fractionation of woody biomass using commercial β-zeolite as catalyst in a flow-through reactor was carried out, leading to a maximum aromatic monomer yield of 20.5 wt.%. Birch, spruce and walnut shells were compared as lignocellulosic feedstocks. β-zeolite acts as a bifunctional catalyst, which prevents lignin repolymerization due to its size-selective properties and also cleaves β-O-4 lignin intralinkage.

Crucial to optimizing system operation, a rate limiting step analysis using different reactor configurations revealed a mixed regime where the rates of both solvolytic delignification and zeolite-catalyzed depolymerization/dehydration affect the net rate of aromatic monomer production. Oxalic acid co-feeding was found to enhance monomer production at moderate concentrations by improving solvolysis, while it caused structural changes to the zeolite and led to lower monomer yields at higher concentrations. Zeolite stability was assessed through catalyst recycling and characterization using NH\textsubscript{3}-TPD, XRD, N\textsubscript{2} physisorption and TGA. Main catalyst deactivation mechanisms were found to be coking and leaching, leading to widening of the pores and decrease of zeolite acidity, respectively.

Introduction

Increasing consumption of fossil resources is a major contributor to anthropogenic global warming, which endangers the existence of numerous lifeforms including humans in the long term\cite{1,2}. Lignocellulosic biomass is a promising alternative to fossil feedstocks in order to sustain human needs in an environmentally friendly manner\cite{3–5}. Despite the great valorization potential of lignocellulosic biomass (consisting of cellulose, hemicellulose and lignin) towards platform molecules\cite{6}, it is still predominantly used in pulp and paper industry through the Kraft pulping process\cite{7}, where the lignin fraction is underutilized as low grade fuel. However, valorization of all three components is essential for biomass to become an economically viable alternative to fossil feedstocks\cite{8}.
Lignin is an organic biopolymer comprised of phenolic building blocks, which are the sole renewable source of monoaromatic compounds. As shown in Figure 1, different valorization approaches strongly affect the fate of the resulting lignin stream. At aggressive pH and temperature conditions used in conventional lignin extractive processes (i.e., Kraft), native ether bonds in lignin are cleaved, leading to the irreversible formation of stable carbon-carbon bonds[9]. Hence, these processes hinder the subsequent production of monoaromatic compounds and lead to a poorly soluble and highly recalcitrant lignin. A[]

### Figure 1: Scheme of different lignocellulose fractionation methods

Lignin is an organic biopolymer comprised of phenolic building blocks, which are the sole renewable source of monoaromatic compounds. As shown in Figure 1, different valorization approaches strongly affect the fate of the resulting lignin stream. At aggressive pH and temperature conditions used in conventional lignin extractive processes (i.e., Kraft), native ether bonds in lignin are cleaved, leading to the irreversible formation of stable carbon-carbon bonds[9]. Hence, these processes hinder the subsequent production of monoaromatic compounds and lead to a poorly soluble and highly recalcitrant lignin. Alternatively, Organosolv processes employ aqueous mixtures of organic solvents at mild conditions, enabling the partial preservation of lignin’s native chemical structure[10] and thus its valorization potential into valuable aromatic monomers[11]. In the so-called “lignin-first” approaches, removal of lignin under organosolv conditions is coupled with an active stabilization step. Particularly, reductive catalytic fractionation (RCF) is a popular lignin-first valorization strategy[12]-[13], where metals such as Pd or Ru are employed as catalysts for the hydrogenation of allylic alcohols, which are highly reactive reactive intermediates that are believed to play a key role during lignin recondensation[14–16]. RCF requires pressurized hydrogen or a hydrogen donor, such as a protic solvent (e.g., MeOH, EtOH) or hemicellulose derived compounds[17][13][18]. The main drawbacks of RCF are the costly high pressure requirements[19], the environmental impact of using fossil-based molecular[20–22], and the catalyst deactivation by poisoning, leaching and sintering[23][24]. Additionally, when RCF is carried out in batch reactors, subsequent separation of lignocellulosic pulp from catalyst becomes a challenging task. This can be avoided by using multi-bed flow-through systems[17][25] or a rotating basket[15], which physically separate biomass from the catalyst.

Very recently, protonic zeolites such as β-zeolite have been reported[26] as suitable catalysts for lignin-first fractionation of birch wood. They have been tested in a batch...
reactor, rendering phenolic monomers and holocellulose-based valuable products such as furfural and ethyl levulinate. Unlike in RCF, the stabilization of monomeric species in the β-zeolite assisted process has been explained by the combined effect of the size-selectivity and the Brønsted acidity of the microporous catalyst[26]. In particular, Subbotina and co-workers argue that the stabilizing role of the zeolites lies on the fact that the acid-catalyzed dehydration of allylic alcohols, which are reactive intermediates commonly known to play a key role during lignin repolymerization, takes place in the relatively small pores of the zeolite, free of higher molecular weight oligomers. Thus, the combined effect of the pore structure and the Brønsted acidity of β-zeolites appears to prevent the recondensation of unstable reactive intermediates, and in this way enables the hydrogen and additive-free lignin conversion into aromatic monomers. This makes the β-zeolite assisted lignin-first process a potential candidate for scale-up. However, beyond the very recent pioneering work by Subbotina et al. in batch reactors, this novel β-zeolite assisted lignin-first process has not been further investigated. Fundamental questions concerning the role of β-zeolite in the context of this complex reaction network (e.g., during depolymerization and/or stabilizations reactions) remains unclear. In addition, other critical issues such as catalyst stability, the suitability of this process for continuous operation and its applicability to other attractive lignocellulosic feedstocks are yet to be explored.

In the present work, we leverage the unique characteristics of flow-through reactors in biomass fractionation[23],[28] to investigate this novel β-zeolite assisted lignin-first process. This technique allows decoupling of solvolytic and catalytic steps, enabling the study of process parameters affecting individual rate steps. Through variations of the reactor configuration (e.g., packing strategy) and process conditions, we carry out a rate limiting step analysis, which is crucial for process intensification purposes. Analysis of the resulting lignin with 2D HSQC NMR spectroscopy is used to study the role of β-zeolite on β-O-4 bond cleavage, and correlate with the monomer yields. Subsequently, the co-addition of oxalic acid as a homogeneous acid was investigated. Due to the physical separation between biomass and catalyst in this reactor configuration, it is also possible to recover the spent zeolite and study its stability upon process conditions. Thorough characterization of the (spent) β-zeolite as well as a series of catalyst recycling experiments, this work provides insights into the deactivation mechanisms. Finally, the versatility of β-zeolite was evaluated by comparing the performance of birch hardwood with other relevant lignocellulosic feedstocks such as spruce as a softwood and walnut shells as an agricultural residue.

**Experimental methods**

Lignocellulosic biomass was drilled, ball milled and sieved to a particle size of 50-150 μm in order to avoid mass transfer limitations during delignification[29]. Milled biomass was pre-extracted and dried. Lignin content of lignocellulosic solids before and after reaction was determined according to NREL procedure[30]. All yields are reported in dry and pre-extracted biomass weight basis.

Experiments were carried out in a modular Swagelok ½” Hastelloy tubular reactor, consisting of two individual tubes of 10 cm in length connected to each other by a threaded element. In order to prevent inefficient solid-liquid contact, the reactor was
placed vertically and packed with 2 mm glass beads and quartz wool. The first reactor contained biomass particles and the second one contained the β-zeolite. To enable operation in flow, zeolites were pelletized, milled and sieved to a particle size of 40-150 µm. Metal gaskets with 5 µm pore size were used on the sides of the reactors to ensure no loss of solid. Zeolites were calcined at a temperature of 550°C for five hours. Experiments in a temperature range of 190-220°C were carried out at a pressure of 50 bars in order to ensure liquid phase operation (Figure S6). A 9:1 v/v ethanol/water solvent mixture was used for all experiments. Solvent composition was selected based on prior studies[26].

Liquid samples were collected every 10 minutes during the first hour of reaction and every 20 minutes during the next two hours. Monomeric compounds in the untreated sample mixture were identified through GC-MS. Monomer yield was quantified through GC-FID with isopropyl phenol as standard and using the effective carbon number (ECN) methodology[31]. For further lignin analysis, solvent removal was performed at 75 mbar and 40°C, followed by a liquid-liquid extraction with ethyl acetate/water 3x10 mL and subsequent solvent evaporation under vacuum, leading to lignin oil. The resulting lignin oil was dissolved in DMSO-d6 to a concentration of 70 mg oil/mL for subsequent 2D HSQC NMR analysis. Similarly, GPC analysis was carried out by dissolving lignin oil to a concentration of 5 mg/mL in tetrahydrofuran.

Spent zeolite was collected after reaction and dried overnight at 105°C. Ammonia temperature programmed desorption (NH3-TPD) was used to characterize zeolite acid sites. Thermogravimetric analysis (TGA) was used to analyze the occurrence of coking. X-ray diffraction (XRD) was employed to study the crystallographic structure of the zeolite. Nitrogen physisorption at 77K was employed to study the microstructure of zeolite samples.

Further details on the experimental procedures and materials can be found in the supplementary information.

Results and discussion

Effect of zeolite addition

To investigate the potential of β-zeolite as a stabilizing agent to produce lignin-based phenolic monomers in flow, experiments were carried out varying weight ratios of biomass and zeolite loadings combined in sequential reactors. In order to ensure a constant bed voidage, silicon carbide was mixed in corresponding amounts with the zeolite and added to the second reactor. As shown in Figure 2, adding a zeolite loading of 1-3 g to 1 g biomass (i.e., zeolite/biomass mass ratio of 1-3) leads to an increase in monomer yields between 12.9 and 19.4 wt.%, which are significantly higher than the 1.7 wt.% yield for the experiment without zeolite. Furthermore, an experiment with a higher biomass to zeolite mass ratio was performed by decreasing the biomass loading in the first reactor to 0.5 g. The corresponding biomass/zeolite mass ratio of 6 did not lead to a significantly higher monomer yield, indicating that monomer production is not limited by catalytic stabilization at these conditions.
Figure 2: Effect of zeolite loading in the aromatic monomer yield. Experiments carried out at standard conditions: Birch wood, T= 220°C, F_s=0.5 mL/min, P= 50 bar with a total duration of 3 hours in segregated reactor configuration. BM= biomass, Z= \( \beta \)-zeolite.

The obtained monomeric aromatic products are assigned as 62-67 wt.% unsaturated aromatics, namely eugenol, isoeugenol and 2,6-dimethoxy-4-propylphenol in accordance with previous reports\cite{26}, while only traces of the corresponding saturated monomers were observed. Moreover, 23-30 wt.% of carbonyl-containing monomers were detected based on syringaldehyde and 4-Hydroxy-3-methoxyacetophenone. Noteworthy, as shown in Figure 2, the product distribution of phenolic monomers was not affected by varying the biomass /catalyst ratio. In addition, \( \beta \)-zeolite also facilitated the production of holocellulose-based products, particularly furfural and ethyl levulinate. An increase in biomass/catalyst mass ratio from 1 to 3 leads to an increase in total sugar derived products yield from 1.6 to 7.1 g sugar derived products/ g initial holocellulose). This outcome is in line with previous studies, where \( \beta \)-zeolite is used to produce furfural and ethyl levulinate from monosaccharides\cite{32}. 
Lignin samples obtained with different zeolite loadings were analyzed by 2D HSQC NMR and the corresponding spectra are shown in Figure 3. Characteristic alpha alkoxy fragments were observed, indicating that α-ethoxylation of the β-O-4 linkage takes place during delignification with ethanol, as suggested earlier. This leads to an increment in lignin solubility and enables efficient delignification. The spectra also reveal the presence of allylic alcohol-containing moieties, which have been identified as possible unstable reactive intermediates, at least partially responsible for undesirable lignin repolymerization. Characteristic β-O-4 signals were observed to decrease with increasing zeolite loading, indicating that acid sites in β-zeolite are involved in the cleavage of these ether bonds.

Based on the observed trends, it is reasonable to question whether the increased in monomeric yield in the β-zeolite assisted process is merely a result of the Brønsted acid catalyzed β-O-4 cleavage. Thus, we compare the performance of 2 g β-zeolite with that of an equivalent concentration of homogeneous oxalic acid (see ESI Section 15). The conversion of birch wood with 0.1 M oxalic leads to a monomer yield of 4 wt.%, which is significantly lower than the yields achieved using β-zeolite. This low monomer yield in the case of the homogeneously catalyzed conversion is attributed to
acid catalyzed lignin repolymerization reactions\cite{34,35}, thereby confirming the synergistic role of the zeolite acidity and its pore structure in preserving high monomeric yields. Consequently, we conclude that there are at least two distinct functions carried out by the zeolite: contribution to depolymerization reactions through ether cleavage, and size-selective properties that enable the hinder bi-molecular recondensation of reactive intermediates through dehydration reaction, as shown in prior study\cite{26}. Given the fact that β-zeolite pores are too small to accommodate lignin fragments larger than dimers (See Figure S20), the depolymerization reaction likely occurs at the outer surface of the zeolite and not inside its pores. According to these findings, a proposed reaction scheme for the lignin transformation from lignocellulose to aromatic monomers is shown in Figure 4.

Figure 4: Reaction scheme for flow-through β-zeolite-assisted lignocellulose fractionation

Rate limiting step analysis

The transformation of in-planta lignin into aromatic monomers using β-zeolite may be governed not only by chemical transformations but also by physical phenomena such as internal/external mass transfer of the reactive species in and around the solid biomass and/or the solid catalyst. Mass transfer limitations can affect the overall monomer generation rate and, in general, they should be avoided for optimal system operation\cite{29}. Specifically for lignocellulosic biomass and microporous zeolites, the system is prone for internal mass transfer limitations due to the interaction of large lignin macromolecules with microporous solids\cite{36}. In order to ensure absence of internal and external mass transfer limitations during delignification, we have studied the effect of biomass particle size in the delignification rate of birch wood (See ESI
Section 16) and concluded that there are no diffusional limitations for particles below 150 \( \mu m \) and a solvent flowrate of at least 0.5 mL/min. To rule out mass transfer limitations for the zeolite-catalyzed reactions, the effect of \( \beta \)-zeolite particle size was evaluated by comparing the performance of 40-80 \( \mu m \) particles (i.e., reference case) with that of 80-150 \( \mu m \) particles. Using larger \( \beta \)-zeolite particles did not cause any significant change in phenolic monomer yield (See Figure S19), demonstrating the absence of diffusional effects around and inside the catalyst particles.

After discarding mass transfer effects, we examined the contribution of the individual conversion steps on the net monomer production rate. As sketched in Figure 4, when exposed to flow-through of ethanol/water at 220\(^\circ\)C, the solid biomass first undergoes solvolytic delignification (i.e., the release and dissolution of lignin fragments from the solid biomass into the liquid stream). Important parameters that influence the rate of this step are solvent composition and temperature (which are kept constant in this part of study). Thus, as the biomass to solvent feed flow ratio is kept constant, the resulting (time-dependent) concentration of solubilized lignin remains comparable throughout the set of experiments presented in this study. Accordingly, the extent of biomass delignification is determined by the total duration of the process (i.e., residence time of the solid, \( t_{\text{solid}} \)), which is set to 3 h in the present study.

Once dissolved in the liquid stream, lignin will undergo \( \beta \)-O-4 solvolytic cleavage, giving rise to the formation of unstable intermediate and consecutive recondensation in the liquid phase (See Figure S21). Subsequent to the \( \beta \)-O-4 solvolytic cleavage and in parallel to the homogeneous recondensation reactions, \( \beta \)-zeolite catalysis includes the \( \beta \)-O-4 cleavage of lignin oligomers and catalytic stabilization of the unstable lignin monomers. Accordingly, we may define \( t_{\text{homo}} \) and \( t_{\text{hetero}} \) as the residence times that determine the progress of the homogeneous and heterogeneous reaction pathways, respectively. For a given flow rate, \( t_{\text{homo}} \) and \( t_{\text{hetero}} \) should be proportional to the volume in between particles and the catalyst volume, respectively. Taking advantage of to the degrees of freedom of a flow-through reactor, we evaluate the performance of different reactor configurations (Figure 5) where \( t_{\text{homo}} \) and \( t_{\text{hetero}} \) are varied independently with the help of a solid diluent (i.e., SiC). Of particular interest is the possibility to decouple the residence time prior to catalytic stabilization from that during catalytic stabilization (e.g., by playing with the void fraction before the catalytic bed) in order to investigate the significance of the individual steps on the overall process.

To study the influence of solvolytic recondensation on the phenolic monomer yield, we first consider a case when the biomass and zeolite are segregated in two reactors (i.e., configuration 1), where \( t_{\text{homo}} \) before the catalytic stabilization (\( t_{\text{homo1}} \)) is approximately the same as that during catalytic stabilization (\( t_{\text{homo2}} \)). This configuration was compared with the case when both reactor zones were filled with a physical mixture of the same amount of biomass and zeolite (i.e., configuration 2, with negligible \( t_{\text{homo1}} \)). Although the total residence time for homogeneous and heterogeneous reactions is comparable in these two configurations, the latter introduces early stage contact between the unstable intermediates and the zeolite bed, thus ensuring their rapid stabilization. On the other hand, by spreading the biomass along the entire reactor, the solubilized lignin that is released from the solid biomass near the reactor exit spends relatively less
amount of time in the reactor. As shown in Figure 5, the physical mixture (i.e., configuration 2) leads to a yield of 9.4%, significantly inferior to the 16.5% of segregated case (i.e., configuration 1), indicating that monomer yield is not limited by solvolytic repolymerization, but rather by the relatively slow formation of reactive intermediates. In other words, prompt stabilization is not required. To verify this we further increased the average liquid residence time in the first reactor ($\tau_{homo1}$) in configuration 4. Here, we halved the biomass loading and solvent flow rate proportionally in order to free some space between the biomass and catalyst beds. To rule out additional effects derived from this decrease in biomass and flow rate, a control experiment was carried out using a single reactor with the same biomass and zeolite loading as seen in configuration 3. Configurations 3 and 4 showed no significant differences in monomer yield, supporting that the observed monomer generation rate is not affected by solvolytic repolymerization.

![Figure 5: Effect of different reactor configurations in the aromatic monomer yield. Experiments carried out at the following conditions: Birch wood, $T=220^\circ C$, $P=50$ bar with a total duration of 3 hours. The masses of lignocellulose, zeolite and silicon carbide are described for each reactor and configuration according to the legend on the left.](image)

So far, we proved that monomer production rate is neither affected by solvolytic repolymerization nor by mass transfer at these reaction conditions. Thus, we now explore the effects of solvolytic delignification and catalytic stabilization (i.e., here understood as the sequence of zeolite catalyzed reactions that include $\beta$-O-4 cleavage of solubilized lignin fragments and subsequent formation of monomers under stabilizing conditions in the zeolite pores) on the overall rate on monomer production by studying the effects of zeolite loading at different temperatures. To that end, the kinetic parameters of these reactions are studied by leveraging the time-resolved data provided by the flow-through system. As shown in Figure S24, cumulative monomer yields show a linear trend during the first 40 minutes of reaction, suggesting a constant reaction rate during this period. Thus, delignification rate was determined by quantifying the dissolved lignin during the initial 40 minute period through liquid-liquid extraction and gravimetry of the resulting oil obtained for temperatures ranging from 190 to 220$^\circ C$. As shown in Figure 6, the apparent activation energy for the delignification rate is 82 ± 6 kJ/mol, on par with literature data for delignification of hardwood under organosolv conditions\cite{25}. Similarly, the monomer production rate was determined by estimating the cumulative monomer yield during the initial period. As displayed in Figure 6, using a zeolite loading of 2 g in a segregated bed configuration leads to an apparent activation energy of 84 ± 3 kJ/mol for the monomer production rate, very similar to that of delignification. The similarity
between these two values would suggest that the overall rate of monomer production is indeed determined by the rate of lignin release, in line with previous literature that describes the delignification as a rather slow process, usually accelerated by the presence of acids \[^{34,37}\]

Nevertheless, it is remarkable that the apparent activation energy of for the monomer production increases up to 115 ± 2 kJ/mol when lowering the zeolite loading to 1 g, while that of the delignification reaction remains the same as it is independent of the catalyst loading. The fact that activation energy based on monomers is a function of zeolite loading suggests that the overall rate of monomer generation is to some extent affected by the solid-catalyzed reactions (particularly when using limited zeolite loadings), as well as solvolytic delignification, particularly (particularly when using sufficiently large zeolite loadings). This is in line with our earlier findings in Figure 2, which showed that zeolite addition leads to a substantial increase in monomer yield within a certain range, and becomes ineffective at high zeolite loading. In this sense, the system operates in a mixed kinetic regime where both solvolytic delignification and catalytic stabilization play a role. Thus, process intensification strategies should target the acceleration of these two steps. In addition, these results also reveal that the true activation energy of the stabilization reactions should be greater than that of the delignification reactions (≥ 115 kJ/mol), suggesting that even higher reaction temperatures will be beneficial for the process.

The systematic rate limiting step analysis suggests that it is necessary to increase both solvolytic and catalytic reaction rates to enhance the phenolic monomer yield. Homogeneous acid addition is known to increase β-O-4 bond cleavage through hydrolysis, leading to a higher delignification rate\[^{38,28}\]. Nevertheless, acid-catalyzed lignin depolymerization may also lead to more severe lignin recondensation\[^{19}\]. Thus, we evaluate the co-addition of a homogeneous acid on the monomer yield. It is well-known that most homogeneous acids lead to compositional and textural modifications of aluminosilicates at high concentrations\[^{39,40}\]. Oxalic acid was selected as the homogeneous acid, as it is completely biodegradable and a more sustainable alternative to the usually strong mineral acids used in lignocellulose
fractionation \cite{41-43}. The effect of oxalic acid addition in different concentrations on the delignification and aromatic monomer yield is shown in Figure 7.

![Figure 7: Effect of acid addition on delignification and aromatic monomer yield. Experiments carried out at standard conditions: Birch wood, T= 220°C, F_s=0.5 mL/min, P= 50 bar with a total duration of 3 hours, 1g biomass, 2g β-zeolite in segregated reactor configuration.](image)

A gradual increase in monomer yield and delignification is observed for an incremental addition of oxalic acid in a concentration between 0 and 0.75 g/L. However, even higher acid concentrations up to 3 g/L render lower monomer yield, despite the monotonic increase in delignification. These results could be explained by the expected increase in the rate of recondensation reactions, leading to higher lignin molar weight products. Nevertheless, gel permeation chromatography (GPC) data showed no clear indications of molar weight increase with increasing acid concentration (See Figure S17). Hence the decrease in monomer yield does not seem to be attributed to acid-catalyzed lignin repolymerization. Another reasonable hypothesis is that increasing concentrations of oxalic acid modifies the microporous and textural properties of the β-zeolite, which is a known phenomenon for various aluminosilicates \cite{44-46}. To assess this hypothesis, N\textsubscript{2} physisorption studies were carried out on spent zeolites with and without acid addition. As shown in Table 1, acid addition leads to a lower zeolite surface area, but also to a smaller pore and micropore volumes, probably having a detrimental effect on the size-selective properties of the zeolite and its ability to inhibit lignin repolymerization. Hence, the combination of oxalic acid with β-zeolite seems to be an attractive strategy that can be further optimized to achieve higher monomer yields, but the prolonged use of zeolite under these conditions may lead to undesirable changes in its microporous structure.

**Stability and regeneration of β-zeolite**

In order to evaluate the stability of β-zeolite as a catalyst in the treatment of lignocellulosic biomass, recycle experiments were carried out according to reactor configuration 1 in Figure 8, by successively replacing biomass in the first reactor while keeping the second reactor’s content unchanged. Recycle experiments were conducted with 2g β-zeolite loading, since it is below the full conversion limit as seen in Figure 2. After the last recycle experiment, the content of the second reactor was emptied and collected for analysis and regeneration following the
same calcination procedure used to activate fresh \( \beta \)-zeolite. The effect of catalyst recycle and regeneration on aromatic monomer yield is displayed in Figure 8.

![Figure 8: Effect of catalyst recycle and regeneration in the aromatic monomer yield. Experiments carried out at standard conditions: Birch wood, \( T = 220^\circ \text{C} \), \( F_s = 0.5 \text{ mL/min} \), \( P = 50 \text{ bar} \) with a total duration of 3 hours, 1g biomass, 2g \( \beta \)-zeolite in segregated reactor configuration. Relative catalyst activity calculated as the monomer yield of each experiment divided by the monomer yield obtained after the first run.](image)

After a total of five recycle experiments, a relative drop of 35% was detected in phenolic monomer yield, while no significant change was observed in product distribution. The progressive decrease in catalytic activity for successive recycle runs is an indication of catalyst deactivation. It was observed that spent zeolites were significantly darker than the fresh ones (See Figure S9), suggesting coke deposition. After thermal regeneration, zeolites restored their original white appearance but catalytic activity was only partially recovered. To understand the possible root causes of the observed deactivation, spent zeolites were analyzed by using TGA, \( \text{N}_2 \) physisorption, \( \text{NH}_3 \)-TPD and XRD. The results provided by these techniques are shown in Figure 9.
XRD patterns showed no significant differences for the main characteristic peaks of β-zeolite [47], with the exception of the regions at 6.7°, 21.5° and 25.6°, which show minor peak development, especially for the five times used and regenerated catalysts. These results indicate that the crystalline structure of β-zeolite is mostly unchanged after a single run, but after repeated recycling and regeneration, minor structural changes take place.

TGA was carried out at a temperature program that ensured sample dewatering in order to provide a quantitative comparison free of moisture effects (See Section 10.2 in SI). The spent catalyst after one run exhibits a significantly higher mass loss than the fresh zeolite, further supporting that catalyst coking takes place. Similar trends in mass loss for the one-time and five-times used zeolites indicate that the amount of coking is not proportional to the total time on stream of the catalyst. However, the mass loss derivative ($\Delta$TGA) is significantly lower for the five times recycled catalyst when compared with fresh zeolite. These results suggest that coke deposits become more recalcitrant with increasing time on stream, potentially requiring higher temperatures for full thermal decoking.

Nitrogen physisorption data allowed to calculate surface area and pore volume for the solid samples, as shown in Table 1. One and five time spent zeolites respectively displayed a significantly lower surface area and pore volume compared with fresh β-zeolite. This is likely due to pore blocking caused by biomass-derived coke deposits, in agreement with TGA data. As a consequence of pore size broadening and despite the occurrence of coking, β-zeolite shows a slight increase in surface area and pore volume upon time on stream.
Table 1: Surface area and pore volume for all solid samples as determined by nitrogen physisorption. *calculated according to t-plot method. Peak temperatures for Lewis and Brønsted acid sites. Acid site concentration obtained by deconvolution (See ESI Section 10.4)

|                  | Surface area [m²/g] | Pore volume [cm³/g] | Micropore volume [cm³/g] | T_Lewis [°C] | T_Bronsted [°C] | Lewis site conc. [mmol/g] | Brønsted site conc. [mmol/g] |
|------------------|---------------------|---------------------|--------------------------|--------------|-----------------|--------------------------|-----------------------------|
| Fresh            | 437                 | 0.263               | 0.151                    | 205          | 371             | 0.075                    | 0.145                       |
| 1 time used      | 358                 | 0.231               | 0.112                    | 182          | 325             | 0.046                    | 0.125                       |
| 1 time used + 3 g/L acid | 302                 | 0.211               | 0.093                    | 189          | 340             | 0.057                    | 0.124                       |
| 5 times used     | 379                 | 0.256               | 0.12                     | 191          | 302             | 0.046                    | 0.073                       |
| Regenerated      | 434                 | 0.286               | 0.136                    | 202          | 350             | 0.047                    | 0.064                       |

Given the relevance of the β-zeolite pore structure to the chemical transformation of lignin, pore size distribution data was obtained for the solid samples. Fresh zeolite shows pore sizes narrowly distributed around 4 nm. Spent zeolites after one and five runs respectively show gradual pore size broadening as seen in Figure 9. Thermal regeneration leads to a full recovery of the original surface area and a higher pore volume than fresh β-zeolite. However, used zeolites show a smaller fraction of the pore volume being comprised by micropores. The observed trend suggests that catalytic activity loss could be caused by zeolite leaching.

NH₃-TPD results shown in Figure 9 display a lower temperature peak at 200°C corresponding to weaker Lewis sites and a broader peak at higher temperatures (350-600°C) for stronger Brønsted acid sites, in agreement with prior literature studies with β-zeolite[48],[49]. The desorption temperature (as indicative of the acid strength) and the corresponding amounts of these acid sites are summarized in Table 1 for all catalyst samples. Used zeolites show a decrease in acidic strength and amount for both Lewis and Bronsted acid sites. The 5 times used zeolite does not show further change in Lewis sites, however, a significant drop in Brønsted acidic strength and concentration was observed. Thermal regeneration restores acidic strength for both acid site types but has no effect on their concentration.

Based on the results obtained with the different characterization techniques employed, we conclude that the main deactivation mechanisms are: 1) coking through carbon deposition, and 2) leaching, which leads to a decrease in the concentration of acidic active sites and pore size broadening, being detrimental for the size-selective properties of β-zeolite in the prevention of recondensation reactions. While the effects of coking can be reversed through thermal treatment, the leaching and observed acidity loss is likely the root cause for the irreversible loss of catalytic activity. Overall, the results of this stability study are meant to highlight attention areas for future development of promising tailor-made microporous aluminosilicates for lignin-first biorefining.

**Effect of different lignocellulosic feedstocks**

As the types of biomass feedstocks vary across the world, it is valuable for future biorefineries to be flexibly operable with a diverse range of lignocellulosic feedstocks from an economic (e.g. logistics) as well as environmental (e.g. biodiversity) perspective. Accordingly, the system was studied using different feedstocks that represent the diversity of lignocellulosic biomass types: birch as a hardwood, spruce as a softwood and walnut shells as an agricultural residue.
The phenolic monomer yield and the extent of delignification for different feedstocks are provided in Figure 10. Compared to the 16.5 wt.% phenolic monomer yield obtained with birch wood, relatively lower yields were obtained from spruce and walnut shells (i.e., 9.8 and 9.4 wt.% of the initial lignin, respectively). Nonetheless, considering the higher native lignin content of spruce and walnut shells into account, the total aromatic monomer production per gram of initial biomass is comparable for all three feedstocks. 2D HSQC NMR analysis of the lignin obtained from spruce wood and walnut shells shows very weak β-O-4 characteristic signals (see Figure S14), indicating extensive ether bond cleavage. All three feedstocks enabled the generation of holocellulose-based furfural and ethyl levulinate in varying yields (see table S1).

The considerably lower delignification extent of spruce signifies that there are possibilities for further increasing monomer yield by using more severe solvolytic conditions such as a higher temperature or acidity. Significant differences in monomeric product distribution were observed for each feedstock. Respectively for birch, spruce and walnut shells, 72 mol%, 19 mol% and 60 mol% of the phenolic products were detected to be single-methoxy aromatics (S units). These differences are in agreement with the ratio of S/G units present in the native structure of these feedstocks\(^{[50,51]}\). Hence, the monomeric product distribution obtained with the different feedstocks is mainly influenced by the in-planta lignin composition and structure.

Overall, all selected feedstocks were successfully valorized using β-zeolite as a stabilizing agent. The comparable yields in terms of lignin-based phenolic monomers as well as holocellulose-based products demonstrate the robustness of β-zeolite in lignocellulose processing. In light of these findings, there is great potential for improving operation conditions as well as designing tailor-made zeolite catalysts to optimize this approach towards an economically and environmentally benign process for lignocellulose valorization.

**Conclusions**

In this study, a one-step β-zeolite assisted fractionation of lignocellulosic biomass in a flow-through reactor is reported, using birch as main feedstock and 9:1 v/v ethanol/water as solvent at 220°C. We conclude that β-zeolite is active in ether bond cleavage as well as in the acid-catalyzed stabilization of reactive intermediates, and that both the zeolite pore structure, as
well as its acidity are key parameters to the success of the lignin-first fractionation strategy. In an effort to optimize the chemically and physically complex process, a systematic approach was followed to identify the limiting steps. Reactor configurations with increasing liquid residence time before zeolite-based stabilization did not lead to a decrease in monomer yield, leading to the conclusion that solvolytic lignin recondensation is not the rate limiting step in aromatic monomer production. By comparing the rates of production of lignin oil and monoaromatics at different temperatures and zeolite loadings, we concluded that solvolytic delignification and zeolite-catalyzed reactions are rate determining steps in the overall production of lignin monomers. Accordingly, promotion of zeolite-assisted stabilization through increase in zeolite/biomass mass ratio from 1 to 6 has a beneficial effect on increasing from 12.9 to 20.5 wt.%. To further accelerate solvolytic delignification, the co-addition of oxalic acid was studied. A volcano curve for different acid concentrations and optimum in 0.75 g/L of acid was obtained. Nevertheless, the addition of acid also led to unwanted modifications in the pore structure of β-zeolite. Catalyst recycle experiments showed a relative drop of 35% in monomer yield over five experimental runs. The catalyst deactivation is attributed to the combined effects of coking and structural modifications of zeolite, such as increase in pore size and loss of acidity through leaching. Finally, in order to demonstrate the versatility of β-zeolite in lignin-first biorefining, spruce wood and walnut shells were considered as alternative feedstocks, leading to comparable monomer yields but providing different product distributions as a result of varying native lignin structure.

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Electronic supplementary information for

β-zeolite assisted lignin-first fractionation in a flow-through reactor

A. Kramarenko[a], D. Etit[a], G. Laudadio[b], F. Neira D’Angelo[a]*

*Department of chemical engineering and chemistry, Sustainable process engineering group, Eindhoven technical university of technology, Het Kranenveld 14 5612 AZ Eindhoven, Nederlands

b [current affiliation] Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA,92037, United States.
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2. Materials

Monomer compounds were purchased from Sigma Aldrich all with purity $\geq 95\%$ : 4-(propan-2-yl)phenol, 4-ethyl-2-methoxyphenol, 4-methyl-2-methoxyphenol 4-allyl-2-methoxyphenol, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol, 2-methoxy-4-[prop-2-enyl]phenol, 1-(4-hydroxy-3-methoxyphenyl)ethanone. Guaiacylglycerol-β-guaiacyl Ether $\geq 95\%$ was purchased from TCI chemicals. Absolute HPLC grade $\geq 99\%$ ethanol and ethyl acetate respectively were purchased from Biosolve. Hydrogen beta zeolite was purchased from Alfa Aesar with Si/Al = 320. Silicon carbide 300 mesh and Pd/Al$_2$O$_3$ 5 wt.% was purchased from Sigma Aldrich. Birch (Betula) and Spruce (Picea) wood were locally grown in Eindhoven, Nederlands and harvested in 2018. Walnuts (Junglans regia) were purchased from www.allnuts.nl.

As schemed below, 2,6-Dimethoxy-4-propylphenol was synthesized from commercially available 2-methoxy-4-[prop-2-en-1-yl] phenol by hydrogenation with Pd/Al$_2$O$_3$ 5 wt.% in a 200 mL stirred reactor with EtOH: H$_2$O 9:1 v/v. The initial concentration of reactant was 1g/L and 1 gram of catalyst was added. Room temperature hydrogen pressure was 10 bars. The reaction was carried out at 150°C for a total duration of 3 hours.

3. Experimental set-up

Solvent was supplied through a 500 mL ISCO pump (details). Liquid outlet is initially collected in a 5 mL volume vessel, which in case of overflow leads to a second larger 500 mL liquid collection vessel. The setup is pressurized with nitrogen through a backpressure regulator. Tubular reactors of 1 cm ID x 10 cm length are connected through a threaded middle joint piece and porous metal gaskets as shown in Figure S- 2.
Each reactor was packed with 1 gram of quartz wool and 1 gram of 2 mm glass beads according to the configuration showed in Figure S-3. Wool and beads ensure that the bed remains static during the experiment and allow for easy and circa loss-free recovery of used biomass and zeolite. The reactor has a total empty volume of 8.4 cm$^3$. The void volume for the packed reactor was measured by filling with water and ultrasound during 1 hour to ensure full liquid penetration in the wood/zeolite and subsequent weighing. For a loading of 1 g of biomass, the void volume is 4.6 cm$^3$ and for a loading of 2 g of zeolite, the void volume is 3.5 cm$^3$.

4. Calculation of bubble point pressure

In order to keep the solvent in liquid phase during the operation, bubble point pressure for 9:1 v/v EtOH/H$_2$O mixture in 150 – 250°C is determined through simulations in Aspen plus software. As provided in Figure S-5, ethanol and water are introduced to the system with flexible volume input in ambient conditions. The resulting mixture at 25°C – 1bar is fed to a heat exchanger, which is programmed to set its pressure to the corresponding bubble point pressure for given temperature.
Regarding the chemical properties, the base method is selected as non-random two liquid model combined with Redlich-Kwong equation of state (NRTL-RK).

![Aspen simulation diagram for bubble point pressure calculations](image)

**Figure S- 5: Aspen simulation diagram for bubble point pressure calculations**

The resulting bubble point pressure in the temperature range of 150 – 250°C is given in Figure below. Since the current experimental setup is operable with a highest pressure of 51 bar, the maximum temperature throughout the experiments is set as 220°C.

![Sensitivity Results Curve](image)

**Figure S- 6: Bubble point pressure of 9:1 v/v EtOH/H2O solvent with respect to temperature**

### 5. Experimental procedure

#### 5.1. Preparation of biomass

Branches of lignocellulcic biomass were drilled using a Bosch GSB 13 RE professional drill and a 16 mm wood drill bit, as show in Figure below. The resulting coarse sawdust was further milled using a planetary ball mill using 5-20 mm zirconia balls at 300 rpm during 10 minutes. The resulting fine sawdust was sieved to a particle size range of 50-150 μm, which has proved to be a particle size small enough to prevent diffusional mass transfer limitations\(^1\). Biomass sawdust was dried and pre-extracted using a Toluene/EtOH 2:1 v/v mixture in a Soxhlet for 6 hours. All experiments were carried out using dry and pre-extracted biomass.
5.2. Preparation of zeolite

Commercial β-zeolite is available as a fine powder which can’t be used as such in the flow-through system due to loss of solids cause by the solvent flow. Therefore zeolite was pelletized at a pressure of 5 tons for a duration of 5 minutes. Pelletized zeolites were milled in a mortar and sieved to the desired particle size between 40 and 150 μm. Subsequently, the zeolite was thermally activated at 550°C for 5 hours.
5.3. Flow-through reaction procedure

First, it is important to degas the pump in order to ensure results consistency. The packed reactors are connected to the system and placed in the oven. The system is pressurized with nitrogen until 10 bars and vented three times in order to remove all oxygen. Subsequently, the system is heated until temperature setpoint, measured with an additional thermocouple inside the oven in order to ensure isothermal operation. Afterwards, the liquid flow rate is started. 5 mL liquid samples are collected at 10 minute intervals during the first hour of time on stream. During the final two hours of the experiment, liquid samples are collected every 20 minutes. Once the total time on stream of 180 minutes is reached, the oven is switched off and the liquid flowrate is stopped. The pressure drop across the system was monitored by comparing the pressure measurements of the pump and the back pressure controller. All experiments were carried out with a pressure drop of 0.7 bars. After reaction completion, the oven was switched off and the flowrate was stopped. The reactors were emptied and the contained biomass and zeolite are dried overnight at 110°C.

5.4. Liquid sample work-up

Liquid samples were processed according to the scheme shown in Figure S-10. For NMR, GPC and GC-MS analysis, samples were liquid-liquid extracted first in order to remove all sugar derived products. For this, samples were dried under 100 mbar and 40°C in rotavap and were extracted with 10 mL of ethyl acetate and 10 mL of water three times. It was observed that after beta-zeolite assisted processing, the resulting lignin is more easily soluble in ethyl acetate and provides a better behavior during the extraction, being also less prone for undesirable emulsions.

![Liquid samples](image)

**Figure S-10: Scheme of liquid sample work-up**
Figure S-11: Liquid/liquid extraction of delignification liquor with (left) and without (right) beta-zeolite assisted fractionation

6. GC-MS

Sample preparation involves liquid-liquid extraction of the untreated sample with ethyl acetate and water, as shown in Figure S-11. The organic phase was isolated and processed under 50 mbar and 40°C until dryness. The resulting lignin oil was resolubilized in acetone and analyzed by GC-MS.

A Shimadzu QP2020 GC-MS was used with a SH-Rxi-1ms capillary column. The analysis method consisted of an initial oven temperature of 50°C kept for 1 minute. Temperature was increased at 15°C/min until 300°C where it was kept for a duration of 7.5 minutes, hence the total analysis duration was 25 minutes. Injection temperature was 250°C and detector temperature was 200°C. Peak characterization was carried out using the available compound library in the Shimadzu software and are well in line with prior work from literature [2].
Figure S-12: GC-MS chromatogram of birch wood lignin obtained at 220°C with 1 gram of biomass and 2 g of β-zeolite.
2 mL aliquots of untreated liquid reaction samples were collected from the reactor. 1.5 mL of 5 g/L isopropyl phenol solution in EtOH: H₂O 9:1 v/v was added. The resulting mixture was filtered through an 0.45 μm teflon syringe filter.

Analysis was performed in a Varian CP-3800 gas chromatographer equipped with a CP-SII-5 CB 30m capillary column and a flame ionization detector. The analysis method consisted of an initial oven temperature of 50°C kept for 1 minute. Temperature was increased at 15°C/min until 300°C where it was kept for a duration of 12.33 minutes, hence the total analysis duration was 30 minutes. Injection temperature was 250°C and detector temperature was 290°C. Monomer yield was calculated for each sample according to effective carbon number principle in agreement with available protocols [3] and using the equations shown below. Main reaction products were identified by injection of available commercial standards. 2,6-Dimethoxy-4-propylphenol is one of the majoritary products and is not commercially available, hence the peak assignation was performed according to the GC-MS sequence, as shown in Figure S-13.
\[ n_{\text{isopropyl phenol}} = \frac{m_{\text{isopropyl phenol in sample}}}{MW_{\text{isopropyl phenol}}} \]

\[ n_{\text{monomer}} = \frac{A_{\text{monomer in sample}}}{A_{\text{decane in sample}}} \times n_{\text{isopropyl phenol}} \times \frac{ECN_{\text{isopropyl phenol}}}{ECN_{\text{monomer}}} \]

\[ m_{\text{monomer}} = n_{\text{monomer}} \times MW_{\text{monomer}} \]

\[ \text{Monomer yield (wt.\%)} = \frac{m_{\text{monomer}}}{m_{\text{initial lignin in biomass}}} \times 100 \]

Figure S-13: GC-FID of a complete set of 12 reaction samples. Overlaid are the chromatograms of pure aromatic monomer compounds.

8. 2D HSQC NMR

A solution of 45 mg of lignin in 0.6 mL of DMSO-d6 were prepared and placed in the corresponding NMR tube. Samples were analyzed and in a Bruker 400 MHz spectrometer according to the standard program HSQC EDETGPSISP where a 1H NMR sample of 32 scans with a relaxation delay of 2 seconds is
coupled to a $^{13}$C HSQC analysis of 16 scans and a relaxation delay of 2 seconds. The resulting spectra was analyzed using MestReNova. Assignment of peaks was carried out according to literature [4,5].

Figure S-14: 2D HSQC NMR of walnut shell lignin

Figure S-15: 2D HSQC NMR spectra of spruce lignin
9. Gel permeation chromatography (GPC)

The molecular weight of the isolated lignin was determined by gel permeation chromatography (GPC) analysis. The analysis was carried out on a Hewlett Packard 1100 series THF-GP. The lignin samples (10 mg) were dissolved in THF with toluene as a flow marker. Prior to analysis, the samples were filtered with a syringe filter (0.45 µm, PTFE). Analysis was performed with PSS WinGPC UniChrom.

Although the presence of zeolite clearly leads to the production of low molar weight products, different acid concentration does not lead to a significantly different result.
10. Solid characterization

10.1. X ray diffraction (XRD)
X-Ray Diffraction is performed by a Rigaku MiniFlex 600. Using Cu Kα radiation, the detector angle 2θ is varied from 5° to 60°.

10.2. Thermogravimetric analysis (TGA)
Thermogravimetric analysis was carried out in a Thermo Analysis TGA Q500. 10 mg of sample were heated from room temperature until a final temperature of 1000°C at a rate of 10°C/min. Weight loss at low temperatures significantly varies between the different analyzed samples, indicating different moisture contents. In order to provide conditions for a rigorous water-free comparison, the temperature program was changed. Samples were heated from room temperature until 110°C at a rate of 10°C/min and kept at constant temperature for one hour. Subsequently temperature was increased from 110°C to 1000°C at a rate of 10°C/min.

10.3. N₂ physisorption
Approximately 100 mg of solid sample was weighed and prepared for analysis by heating at 150°C under N₂ flow. N₂ physisorption was carried out in a Micromeritics Tristar at 77K. BET area, pore volume and pore size distribution have been calculated with Micromeritics software available at the device.

10.4. Ammonia temperature programmed desorption (NH₃-TPD)
Ammonia temperature programmed desorption was carried out in a Micromeritics AutoChem II chemisorption analyzer. 100 mg of sample were heated to a temperature of 500°C under a helium flow of 10 mL/min for one hour. Temperature was reduced to 100°C under a helium flow of 10 mL/min for one hour. The sample was saturated under using a gas mixture of NH₃/He 5% under a flow of 10 mL/min for 2 hours. Temperature was increased until 700°C at a rate of 20°C/min. Amount of desorbed ammonia was determined by calibration with gas standards. Curve deconvolution was carried out in Origin 2019, as shown in Figure S-18. A third peak with maxima at approximately 600°C was observed. However, as reported previously [6], this peak is related to zeolite disproportionation and is not representative of the zeolite acidity.
Figure S-18: Deconvoluted NH3 TPD signals for each one of the samples a) Fresh zeolite after calcination. b) Used zeolite after one experiment at 220°C without acid. c) Used zeolite after one experiment at 220°C with 3g/L of oxalic acid. d) Used zeolite after five recycle experiments at 220°C without acid. e) Thermally regenerated zeolite after five recycle experiments at 220°C without acid

11. Reproducibility of the standard case and the effect of zeolite particle size

Experiments were carried out at standard conditions with 1 g of biomass loading in the first reactor and 2 g of zeolite in the second reactor at two different particle sizes. As shown in Figure S-19, four experiments to check the reproducibility resulted in aromatic monomer yields in the range of 15.5 – 17.3 wt.%, resulting an average and standard deviation of 16.5 ± 0.9 wt.%. In addition to the consistency of
overall yields, as also seen in Figure S-19, distribution of aromatic products showed a consistent trend as well. Finally, as also provided in Figure S-19, larger zeolite particle size resulted in a yield of 17.3 wt.% with similar product distribution, confirming the insignificance of mass transfer limitations in this range.

Figure S-19: Monomer product distribution for reproducibility experiments carried out at different zeolite particle size.

12. Different feedstocks composition

Table S-1: Monomeric product distribution for different lignocellulosic feedstocks

|                          | Birch | Spruce | Walnut Shell |
|--------------------------|-------|--------|--------------|
| Initial biomass (mg)     | 1000  | 1000   | 1000         |
| Lignin content of initial biomass (mg) | 216   | 280    | 315          |
| Holocellulose content (mg) | 674   | 604    | 511          |
| Furfural produced (mg)   | 20    | 4      | 20           |
| Ethyl levulinate produced (mg) | 7     | 9      | 3            |
| Monomeric lignin-based products (mg) | 36    | 27     | 30           |
| Yield$_1$ (mass monomers/initial lignin weight) | 16.5% | 9.8%   | 9.4%         |
| Yield$_2$ (mass monomers/initial biomass weight) | 3.1%  | 2.7%   | 3.0%         |
| Yield$_3$ (mass sugar derived products/initial mass holocellulose) | 3.9%  | 2.2%   | 4.5%         |

13. Lignin oligomers size considerations

Beta zeolite has a tridirectional pore structure with two large distinct pore systems. One of the pore systems consists of straight 12-membered ring channels with a free aperture of 6.6 x 6.7 Å along the [1 0 0] axis. The second pore system consists of zig zagged 12-membered ring channels with dimensions of 5.6 x 5.6 Å along the [0 0 1] axis. Lignin fragments with more than two aromatic rings (dimers) are too large to fit in these small pores, hence we hypothesize that depolymerization takes place on the external surface of the zeolite and not inside the pores.
Figure S-20: Estimation of characteristic dimensions of different lignin oligomers and comparison with β-zeolite pore size

14. Different reactor configurations

Figure S-21: Simplified reaction mechanism with reactions described as a function of characteristic reaction times: $t_{\text{solid}}$, $t_{\text{homo}}$, $t_{\text{hetero}}$. (Liquid)
Where:

\[ \tau_{\text{homo}} = \frac{V_R \varepsilon_{\text{void}}}{Q_{v,l}} \]

\[ \tau_{\text{hetero}} = \frac{W_{\text{cat}}}{Q_{v,l}} \]

Where:

\( \tau_{\text{homo}} \) = Residence time for homogeneous reactions in liquid phase [min]

\( \tau_{\text{hetero}} \) = Residence time for heterogeneous reactions catalyzed by zeolite [min]

\( W_{\text{cat}} \) = Weight of \( \beta \)-zeolite catalyst [g]

\( Q_{v,l} \) = Volumetric flowrate of liquid in the reactor [mL/min]

\( \varepsilon_{\text{void}} \) = reactor voidage [m\(^3\) void/ m\(^3\) reactor]

15. Effect of acid addition without zeolite

In order to prove that \( \beta \)-zeolite has shape-selective properties and not only acts as a source of acid sites, an experiment was carried out using exclusively an homogeneous acid in the absence of b-zeolite in the reaction medium. The concentration of acid sites in \( \beta \)-zeolite according to NH\(_3\)-TPD is approximately 200 mM/g. Zeolite equivalent acidity was calculated as the moles of acid sites divided by the void volume of the reactor. Hence an equivalent pH of 1.2 was calculated. Consequently an experiment using 1g of birch wood and a 0.1M Oxalic acid concentration in the solvent was performed in the flow-through reactor at 0.5 mL/min of liquid flowrate and a total duration of 3 hours at 220 °C.

16. Effect of solvent flowrate and biomass particle size on delignification rate

Effects of external and internal mass transfer for birch wood have been evaluated by performing delignification experiments with varying particle size and solvent flowrate. The delignification rate is expressed as \( \text{L}_{\text{Reactor}}/L_0 \), being \( L_0 \) the initial amount of lignin in the wood and \( L_{\text{Reactor}} \) the amount of lignin remaining in the reactor, which is the sum of the lignin remaining in the wood and the lignin dissolved in the liquid inside the reactor at a a given reaction time (\( L_{\text{Reactor}} = L_{\text{wood}}(t) + L_{\text{liquid}}(t) \)). The experiments were carried out in the same flow-through reactor used in the present study at 200°C but with a different solvent mixture consisting of MeOH/H\(_2\)O 50/50% vol., which is known to be a more efficient solvent..
mixture in the delignification of lignocellulosic biomass than EtOH/H₂O 90/10% vol[7], hence providing a higher delignification rate. Consequently these findings regarding the effect of solvent flowrate and biomass particle size can be applied to the experiments carried out with EtOH/H₂O 90/10% vol.

As shown in Figure S23, an increase in solvent flowrate from 0.5 to 1 mL/min has no significant effect on delignification rate, indicating that there are no external mass transfer limitations for the studied liquid flowrate range. An increase in biomass particle size leads to a slower delignification for a particle size above 150 μm, which is in agreement with recent studies carried out in batch reactors[1]. Consequently, experiments carried out at \( F_L = 0.5 \) mL/min and \( 150 \text{ μm} > d_{p,\text{biomass}} > 50 \text{ μm} \) with EtOH/H₂O 90/10% vol. are free of internal and external mass transfer limitations, hence the system is operated within the kinetic delignification regime.

Figure S-23: Left: Effect of liquid solvent flowrate on delignification rate of birch wood at \( d_{p} = 50-100 \text{μm} \). Right: Effect of particle size on delignification rate of birch wood at \( F_L = 0.5 \) mL/min
17. Reaction experiment conditions

*Table S-2: Experimental conditions for the reported reaction experiments*

| Experiment No. | T (°C) | Flow Rate (ml/min) | Oxalic Acid (g/L) | Feedstock Type | Feedstock Mass (mg) | Zeolite Mass (mg) | Zeolite Size (µm) | Note                  |
|----------------|--------|--------------------|-------------------|----------------|---------------------|------------------|-------------------|-----------------------|
| 1              | 220    | 0.5                | -                 | Birch          | 1000                | 0                | -                 |                       |
| 2              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Reproducibility (1)   |
| 3              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Reproducibility (2)   |
| 4              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Reproducibility (3)   |
| 5              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Reproducibility (4)   |
| 6              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Recycled zeolite      |
| 7              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Recycled zeolite      |
| 8              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Recycled zeolite      |
| 9              | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Recycled zeolite      |
| 10             | 220    | 0.5                | -                 | Birch          | 1000                | 1400             | 40-80             | Re-calcined           |
| 11             | 220    | 0.5                | -                 | Birch          | 1000                | 1400             | 40-80             |                       |
| 12             | 220    | 0.5                | -                 | Birch          | 1000                | 1000             | 40-80             |                       |
| 13             | 220    | 0.5                | -                 | Birch          | 1000                | 3000             | 40-80             |                       |
| 14             | 220    | 0.5                | -                 | Birch          | 500                 | 3000             | 40-80             |                       |
| 15             | 220    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             | Configuration 2       |
| 16             | 220    | 0.25               | -                 | Birch          | 500                 | 1500             | 40-80             | Configuration 4       |
| 17             | 220    | 0.25               | -                 | Birch          | 500                 | 1500             | 40-80             | Configuration 3       |
| 18             | 220    | 0.5                | 1.5               | Birch          | 1000                | 2000             | 80-150            |                       |
| 19             | 220    | 0.5                | 1.5               | Birch          | 1000                | 2000             | 40-80             |                       |
| 20             | 220    | 0.5                | 0.75              | Birch          | 1000                | 2000             | 40-80             |                       |
| 21             | 220    | 0.5                | 3                 | Birch          | 1000                | 2000             | 40-80             |                       |
| 22             | 220    | 0.5                | 0.375             | Birch          | 1000                | 2000             | 40-80             |                       |
| 23             | 200    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             |                       |
| 24             | 190    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             |                       |
| 25             | 210    | 0.5                | -                 | Birch          | 1000                | 2000             | 40-80             |                       |
| 26             | 210    | 0.5                | -                 | Birch          | 1000                | 1000             | 40-80             |                       |
| 27             | 200    | 0.5                | -                 | Birch          | 1000                | 1000             | 40-80             |                       |
| 28             | 190    | 0.5                | -                 | Birch          | 1000                | 1000             | 40-80             |                       |
| 29             | 220    | 0.5                | -                 | Spruce Shells   | 1000                | 2000             | 40-80             |                       |
| 30             | 220    | 0.5                | -                 | Walnut Shells   | 1000                | 2000             | 40-80             |                       |
## 18. Reaction experiment results

**Table S-3: Monomer yields for all reported experiments**

| Experiment No. | 4-ethyl-2-methoxy phenol | 4-allyl-2-methoxy phenol (Eugenol) | 2-methoxy-4-(prop-1-en-1-yl)phenol (Isoeugenol) | 1-(4-hydroxy-3-methoxyphenyl) ethanone | 2,6-dimethoxy-4-propylyphenol | 4-hydroxy-3,5-dimethoxy benzaldehyde | 2,6-dimethoxy-4-(prop-1-en-1-yl)phenol | 4-(3-hydroxypropyl)-2,6-dimethoxy phenol | Total Yld (wt.% lignin) |
|----------------|--------------------------|-----------------------------------|-----------------------------------------------|--------------------------------------|----------------------------------|---------------------------------------|---------------------------------------|-------------------------|------------------------|
| 1              | 0.0%                     | 0.0%                              | 0.1%                                          | 0.0%                                 | 0.2%                             | 1.4%                                  | 0.0%                                  | 1.7%                    | 15.9%                  |
| 2              | 0.1%                     | 0.1%                              | 0.5%                                          | 3.2%                                 | 0.5%                             | 1.7%                                  | 8.6%                                  | 1.2%                    | 17.1%                  |
| 3              | 0.2%                     | 0.2%                              | 0.5%                                          | 2.8%                                 | 0.6%                             | 1.5%                                  | 10.4%                                 | 1.0%                    | 15.4%                  |
| 4              | 0.2%                     | 0.0%                              | 0.4%                                          | 2.7%                                 | 0.4%                             | 1.5%                                  | 9.4%                                  | 0.8%                    | 17.3%                  |
| 5              | 0.1%                     | 0.1%                              | 0.4%                                          | 2.5%                                 | 1.0%                             | 1.6%                                  | 10.0%                                 | 1.5%                    | 16.3%                  |
| 6              | 0.0%                     | 0.3%                              | 0.6%                                          | 2.9%                                 | 0.7%                             | 1.6%                                  | 9.2%                                  | 1.1%                    | 14.6%                  |
| 7              | 0.0%                     | 0.1%                              | 0.6%                                          | 2.4%                                 | 0.2%                             | 1.2%                                  | 9.0%                                  | 1.2%                    | 13.2%                  |
| 8              | 0.0%                     | 0.0%                              | 0.5%                                          | 2.6%                                 | 0.0%                             | 1.3%                                  | 7.7%                                  | 1.0%                    | 11.8%                  |
| 9              | 0.0%                     | 0.4%                              | 0.5%                                          | 2.1%                                 | 0.1%                             | 1.3%                                  | 6.6%                                  | 0.9%                    | 12.3%                  |
| 10             | 0.0%                     | 0.2%                              | 0.5%                                          | 2.3%                                 | 0.1%                             | 1.1%                                  | 7.1%                                  | 1.0%                    | 15.7%                  |
| 11             | 0.0%                     | 0.3%                              | 0.6%                                          | 2.7%                                 | 0.2%                             | 1.7%                                  | 8.6%                                  | 1.4%                    | 12.9%                  |
| 12             | 0.1%                     | 0.1%                              | 0.7%                                          | 2.9%                                 | 0.2%                             | 0.9%                                  | 7.9%                                  | 0.1%                    | 19.4%                  |
| 13             | 0.2%                     | 0.3%                              | 0.5%                                          | 2.9%                                 | 1.0%                             | 2.2%                                  | 11.2%                                 | 1.2%                    | 20.5%                  |
| 14             | 0.1%                     | 0.1%                              | 0.5%                                          | 2.9%                                 | 1.1%                             | 1.8%                                  | 12.4%                                 | 1.3%                    | 14.1%                  |
| 15             | 0.1%                     | 0.4%                              | 0.5%                                          | 1.9%                                 | 0.2%                             | 1.2%                                  | 4.2%                                  | 0.8%                    | 18.3%                  |
| 16             | 0.0%                     | 0.1%                              | 0.5%                                          | 2.3%                                 | 0.3%                             | 2.0%                                  | 7.7%                                  | 1.2%                    | 11.6%                  |
| 17             | 0.0%                     | 0.2%                              | 0.4%                                          | 2.1%                                 | 0.5%                             | 1.3%                                  | 9.7%                                  | 0.0%                    | 17.3%                  |
| 18             | 0.1%                     | 0.2%                              | 0.6%                                          | 2.8%                                 | 0.5%                             | 1.5%                                  | 10.5%                                 | 1.1%                    | 18.5%                  |
| 19             | 0.1%                     | 0.1%                              | 0.8%                                          | 3.5%                                 | 1.6%                             | 1.3%                                  | 10.6%                                 | 0.5%                    | 20.1%                  |
| 20             | 0.1%                     | 0.2%                              | 0.6%                                          | 3.0%                                 | 0.8%                             | 2.0%                                  | 11.6%                                 | 1.8%                    | 17.1%                  |
| 21             | 0.1%                     | 0.1%                              | 0.5%                                          | 2.5%                                 | 0.8%                             | 1.6%                                  | 10.0%                                 | 1.5%                    | 18.3%                  |
| 22             | 0.0%                     | 0.1%                              | 0.6%                                          | 2.6%                                 | 0.9%                             | 2.0%                                  | 10.4%                                 | 1.7%                    | 11.6%                  |
| 23             | 0.0%                     | 0.0%                              | 0.4%                                          | 2.2%                                 | 0.0%                             | 1.0%                                  | 7.0%                                  | 1.0%                    | 9.8%                   |
| 24             | 0.0%                     | 0.0%                              | 0.4%                                          | 1.8%                                 | 0.0%                             | 1.2%                                  | 5.3%                                  | 1.2%                    | 18.8%                  |
| 25             | 0.0%                     | 0.1%                              | 0.6%                                          | 2.8%                                 | 0.5%                             | 1.6%                                  | 10.4%                                 | 2.9%                    | 12.4%                  |
| 26             | 0.0%                     | 0.1%                              | 0.7%                                          | 1.9%                                 | 0.0%                             | 1.6%                                  | 7.5%                                  | 0.5%                    | 6.2%                   |
| 27             | 0.0%                     | 0.0%                              | 0.5%                                          | 0.9%                                 | 0.0%                             | 0.7%                                  | 2.7%                                  | 1.3%                    | 3.4%                   |
| 28             | 0.0%                     | 0.0%                              | 0.3%                                          | 0.7%                                 | 0.0%                             | 0.1%                                  | 1.8%                                  | 0.4%                    | 9.8%                   |
| 29             | 0.8%                     | 0.5%                              | 1.3%                                          | 5.3%                                 | 0.3%                             | 1.2%                                  | 0.5%                                  | 0.0%                    | 9.4%                   |
| 30             | 0.2%                     | 0.0%                              | 0.6%                                          | 2.6%                                 | 0.1%                             | 1.1%                                  | 4.3%                                  | 0.4%                    | 9.4%                   |
19. Kinetic measurements

![Graph of cumulative yield vs. time on stream for different temperatures with R² values.]

**Figure S-24**: Period of constant monomer production rate for 2g β-zeolite loading

**Figure S-25**: Period of constant monomer production rate for 1g β-zeolite loading

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