2-step lignin-first catalytic fractionation with bifunctional Pd/β-zeolite catalyst in a flow-through reactor

A. Kramarenko,[a] A. Uslu,[a] D. Etit,[a, b] and F. Neira D’Angelo*[a]

This work demonstrates an additive and hydrogen-free 2-step lignin-first fractionation in flow-through. First, solvolytic delignification renders lignin liquors with its native chemical structure largely intact; and second, β-zeolite catalytic depolymerization of these liquors leads to similar monomer yields as the corresponding 1-step fractionation process. Higher delignification temperatures lead to slightly lower β-O-4 content in the solvated lignin, but does not affect significantly the monomer yield, so a higher temperature was overall preferred as it promotes faster delignification. Deposition of Pd on β-zeolite resulted in a bifunctional hydrogenation/dehydration catalyst, tested during the catalytic depolymerization of solvated lignin with and without hydrogen addition. Pd/β-zeolite displays synergistic effects (compared to the Pd/γ-Al2O3 and β-zeolite tested individually and as a mixed bed), resulting in higher monomer yield. This is likely caused by increased acidity and the proximity between the metallic and acid active sites. Furthermore, different β-zeolite with varying SAR and textural properties were studied to shed light onto the effect of acidity and porosity in the stabilization of lignin monomers. While some of the catalysts showed stable performance, characterization of the spent catalyst reveals Al leaching (causing acidity loss and changes in textural properties), and some degree of coking and Pd sintering.

Introduction

One of the most pressing needs in the chemical industry today is the shift from polluting and finite fossil feedstocks towards a more sustainable and green alternative for the production of fuels and chemicals. Lignocellulosic biomass can play a key role in this transition.[1,2] Among the various alternatives explored so far to valorize this chemically rich feedstock, biomass fractionation into its primary constituents (i.e., cellulose, hemicellulose and lignin) and subsequent upgrading of the separate fractions into building blocks (i.e., bio-refining) is regarded as the most economically feasible biorefinery. A promising strategy recently developed for lignocellulose valorization is the so-called lignin-first,[3] also known as reduc-tive catalytic fractionation (RCF) or catalytic upstream biorefining process (CUB).[3] This approach combines solvolytic removal of lignin from the lignocellulosic matrix (i.e., delignification) with the depolymerization of the solubilized lignin fragments and the catalytic stabilization thereof.[3,14] Lignin-first typically involves the use of organic protic solvents (e.g., MeOH, EtOH, BuOH),[12] an heterogeneous redox catalyst (e.g., supported Pd, Ru, Ni),[13,14] and a reducing agent such as pressurized H2 or an internal hydrogen donor derived from biomass (e.g., reducing sugars, formic acid).[15,16] This approach results in a highly depolymerized lignin oil and a near-theoretical maximum yield of aromatic lignin monomers (i.e., 40–50 wt.% vs. 5–10 wt.% obtained in traditional delignification methods).[17–19] Carbohydrates remain relatively unaltered during this process,[20] enabling facile downstream valorization (e.g., enzymatic hydrolysis).

In view of upscaling this technology,[21] a few works have looked at decoupling this conversion in 2 steps (i.e., solvolsysis and catalytic depolymerization), thereby preventing the need to mix solid biomass and catalysts, and allowing for independent optimization of the process conditions for each step.[22,23] Using batch reactors and Pd-based catalyst, the 2-step process resulted in a significantly lower aromatic monomer yield than the 1-step counterpart, suggesting that solvated lignin undergoes rapid, undesired repolymerization. Therefore, a 2-step lignin-first valorization in batch is not a promising strategy for scale up. Although the vast majority of lignin-first related literature is based on batch reactor studies, some contributions have been focused on lignin-first fractionation in continuous flow reactors.[24–27] More concretely, a recent study involving 2-step lignin-first fractionation has shown that solvated native-like lignin in MeOH can be obtained in a flow-through reactor,[28] where lignin liquor is rapidly separated from the biomass bed. Remarkably, this nickel catalyzed 2-step lignin-first
approach in flow yielded the same amount of monomers as its 1-step homologue (i.e., 35 wt.%). Despite its promising features, these lignin-first strategies suffer from a few bottlenecks that hamper its scale-up potential. Fast deactivation of the (expensive) metal catalysts and the use of elevated hydrogen pressures lead to high operational costs.\[29–31\]

Recent work has shown that ß-zeolite can be used as a catalyst to depolymerize lignin and effectively prevent its repolymerization through dehydration and size selectivity under lignin-first conditions, leading to high aromatic monomer yields (i.e., 20 wt.%)[32,33] Although the monomer yields were not as high as for other lignin-first processes with mineral acids, metal catalysis and high pressure H\(_2\), the absence of all these elements enables operation at lower pressures, cheaper reactor materials and simpler downstream separation. These factors make the ß-zeolite assisted fractionation an economically attractive process that could find its place a future biorefinery concept. Nevertheless, previous work on this reaction has focused on the 1-step strategy, whereas a 2-step strategy would be more desirable. Despite the fact that ß-zeolite shows better performance under 1-step lignin-first conditions than other zeolite frameworks,[32] very little is known regarding the influence of other relevant parameters such as ß-zeolite acidity or surface morphology. Such information would be key to envision and further optimize a 2-step fractionation strategy in which the process conditions for lignin solvolysis and zeolite assisted depolymerization/stabilization of lignin liquors are tuned independently. Additionally, given the well-established effect of transition metal catalysis on increasing monomer yield during lignin-first fractionation a plausible optimization strategy could involve the combination of metal and zeolite catalysis for this reaction.\[8,34,35\] Even though the use of transition metal catalyst supported on zeolites has been extensively studied for high temperature biomass conversion strategies such as pyrolysis with good results,\[36,37\] the use of zeolite-supported metal catalysts under lignin-first conditions is a field that remains largely unexplored. Particularly the case of metal supported ß-zeolite for lignin-first has not been investigated, to the best of our knowledge. In the present work, as illustrated in Figure 1, we compare the 1-step and 2-step lignin-first fractionation strategies by using EtOH:H\(_2\)O 9:1 v/v as a solvent and ß-zeolite as catalyst in order to assess whether a native-like lignin can be obtained under these conditions. Leveraging the optimization opportunities that a 2-step process offers, we evaluate the effect of delignification temperature on the final monomer yield. Moreover, we deposited Pd in ß-zeolite through ion exchange and evaluated its performance in the 2-step process approach. By harnessing the unique capabilities of flow-through reactors we carry out experiments with different bed configurations in order to study the potential synergistic effects of the different tested catalysts and elucidate the reaction mechanism. Additionally, three different ß-zeolites with varying acidity and different porosity properties are used as supports for Pd deposition. The catalytic performance and stability of the resulting supported catalysts are tested. Finally, the used catalysts are analyzed by using different solid characterization techniques to elucidate possible deactivation mechanisms.

Results and Discussion

1-step vs. 2-step zeolite-assisted lignin-first lignocellulose fractionation

In order to investigate the effect of performing zeolite-assisted lignocellulose fractionation in 1 and 2 steps respectively, different experiments were carried out with the a commercial sample of ß-zeolite (henceforth referred as ß-Z) in the flow-through setup according to the reactor configurations shown in Figure 1. Figure 2 compares the monomer yield for the 1-step and the 2-step processes. To further assess the stability of the delignification liquor obtained after the first fractionation step,
The liquor was aged for four weeks before catalytic conversion. Figure 2B shows the comparison of cumulative and steady state monomer yields for the 1 and 2-step process configurations respectively. The cumulative yield for the 2-step process has been calculated as the steady state monomer generation rate multiplied by the total time on stream. The results in Figure 2 show that there is no significant difference in the monomer yield achieved between the 1-step and 2-step processes, even after the delignification liquor is aged for a time period of four weeks. 2D HSQC NMR analysis indicated that the delignification liquor obtained after first step delignification contains ether lignin intralinkages, which can be catalytically cleaved to form stable aromatic monomers. The liquor obtained after the second catalytic conversion step does not show any ether linkage characteristic signals in NMR, indicating that lignin has been significantly depolymerized. Overall, these results suggest that oligomeric lignin solvated in EtOH:H₂O 9:1 v/v is chemically stable and can be readily converted into aromatic monomers in a second catalytic step without significant loss of monomeric yield due to undesirable lignin repolymerization.

These findings, which are in line with a very recent work on the 2-step lignin fractionation using MeOH solvolysis followed by a Ni/C catalyzed hydrogenation,[32] are a very important milestone towards process scale-up. Additionally, zeolite-assisted lignin-first fractionation leads to the formation of furfural and ethyl levulinate.[32] This is a result of the acid-catalyzed dehydration of solubilized C5 and C6 sugars.[38,40] As shown in Figure 2B, the 2-step process results in a lower yields to sugar derived products than the 1-step homologue. More concretely, ethyl levulinate yields shows a significant drop when the process is carried out in 2-step, which could be caused by the unstability of glucose in the reaction medium.

An important feature of the 2-step zeolite-assisted lignocellulosic fractionation is that it opens the possibility for separate optimization of process conditions for each individual step. A relevant parameter to further optimize the 2-step process is the delignification temperature in the first step. Prior studies show that increasing delignification temperature leads to higher delignification rate and greater lignin removal from the lignocellulosic matrix.[24] However, it has also been demonstrated that an increase in temperature can lead to solvolytic cleavage of ether bonds,[38,42,43] which can decrease the monomer yield obtained after catalytic processing of the solvated lignin.[24] Therefore we hypothesized that an optimum in delignification temperature with respect to monomer yield can be found.

We investigated the effect of first step delignification temperature by performing four separate delignification experiments in the flow-through reactor setup at 160, 180, 200 and 220°C respectively. This resulted in four different delignification liquor solutions with lignin concentrations ranging from 0.6 to 1.8 mg mL⁻¹. In order to provide a rigorous comparison, the lignin concentration in each solution was adjusted to a value of 1 mg mL⁻¹ either by solvent addition or by solvent evaporation, prior to the subsequent catalytic conversion step (See details in SI Section 9). β-O-4 relative abundance was assessed on each lignin solution by 2D HSQC NMR analysis. Because cross peaks are not exactly proportional to the concentration of chemical groups in the chemical sample, this technique can only provide semi-quantitative comparative results.[39,40] Consequently, the relative abundance of β-O-4 moieties is reported using the delignification liquor obtained at 160°C as basis. As shown in Figure 3, regardless of the greater extent of depolymerization (i.e., down to a relative 25% lower ether content of the delignification liquor) upon increasing the delignification temperature, the monomer yield after the catalytic conversion with β-Zi (i.e., yield of the second step only) remains nearly unaffected. Consequently, the overall monomer yield for the 2-step process increases monotonically with increasing delignification temperature as a result of increasing delignification rate. Therefore, no optimum in delignification temperature was found within the conditions explored in this study, with the greatest monomer yield at the highest delignification temperature (i.e., 220°C). Note that even greater temperatures may yield greater amounts of monomers, but they were not achievable in the current experimental setup. Moreover it is relevant to note that higher delignification temperatures have
been linked to higher rates of solvolytic ether cleavage and lignin repolymerization,\textsuperscript{[47]} which is in line with our observations regarding lignin molar weight distributions measured for samples obtained at different delignification temperatures (See ESI Section 12).

Our results contrast with prior 2-step lignin-first studies where a loss of monomer yield was reported if compared with the 1-step process.\textsuperscript{[22,48]} Nevertheless, unlike the present work, those studies were carried out in a batch reactor in the presence of homogeneous acid, leading to undesirable lignin repolymerization. According to prior work focused on decoupling lignin-first fractionation in batch reactor,\textsuperscript{[47]} solvated lignin significantly repolymerizes if maintained at 200 °C for longer than two hours before contacting with the catalyst, even in the absence of homogeneous acids. Therefore, we conclude that the successful demonstration of the 2-step lignin-first process in the present work is enabled by the homogeneous acid-free conditions and short residence times of the solvated lignin provided by the flow-through reactor system. Nevertheless, it is important to note that despite the indications of intralignin ether cleavage and lignin repolymerization, no significant effect was observed on the monomer yield obtained at increasing delignification temperatures. We hypothesize that the rate of monomer generation in the second process step might be limited by catalyst activity and not by the chemical structure of solvated lignin. For this reason, in order to ascertain the consequences of decoupling lignin-first processes in 2 steps, it would be insightful to evaluate appropriate catalysts and conditions (i.e.: transition metal catalysts and high H\textsubscript{2} pressures) that enable achieving near theoretical maximum monomer yields.\textsuperscript{[50]}

**Bifunctional Pd/β-zeolite supported catalyst**

In this section, β-zeolite catalytic depolymerization of solvolyzed lignin (i.e., the second step of the 2-step biomass fractionation) is compared with the Pd catalyzed hydrogenation of the same liquors, which is a benchmark in the field of lignin-first fractionation.\textsuperscript{[11]} Prior catalytic lignin-first studies involving β-zeolite and metallic hydrogenation catalysts have respectively shown that the use of flow-through reactors provides monomer yields comparable to those obtained with conventional batch systems.\textsuperscript{[29,32,33]} We leveraged the unique capability of the flow reactor to create a sequence of different catalyst beds (i.e., using mixtures of Pd supported catalysts and/or β-zeolite according to the configurations shown in Figure 4) and evaluated the impact on product distribution and yield. Although not required for the β-zeolite assisted process, all tests discussed in this section were conducted under hydrogen flow in order to account for possible effects of the biphasic (gas-liquid) flow through the catalyst bed. The effect of hydrogen flow and total pressure were optimized for maximum monomer yield (see SI for details). The minimum working pressure was 45 bar to ensure liquid phase operation. Further pressure increase until 60 bar (i.e., 15 bar of hydrogen) did not show any significant effect on monomer yield. Even higher pressures were not explored due to equipment limitations, but most likely would render higher monomer yields. Note that Pd-catalyzed reductive catalytic fractionation is typically carried out at pressures of up to 250 bar in batch reactors.\textsuperscript{[51]} Similarly, hydrogen flowrate between 1 and 10 NmL min\textsuperscript{-1} does not show a significant effect on the monomer yield. For further testing, 60 bar and 5 NmL H\textsubscript{2} min\textsuperscript{-1} were selected.

In order to assess for potential synergistic effects, we first studied the performance of Pd and β-zeolite separately according to the 2-step process described above. These experiments were carried out using Pd/γ-Al\textsubscript{2}O\textsubscript{3} and β-Z, zeolite (i.e., configurations 2 and 3, respectively). The performance of γ-Al\textsubscript{2}O\textsubscript{3} alone was tested as well, (i.e., configuration 1) leading to negligible 1.4 wt.% monomer yield. Thus, we conclude that γ-Al\textsubscript{2}O\textsubscript{3}, when present in the other configurations, does not contribute significantly to the monomer yield. However, in the results in Figure 4B, Pd/γ-Al\textsubscript{2}O\textsubscript{3} and β-Z, zeolite provided similar aromatic monomer yields, in fact slightly higher in the zeolite case. Nevertheless, important differences are seen with respect to product distribution. The products obtained with Pd/γ-Al\textsubscript{2}O\textsubscript{3} were comprised mostly of hydroxypropy1-chain phenols, namely 2,6-dimethoxy-4-hydroxypropylphenol. This is the result of the...
hydrogenation of unstable intermediate allylic alcohols into stable monomeric species (i.e., reaction R₂ in Figure 4B).

On the other hand, the product distribution obtained with ß-zeolite is mostly comprised of unsaturated-chain monomers, namely 2,6-dimethoxy-4-propylphenol, resulting from the dehydration of the unstable allylic alcohols (reaction R₄ in Figure 4).

Both routes lead to the conversion of allylic alcohols (which would otherwise lead to repolymerization reactions) as stabilizing strategy. On the other hand, unsaturated-chain monomers (i.e., the products of R₂) have also been pointed as a potential source for undesirable lignin repolymerization.[29] Nevertheless, additional tests performed in a batch reactor with isoeugenol as model compound at 200 °C for a total reaction time of 3 hours showed no conversion of isoeugenol. This suggests that the main unstable intermediates in the proposed reaction mechanism are the allylic alcohols (namely coniferyl and sinapyl alcohol) whereas unsaturated-chain monomers do not contribute significantly to loss of monomer yield.

Next, we assess the combination of Pd/γ-Al₂O₃ and ß-zeolite in configurations 4 and 5, where the same loading of each catalyst as in configurations 2 and 3 were placed as two segregated beds with alternating order of catalysts. According to the most commonly accepted rationale, starting with the zeolite bed followed by the Pd-based catalyst (i.e., configuration 4) would favour acid-catalysed depolymerization followed by reductive stabilization of the reactive intermediates, and as such, would lead to the highest monomer yield. Nevertheless, configurations 4 and 5 render very similar monomer yields. While the role of Pd-based catalysts on lignin depolymerization through ß-O-4 cleavage is also well established,[30] that of ß-zeolites on the stabilization of lignin monomers through dehydration of the allylic alcohols has been proposed only very recently.[32] In line with our previous study,[33] these results further emphasize that the acidic sites of ß-zeolite do not only prompt depolymerization reactions but also play a key role in the stabilization of lignin monomers.

With respect to the product distributions from configurations 4 and 5, these are very similar to those of configurations 3 and 2, respectively. It appears that the first catalytic bed determines the final monomer distribution while the second bed plays a relatively minor role. Interestingly, only configuration 4 shows a significant amount of 2,6-dimethoxy-4-propylphenol, which is likely formed as the result of consecutive zeolite catalysed dehydration and Pd catalysed hydrogenation reactions accord-
ing to reaction scheme in Figure 4 (i.e., reactions $R_4$ and $R_5$, respectively). The limited yield to 2,6-dimethoxy-4-propylphenol in the configuration 5 suggests that β-zeolite is not an effective catalyst to dehydrate the hydroxyl groups on aliphatic chains (i.e., $R_6$).

Finally, configurations 6 and 7 involve the use of physically mixed Pd/γ-Al$_2$O$_3$ and β-Z, zeolite as well as the Pd supported on β-Z, using the same loadings of Pd and β-Z, as the previous configurations 2 and 3. The results in Figure 4 reveal that increasing the proximity between the different active sites in configurations 6 and 7 lead to the highest monomer yield among all studied configurations (i.e., 22.8 and 19.7 wt.% for the Pd/β-Z, and the physical mixture, respectively). Product distributions were also significantly different for both catalyst configurations. The product of the physical mixture in configuration 6 is mostly comprised by hydroxypropyl-chain monomers (i.e., products of the Pd-catalyzed route), while Pd/β-Z is resulted in a mixture of both hydroxypropyl-chain and saturated-chain monomers. The addition of Pd to β-Z, appears to promote the dehydration rate $R_4$, when compared to the physical mixture of Pd/Al$_2$O$_3$ and β-Z. This could be explained by an increase of the acidity of the zeolite catalyst upon addition of the palladium.

Characterization of the zeolite before and after palladium deposition showed that the acidity of the supported catalyst measured by NH$_3$-TPD significantly increased after Pd deposition, which can have a significant effect on monomer yield.[34,35] On the other hand, nitrogen physisorption showed that palladium deposition on β-zeolite does not affect surface area neither pore size or pore volume of the resulting catalyst. TEM image analysis showed that the palladium is distributed in clusters of 11.2 nm in average, which are most likely located in the outer surface of the zeolite, since the zeolite does not contain mesopores where palladium clusters of such size could be located. Thus, we speculate that finely dispersed Pd in close proximity to β-Z, acid sites provides a higher monomer stabilization rate.

### Performance of Pd deposited in different β-zeolites

Although the catalytic activity of β-zeolite has proven more effective in lignin depolymerization and stabilization than other zeolite frameworks,[32] the specific role of crucial properties such as zeolite acidity and microporous structure during lignin-first processes have not been studied and therefore remain unclear. To investigate these effects, three different commercial β-zeolites, namely β-Z$_1$, β-Z$_2$, and β-Z$_3$, were chosen for comparison due to their distinctive acidities, as evidenced by their Si/Al ratios in Table 1. Additionally, while β-Z$_1$ and β-Z$_2$ are predominantly comprised by micropores, β-Z$_3$ contains a large volume of mesopores, providing additional insights on the role of the pore structure in this reaction. The activity of these different β-zeolites, as well as that of commercial ZSM-5 and Ferrierte zeolite frameworks have been tested at different weight hour space velocities by changing the catalyst loading in the reactor, as shown in Figure 5.

Figure 5 shows that β-Z$_2$ and β-Z$_3$ (i.e., the most acidic zeolites) provide a higher activity at moderate WHSV than β-Z$_1$. However, there is no significant difference between the monomer yield achieved with β-Z$_2$ and β-Z$_3$. Given the differences in properties between the different β-zeolites, it is possible to infer that zeolite acidity is a relevant parameter in zeolite-assisted lignin-first valorization, however at lower WHSV all tested β-zeolites show very similar monomer yields. These results also imply that mesoporosity, which is much greater for β-Z$_3$ than for (the similarly acidic) β-Z$_2$, does not have a major effect on monomer yield. All β-zeolites show much higher monomer yields than ZSM-5 and Ferrierte. This is most likely due to the smaller β-member ring in ZSM-5 and Ferrierte,

### Table 1. Structural, acid and compositional properties of fresh and spent supported Pd/β-zeolite catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>$V_{tota}$ [cm$^3$/g]</th>
<th>$V_{micr}$ [cm$^3$/g]</th>
<th>$T_{peak}$ [°C]</th>
<th>$T_{BETmax}$ [°C]</th>
<th>$C_{Brønsted}$ [mmol/g]</th>
<th>$C_{Lewis}$ [mmol/g]</th>
<th>Si/Al (wt.%</th>
<th>Pd leach [wt.%]</th>
<th>Al leach [wt.%]</th>
<th>Pd $\Delta D$ [nm]</th>
<th>Zeo. $\Delta D$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Z$_{1, Pd}$ fresh</td>
<td>595</td>
<td>0.343</td>
<td>0.195</td>
<td>176</td>
<td>326</td>
<td>0.072</td>
<td>0.140</td>
<td>360</td>
<td>–</td>
<td>–</td>
<td>11.2</td>
<td>20.5</td>
</tr>
<tr>
<td>β-Z$_{1, Pd}$ spent</td>
<td>438</td>
<td>0.303</td>
<td>0.131</td>
<td>175</td>
<td>303</td>
<td>0.060</td>
<td>0.071</td>
<td>–</td>
<td>5.2%</td>
<td>16%</td>
<td>14.9</td>
<td>26.4</td>
</tr>
<tr>
<td>β-Z$_{2, Pd}$ fresh</td>
<td>515</td>
<td>0.319</td>
<td>0.166</td>
<td>207</td>
<td>318</td>
<td>0.431</td>
<td>0.549</td>
<td>–</td>
<td>38%</td>
<td>24%</td>
<td>21.4</td>
<td>32.1</td>
</tr>
<tr>
<td>β-Z$_{2, Pd}$ spent</td>
<td>313</td>
<td>0.244</td>
<td>0.100</td>
<td>200</td>
<td>310</td>
<td>0.227</td>
<td>0.342</td>
<td>–</td>
<td>4.9%</td>
<td>14%</td>
<td>28.5</td>
<td>35.1</td>
</tr>
<tr>
<td>β-Z$_{3, Pd}$ fresh</td>
<td>499</td>
<td>0.821</td>
<td>0.126</td>
<td>223</td>
<td>348</td>
<td>0.556</td>
<td>0.613</td>
<td>25%</td>
<td>–</td>
<td>–</td>
<td>3.3</td>
<td>16.5</td>
</tr>
<tr>
<td>β-Z$_{3, Pd}$ spent</td>
<td>334</td>
<td>0.704</td>
<td>0.085</td>
<td>185</td>
<td>302</td>
<td>0.343</td>
<td>0.559</td>
<td>5.4%</td>
<td>17%</td>
<td>4.4</td>
<td>20.3</td>
<td></td>
</tr>
</tbody>
</table>

[a]: Micropore volume, determined by t-plot method. [b]: Concentrations and temperatures of Bronsted or Lewis acid sites determined by NH$_3$-TPD deconvolution. [c]: Based on initial content of Pd and Al in the fresh catalyst. [d]: Average Pd particle size determined by TEM image analysis. [e]: Zeolite average crystallite size determined by Scherrer equation.
which has difficult accessibility for large lignin oligomers than the larger 12-member ring in β-zeolite.

Next, we hypothesized that Pd deposition in more acidic zeolites could further increase monomer yield. For this, we deposited 1 wt.% Pd through on all three β-zeolites and compared their performance. Additionally, given the negative impact in process economics of using gaseous hydrogen, we deposited 1 wt.% Pd through on all three β-zeolites for the absence of molecular hydrogen, the system is not operated with catalyst excess (which would otherwise obscure catalyst deactivation studies),[30] the loadings were adjusted according to the different Pd/β-zeolite activities. Consequently, initial monomer yields in stabilization studies are lower than those shown in Figure 6.

As shown in Figure 7, β-Z2, Pd showed no signs of deactivation during the first 8 hours of which ultimately enables reaction R3 to take place. After starting hydrogen feeding, the liquid samples adopt a lighter colour, as shown in Figure 6D. The presence of molecular hydrogen accelerates the reaction R3 and therefore leads to the formation of 2,6-dimethoxy-4-hydroxypropylphenol. This indicates that hydrogenation R1 is slow, meaning that β-zeolite cannot effectively dehydrate 2,6-dimethoxy-4-hydroxypropylphenol. According to NH3-TPD data and unlike for β-Z1, Pd deposition on β-Z2 and β-Z3 did not lead to an increase in acidity. Also, unlike β-Z1, β-Z2 and β-Z3 did not show an increase in monomer yield upon feeding molecular hydrogen. This could be attributed to hydrogen spillover in the case of β-Z1, which has a significantly greater metal/acid site ratio,[34,35] than the already very acidic β-Z2 and β-Z3.

Stability of different supported Pd/β-zeolite catalysts

Catalyst stability of the different supported Pd/β-zeolite samples was evaluated by using a 2-step process approach. This approach allows to evaluate catalyst stability under steady state conditions, providing an accurate representation of the true catalytic performance at longer times on stream. For this purpose, five biomass beds containing 1 g of birch sawdust each were delignified at the standard conditions used throughout the present work. The resulting delignification liquor was combined and fed through a Pd/β-zeolite catalyst bed at 220°C 60 bar, a liquid flowrate of 0.5 mL min⁻¹ and a hydrogen flowrate of 5 NmL min⁻¹ for a total time on stream of 14 hours. To ensure that the system is not operated with catalyst excess (which would otherwise obscure catalyst deactivation studies),[30] the loadings were adjusted according to the different Pd/β-zeolite activities. Consequently, initial monomer yields in stabilization studies are lower than those shown in Figure 6.

As shown in Figure 7, β-Z2,Pd displayed the fastest and most severe deactivation from all three catalysts tested. Monomer yield declined by 44% relative to the initial monomer yield. β-Z2,Pd showed no signs of deactivation during the first 8 hours of

Figure 6. Performance of different Pd/β-zeolite supported catalysts. First step delignification conditions: 1 g birch sawdust, 220°C, 50 bar, F1 = 0.5 mL min⁻¹, 3 hr total time on stream. Conditions for second step: 220°C, 60 bar, F1 = 0.5 mL min⁻¹, 2 g catalyst with 1 wt.% Pd. Dashed vertical lines symbolize the start of hydrogen flowrate F2 = 5 NmL min⁻¹. A) β-Z1; B) β-Z2; C) β-Z3; D) Color change in liquid reaction samples with and without hydrogen flowrate.

Figure 5. Effect of weight hour space velocity of different zeolites in the obtained monomer yield. First step delignification conditions for all experiments: 1 g birch sawdust, 220°C, 50 bar, F1 = 0.5 mL min⁻¹, 3 hr total time on stream. Second step conditions: 220°C, 50 bar, F1 = 0.5 mL min⁻¹, 2 hr total time on stream, zeolite loading 0.5–3 g. For more details see SI Section 11.
time on stream, but later on yield dropped 17% relative to initial monomer yield. Finally "β-Z₁₃Pd" showed no visible deactivation during the whole duration of this test. Catalyst characterization results are collected in Figure 8 as well as in Table 1.

TGA analysis (Figure 8A) shows that all catalysts were affected by carbon deposition, although not to a great extent. Recent Kraft lignin valorization studies under supercritical ethanolysis conditions assisted by Pd deposited on mesoporous "β-zeolite" reported that the presence of mesopores could inhibit coke formation. However, our TGA results on zeolites with different mesoporosity (i.e., β-Z₁₃Pd and β-Z₃₃Pd) are not in line with these findings, which is likely due to the differences in chemical structure between Kraft lignin and the solvated lignin used in the present work. Next, NH₃-TPD analysis (Figure 8B and Table 1) show that all catalysts suffer a decrease in both acid strength and concentration of (Lewis and Brønsted) acid sites. ICP-AES analysis reveal a significant and comparable decrease of aluminium content for all tested catalysts. Thus, aluminium leaching is likely causing the loss of catalyst acidity. With respect to Pd, although there seems to be a slight weight loss of ca. 5 wt.% of the originally deposited metal, given the small amounts of metal in the original samples, we conclude that there are no strong indications of palladium leaching. N₂-physisorption allowed to calculate surface area, pore volume and pore size distribution. A decrease in BET surface area is observed for all studied catalysts, as well as a decrease in micropore volume. This suggests that zeolite micropore blocking could potentially decrease the accessibility of species to the remaining zeolite acid sites. XRD analysis shows that although there are no major changes in the crystallographic structure of the catalysts, there is an increase in average crystallite size. Finally, the palladium particle size distribution measured by TEM (see details in SI) reveal that the average palladium particle size of β-Z₃₃Pd is significantly smaller than for the other two supported catalysts. This is most likely due to the mesoporous structure of this zeolite, which allows palladium to be deposited inside the pores, while it likely agglomerates on the outer surface of the other two zeolites. However, the average
palladium particle sizes increase after the stability test for all studied catalysts. Therefore, despite the promising performance of \( \beta-Z_{\text{sol}} \) during the stability tests, there are indications of several deactivation mechanisms taking place during this reaction, which could lead to a decrease in catalyst performance at even longer times on stream. Thus, further studies on catalyst stability will be key to assess scalability of this process.

**Conclusions**

In the present work the 2-step zeolite assisted lignin-first fractionation in a flow-through reactor is explored. A comparison between 1-step and 2-step processes revealed that there is no monomer yield difference between both process configurations, indicating that the obtained solvated lignin after the first step contains ether bonds that can be catalytically valorized into aromatic monomers even after an aging period of four weeks. Although lower delignification temperatures in the first step rendered solvated lignin with higher ether content, this has no significant effect in the catalytic performance of the second process step and therefore the first step should be carried out at the highest temperature in order to maximize delignification. A bifunctional catalyst was synthesized by depositing palladium on \( \beta \)-zeolite through ion exchange, which enables lignin depolymerization and subsequent stabilization through the combined effect of zeolite-catalyzed dehydration and palladium-catalyzed hydrogenation. The performance of this catalyst was evaluated through the optimized 2-step process and a synergistic effect was found, which can be to some extent caused by the increase in acidity observed after Pd deposition. Moreover, different commercial \( \beta \)-zeolites of varying acidity and pore structure were used as palladium support, so their catalytic performance and stability could be compared. Pd supported in all three different \( \beta \)-zeolites resulted in similar aromatic monomer yields. Finally, the stability of palladium deposited on different \( \beta \)-zeolites was tested, revealing that high acidity mesoporous zeolite displayed excellent stability, showing no significant drop in monomer yield for a total time on stream of 14 hours. Pd deposited on \( \beta \)-zeolite (highly acidic and mesoporous) displayed the highest stability among all tested catalysts. However, characterization of the spent catalysts revealed signs of carbon deposition, which causes a decrease of catalyst surface area and blocking of zeolite micropores and acid sites; acidity loss likely due to aluminum leaching and, increase of palladium particle size. Thus, further studies on catalyst stability will be key to assess scalability of this process.

Experiments were carried out in a modular Swagelok \( \frac{3}{4}'' \) 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. To enable operation in flow, \( \beta \)-zeolites was calcined at 550 °C for five hours, 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.

For the one-step experiments, the first reactor contained 1 g of biomass particles and the second one contained the 2 g of \( \beta \)-zeolite, 9:1 EtOH/H\(_2\)O v/v was used as solvent at 220 °C, 50 bar of pressure and a liquid flowrate of 0.5 mL min\(^{-1}\) was employed. For the two-step experiments only one tubular reactor was used for each step, where 1 g of birch wood sawdust was fractionated for a total time on stream of 3 hours, leading to a total volume of 90 mL of delignification liquor containing solubilized lignin and polysaccharide oligomers. The delignification liquor was stored in a closed transparent glass container at room temperature. In the second step, the resulting delignification liquor was subjected to a catalytic treatment with a flowrate of 0.5 mL min\(^{-1}\) in a packed bed with 2 g of \( \beta \)-zeolite prepared in the same way as in the 1-step process approach. Palladium was deposited on the different types of \( \beta \)-zeolite through ion exchange following the experimental procedures reported elsewhere,\(^{[59,60]} \) leading to a supported catalyst with a palladium loading of 1 wt.%. ICP-AES was used to determine the Pd loading in the synthesized catalyst.

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.\(^{[19]} \) For further lignin analysis, solvent removal was performed at 75 mbar and 40 °C, followed by a liquid-liquid extraction with ethyl acetate/water 3×10 mL and subsequent solvent evaporation under vacuum, leading to lignin oil. The resulting lignin oil was dissolved in DMSO-d\(_6\) to a concentration of 70 mg oil mL\(^{-1}\) for subsequent 2D HSQC NMR analysis.

Spent catalysts were collected after reaction and dried overnight at 105 °C. Ammonia temperature programmed desorption (NH\(_3\)-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 zeolites. Nitrogen physisorption at 77 K was employed to study the microstructure of zeolite samples. Transmission electron microscopy (TEM) was used to determine Pd dispersion in the supported catalyst.

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

**Conflict of Interests**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.
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