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Zeolite-assisted lignin-first fractionation of lignocellulose: Overcoming lignin recondensation via shape-selective catalysis

Elena Subbotina^[b], Alexandra Velty^[a], Joseph S. M. Samec^{*[b]} and Avelino Corma^{*[a]}

Abstract: Organosolv pulping releases reactive monomers from both lignin and hemicellulose via the cleavage of weak C–O bonds. These monomers recombine to form undesired polymers through the formation of recalcitrant C–C bonds. Different strategies have been developed to prevent this process by stabilising the reactive monomers (i.e., lignin-first approaches). To date, all reported approaches rely on the addition of capping agents or metal-catalysed stabilisation reactions, which usually require high pressures of hydrogen gas. Herein, we report a metal- and additive-free approach that uses zeolites as acid catalysts to convert the reactive monomers into more stable derivatives under organosolv pulping conditions. Experiments with model lignin compounds showed that the recondensation of aldehydes and allylic alcohols produced by the cleavage of β -O-4' bonds was efficiently inhibited by the use of protonic BETA zeolite. By applying a zeolite with a preferred pore size, the bimolecular reactions of reactive monomers were effectively inhibited, resulting in stable and valuable monophenolics. The developed methodology was further extended to birch wood to yield monophenolic compounds and value-added products from carbohydrates.

Introduction

Lignocellulose is the most available source of biomass. Unlike crude oil, which is the most utilised source for the production of chemicals and fuels, biomass is renewable and carbon neutral. Thus, the development of methods for biomass valorisation into platform chemicals or fuel precursors is of high importance. Lignocellulose comprises three main components: lignin, cellulose, and hemicellulose. Lignin is an aromatic heteropolymer that is linked together via C–C and C–O bonds and is mainly derived from three monolignols: coniferyl, *p*-coumaryl, and sinapyl alcohols. Hemicellulose and cellulose are polysaccharides with different structural properties. Cellulose is a regular crystalline polymer consisting of glucose, while hemicellulose is an irregular amorphous polymer comprising C-5 and C-6 sugars. To utilise lignocellulose in the most efficient way, it is desirable to simultaneously transform all three of its components into value-added products. Given the dissimilarity between the structures of cellulose, hemicellulose, and lignin along with the fact that they are crosslinked with each other through covalent bonds, it is challenging to transform all three

components in a single process. As a result, the pulping industry currently only utilises the cellulose fibres.

Acid-catalysed pulping is a promising approach for the catalytic fractionation of biomass since potentially all three components can be transformed into valuable monomeric products.^[1] The main drawback of this approach is the formation of reactive intermediates during the depolymerisation of lignin; these intermediates then react to form dimeric, oligomeric, and polymeric byproducts via C–C bond formation^[2] (Figure 1). To avoid the repolymerisation of lignin during acid-catalysed pulping, Luterbacher and co-workers developed an approach in which lignin with a native structure is isolated.^[3] This was achieved by the addition of formaldehyde, which resulted in the formation of an acetal structure with the 1,3-diols of lignin and prevented the formation of reactive benzylic carbocations. The isolated lignin acetal could then be further converted into monomeric products via hydrogenolysis. Barta and co-workers reported another approach that circumvented the repolymerisation of lignin by stabilising the reactive aldehydes via their transformation into acetals upon the addition of ethyleneglycol (Figure 1B).^[4] Acetal formation with methanol has also been reported.^[5] The Rh-catalysed *in situ* decarbonylation of reactive aldehydes formed during the triflate-catalysed cleavage of lignin was recently reported by Bruijninx and co-workers (Figure 1B).^[6] All the strategies mentioned above require a metal or a stoichiometric amount of capping agent and mainly focus on the conversion of lignin. Thus, the lack of a simple and additive-free process allowing the simultaneous conversion of the three components of lignocellulose motivated us to seek an alternative approach.

Regarding cellulose and hemicellulose valorisation, various studies have reported the conversion of cellulose, xylose, and glucose into furfural, 5-hydroxymethylfurfural (5-HMF), and levulinic acid. Furfural is industrially produced from lignocellulosic biomass in the presence of sulphuric acid via the hydrolysis and dehydration of pentoses.^[7] The production of furfural has several drawbacks related to the use of homogeneous acids, including corrosion and the production of a large amount of humins. Thus, optimising cellulose conversion and furfural production continues to be of great interest.

Recently, the release of a substantial amount of monophenolic compounds (allylic alcohols) from lignin during organosolv pulping due to the cleavage of ether linkages was reported, even in the absence of a transition metal catalyst (Scheme 1).^[8] However, the released monomers are not stable under pulping conditions and thus condense to form new polymers through C–C bonds. As a result, the main role of the catalyst in a lignin-first approach is to convert the released allylic alcohols into stable monomers to avoid recondensation. Most commonly, transition metals and hydrogen gas are used to produce reduced and thus stable monomers.^[8c]

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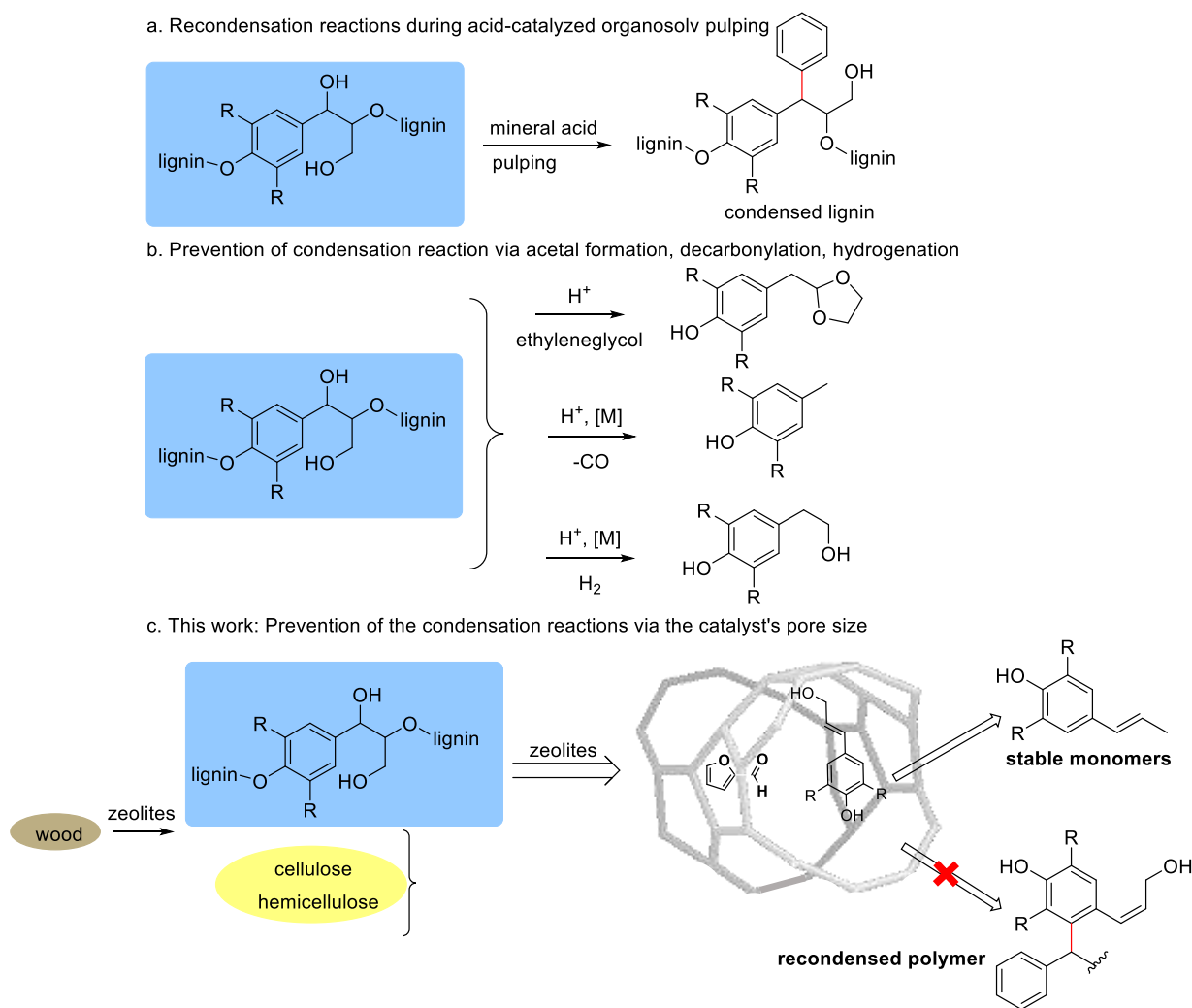
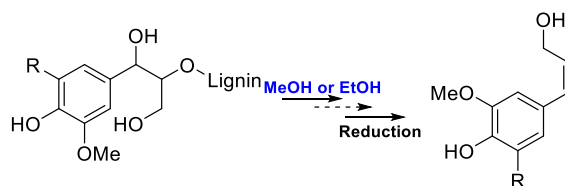


Figure 1. A. Recondensation reactions during acid-catalysed pulping. B. Prevention of recondensation reactions of C-2 aldehydes during the pulping of biomass (previous reports). C. This work: prevention of condensation reactions by diffusion control based on the size and topology of the zeolite pores.

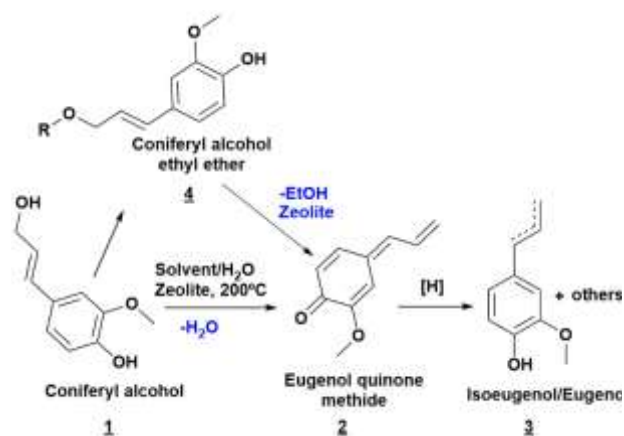
Considering all the above aspects, we decided to take advantage of the catalytic properties of protonic zeolites during the organosolv pulping of lignocellulose to stabilise the monomers released from all components (cellulose/hemicellulose and lignin). Zeolites are porous systems with high surface areas and shape/size selectivity along with the ability to accommodate different metals in their frameworks, resulting in acid/base or redox properties. The substitution of aluminium for silicon in a silica covalent framework induces a charge imbalance that must be compensated by a cation. When this cation is an ammonium ion, its thermal decomposition generates a proton as a compensatory cation, thereby producing a protonic zeolite with

strong Brønsted acid sites. Moreover, the thermal stability of zeolites allows them to be readily reused.

Therefore, we envisioned protonic zeolites as good candidates to convert the released allylic alcohols and products derived from sugars into stable products via elimination, reduction, and isomerisation reactions. Furthermore that zeolites might be able to lower the rate of bimolecular condensations of allylic alcohols by pore size constraints and diffusion control,^[9] eliminating the need for trapping agents and transition metals. In this study, we performed model studies and organosolv pulping of birch wood in the presence of zeolites. The lignocellulosic feedstock underwent solvolytic depolymerisation and released reactive allylic alcohols,



Scheme 1. Release of allylic alcohols during the organosolv pulping of lignocellulose.



Scheme 2. Scheme of the reaction of conferyl alcohol **1** under organosolv pulping conditions in the presence of BETA-1 zeolite.

which were transformed inside the pores of zeolites at Brønsted acid active sites into stable monophenolic products. Moreover, hemicellulose and cellulose were transformed into furfural, levulinic acid, 5-HMF, and their derivatives. The proposed strategy represents a new type of lignin-first approach in which the stabilisation of monomers derived from the pulping of biomass occurs via shape-selective catalysis.

Results and discussion

A) Study on lignin model compounds

During the organosolv pulping of lignocellulose, the depolymerisation of lignin releases lignin fragments and allylic alcohols. Conferyl and sinapyl alcohols are the two main monomers obtained from the solvolytic cleavage of hardwood lignin. Along with the reactivity of allyl alcohol, conferyl has an additional site of reactivity for recondensation in the 5 position of the aromatic ring; thus, it is more prone to form new C–C bonds. To investigate the reactivity of released allylic alcohols during the organosolv pulping of lignocellulose in the presence of zeolites with Brønsted acid sites, we studied the reactivity of the most reactive allylic alcohol (i.e., conferyl alcohol **1**). Two commercial zeolites with Si/Al ratios of approximately 12–13 (BETA and HY zeolites) were selected. Both of these zeolites offer large pore structures that allow the diffusion of large molecules. However,

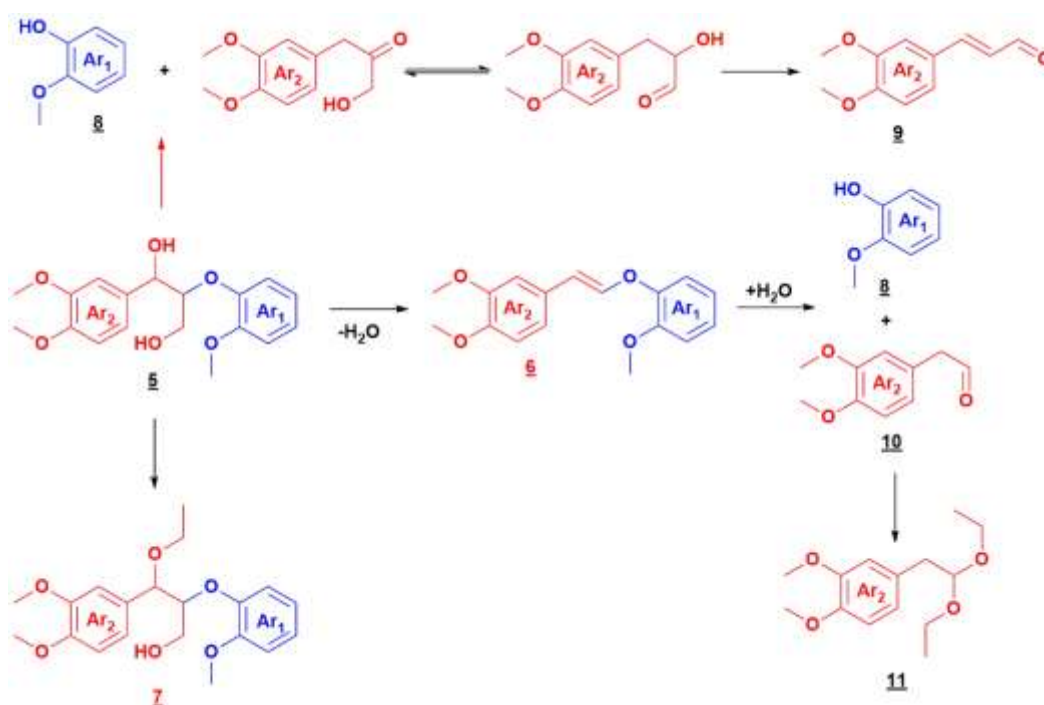
there is one important structural difference; large cavities are present in HY zeolite but absent in BETA zeolite. The presence of cavities in HY zeolite promotes bimolecular reactions and stabilises voluminous transition states. BETA zeolite has a tridirectional pore structure constituted by two large pores systems without cavities. One type of the pore system consists of straight 12-membered ring channels with a free aperture of 6.6×6.7 Å along the [100] axis. The second pore system consists of zigzag 12-membered ring channels with dimensions of 5.6×5.6 Å along the [001] axis. Ultrastable HY zeolite has a tridirectional, large pore structure consisting of sodalite cages (supercages) connected through hexagonal prisms. The pores are formed by 12-membered rings with free apertures of 7.4 Å. The characterisation and preparation of the samples are described in the supporting information (SI).

When conferyl alcohol **1** was subjected to organosolv pulping conditions at 200°C in EtOH/H₂O mixed solvent and in the presence of BETA-1 zeolite, quinone methide **2** and reduced products **3** (*cis*- and *trans*-isoeugenol and eugenol) were the main products obtained (78% total monomer yield; Scheme 2; Table 1, entry 1; Table S8; Scheme S1). When conferyl alcohol was treated under the same reaction conditions but without zeolite, the main product was conferyl alcohol ethyl ether (**4**), which was obtained in 40% yield (Table S8, Entry 10). However, when the reaction was performed in the presence of homogeneous mineral acid (HCl), only traces of monomers were detected, and the reaction vessel was corroded (Table S8, Entry 9). These results show that zeolite was able to stabilise the allyl alcohol **1** through reductive dehydration and isomerisation. To determine the reducing agent, the effects of several solvents and additives on the yield and composition of products were evaluated. The results are reported in Table 1 (entries 1–3). Interestingly, a high ratio of **2** to **3** (2.6) was obtained when MeOH (poor hydride donor) was used as a solvent. The use of EtOH as solvent resulted in a ratio of 0.3. When using *i*-PrOH (strong hydride donor), product **3** was formed in 70% yield, while no product **2** was detected. During the pulping process of lignocellulose, sugars and formic acid are released. Since these compounds are known to act as reducing agents, the reactivity of allyl alcohol **1** was also studied in the

Table 1. Catalytic conversion of conferyl alcohol **1** over zeolites.

Entry	Catalyst	Solvent/additive, mL (mg)	Yield of 2 , %	Yield of 3 , %	Total yield of monomers, %
1	BETA-1	EtOH/H ₂ O (4.5/0.3)	16	57	78
2	BETA-1	MeOH/H ₂ O (4.5/0.3)	18	7	29
3	BETA-1	<i>i</i> PrOH/H ₂ O (4.5/0.3)	0	70	80
4	BETA-1	EtOH/H ₂ O/HCOOH (4.5/0.3/0.1)	15	42	61
5	BETA-1	EtOH/H ₂ O/xylose (4.5/0.3/10)	13	46	62
6	HY-2	EtOH/H ₂ O (4.5/0.3)	0	23	28
7	HY-3	EtOH/H ₂ O (4.5/0.3)	0	20	22
8	HY-1	EtOH/H ₂ O (4.5/0.3)	0	16	25

Reaction conditions: 20 mg catalyst, 6 mg model compound **1**, *t* = 0.5 hours, *T* = 200°C. BETA-1 (Beta zeolite, Si/Al = 12.5), HY-1 (Y zeolite, Si/Al = 15), HY-2 (Y zeolite, Si/Al = 20), HY-3 (Y zeolite, Si/Al = 30).



Scheme 3. Scheme for the β -O-4' cleavage of model dimer under organosolv pulping conditions

presence of xylose and formic acid. However, the yields of products **2** and **3** were similar to those obtained in the absence of xylose and formic acid (Table 1, entries 4 and 5). Based on the abovementioned results, we can conclude that the solvent acts as a reducing agent under the applied reaction conditions. When the reaction was performed for a longer time in isopropanol, no decrease in monomer yield was observed (SI, Figure S6b). A slight decrease in monomer yield was observed in the case of ethanol (SI, Figure S6a), which can be attributed to the slower conversion of quinone methide **2** into the products **3** and its participation in side reactions. These results show that BETA zeolite possesses adequate catalytic properties for the conversion of coniferyl alcohol into quinone methide and propenyl phenol derivatives.

When coniferyl alcohol **1** was subjected to organosolv pulping conditions in the presence of HY zeolite, the total yield of monomers was much lower. This can be attributed to the recondensation reactions that can occur with less steric limitation within the large cavities of HY zeolite (Table 1, Entries 6–8).

Lignin is a polymeric molecule consisting of three monolignols that couple to each other to form C–O linkages (mostly α -O-4', β -O-4', and 4-O-5') and C–C linkages (e.g., 5-5', β -1, β -5', and β - β'). The etheric β -O-4' linkage is the dominant linkage and accounts for up to 60% of total linkages in hardwood. Since C–O ether bonds are significantly weaker than C–C bonds, the β -O-4' linkage is a model linkage that is commonly studied in the investigation of lignin depolymerisation. During organosolv pulping, fragments of lignin can be released in the form of oligomers and dimers. Thus,

Table 2. Catalytic results obtained for the β -O-4' cleavage of model dimer **5** in the presence of BETA-1 zeolite.

Solvent	Conv. %	2 , %	3 , %	10 , %	11 , %	6 , %	7 , %	Sum, %		Balance, %	
								(2)	(3 + 10 + 11)	Ar ₁ (2 + 6 + 7)	Ar ₂ (3 + 10 + 11 + 6 + 7)
Dioxane	100.0	57.8	8.9	13.9	0.1	25.7	0.0	57.8	22.9	83.4	48.6
Dioxane ^b	5.0	0.8	0.0	0.0	0.0	0.4	0.0	0.8	0.0	96.3	95.4
ACN	73.2	34.8	1.7	13.1	0.0	28.0	0.0	34.8	14.8	89.6	69.6
ACN ^b	2.1	1.2	0.0	0.0	0.0	0.5	0.0	1.2	0.0	99.6	98.4
Ethanol	93.4	27.8	8.3	5.6	2.0	4.2	50.0	27.8	15.9	88.6	76.7
Ethanol ^b	94.3	33.5	9.7	2.4	2.4	2.0	43.8	33.5	14.5	85	65.9
Ethanol ^{a, b}	3.7	2.3	0.0	0.0	0.0	0.8	0.4	2.3	0.0	99.8	97.5
IPA*	92.1	37.0	12.9	4.0	0.2	4.6	30.5	37.0	17.2	79.9	60.1
IPA ^{a, b}	4.4	0.8	0.0	0.0	0.0	0.4	0.0	0.8	0.0	96.7	96.0

Reaction conditions: 16.5 mg BETA-1 (Si/Al = 12.5), 60 mg model compound **5**, 2 mL solvent, 40 mg water, reaction time = 2 h, temperature = 200°C, dodecane used as a standard. ^a 180°C for 3 h. ^b Without catalyst. Balances for **Ar**₁ and **Ar**₂ correspond to the total yields of products containing **Ar**₁ and **Ar**₂, respectively.

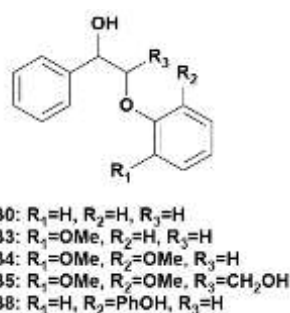
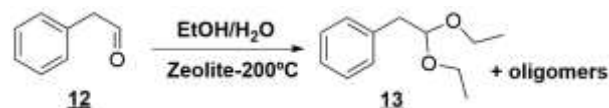


Figure 2. Model compounds.

herein, we studied the reactivity of protonic BETA zeolite towards the cleavage of the β -O-4' bond. The 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol substrate **5** was used as an advanced lignin dimer model (Scheme 3) to study ether cleavage under organosolv pulping conditions in different solvents and in the presence of BETA zeolites. Products **8–11** were obtained from the cleavage of the β -O-4' bond of model compound **5**, providing evidence that BETA zeolite enables the acidolysis of the β -O-4' ether linkage (Table 2). However, the products of β -O-4' cleavage were obtained in low to moderate yields, and a substantial amount of dimer (**5**, **6**, and **7**) was detected in the reaction mixture. In order to evaluate the influence of the steric factors on the transformation, the acidolysis of simplified dimers with different sizes and steric hindrance in the presence of BETA-1 zeolite were also studied (Tables S11 and S12, Figure 2). The absence of any substituents on one of the aromatic rings allows to eliminate electronic factors and thus enables us to study the difference in the reactivity of the model compounds induced only by steric effects. The results show that the acidolysis of dimer compounds with controlled molecular size (**33**, **34**, and **35**) can be successfully carried out in the presence of BETA-1 zeolite, matching the reaction conditions for each dimer. Nevertheless, in the case of the bulky dimer **38**, only dehydration was observed (Figure 2). The results of the reaction with dimer **30** in the presence of two different zeolites with similar acidity but different pore sizes [Beta (12-R pores) and ZSM-5 zeolite (10-R pores)] indicate that acidolysis cannot take place in the presence of ZSM-5 zeolite (Table S11). In the case of ZSM-5 zeolite, the smaller pore size prevented the model substrate **30** from diffusing inside the pores. This indicates that the acidolysis of the β -O-4' linkage occurs inside the pore system of the catalyst and cannot occur on the surface. Therefore, we assume that steric factors and the control of diffusion inside the pores contribute to the lower rate of conversion of dimer **5** in comparison to allylic alcohol **1**. Furthermore, we conclude that the main pathway for the formation of monomers must be the homolysis of β -O-4' bond and the stabilisation of released monomers in the pores of zeolite. Considering that C2-aldehydes (e.g., product **9**) are very reactive toward self-condensation, the stability of phenylacetaldehyde under organosolv pulping conditions was studied. Phenylacetaldehyde that is readily available, very reactive, and without steric impediment was chosen as a model substrate. Reactions were conducted with different concentrations of phenylacetaldehyde and substrate/catalyst ratios to compare the rates of aldehyde self-condensation in the presence of BETA and HY zeolites. When the yield of C2-aldehyde was plotted against reaction time (Figure 3, Scheme 4, Tables S9 and S10) in the presence of BETA-1 and HY-1 zeolites, a constant decrease in yield with reaction time was observed regardless of the reaction conditions. Recondensation reactions proceeded at a much



Scheme 4. Scheme of the reaction of phenylacetaldehyde in the presence of zeolite.

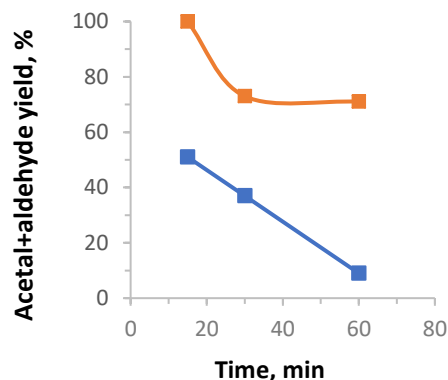


Figure 3. Phenylacetaldehyde (**12**) and phenylacetaldehyde diethylacetal (**13**) yields plotted as a function of time when **12** was subjected to organosolv pulping conditions in the presence of BETA-1 and HY-1 zeolites. ■ BETA-1 (catalyst/substrate = 11, substrate 1.1 mg/mL), ■ HY-1 (catalyst/substrate = 11, substrate 1.1 mg/mL).

higher rate in the presence of HY zeolite compared to BETA zeolite. These results show that the zeolite topology and pore size can control and minimise the recondensation reactions, which take place inside the pores. The pore structure of BETA-1 zeolite does not have cavities like the structure of HY zeolite; thus, the reaction in the presence of BETA-1 zeolite results in a lower oligomerisation rate of phenylacetaldehyde.

The acidolysis of different dimeric models showed that the acidolysis process takes place inside the pores of the catalyst and is controlled by steric factors and diffusion. The results obtained with bulky dimer **38** revealed that BETA-1 cannot catalyse the acidolysis of large lignin fragments (polymeric or oligomeric). The results with model **5** showed that the cleavage of dimeric lignin fragments occurs to a limited extent. The results of monomeric model **1** showed that the system of pores in zeolite can hinder bimolecular condensation due to steric factors, and that BETA zeolite is a good candidate to stabilise allylic alcohols released from organosolv pulping in the presence of a reducing agent such as ethanol or isopropanol.

B) Study of birch wood

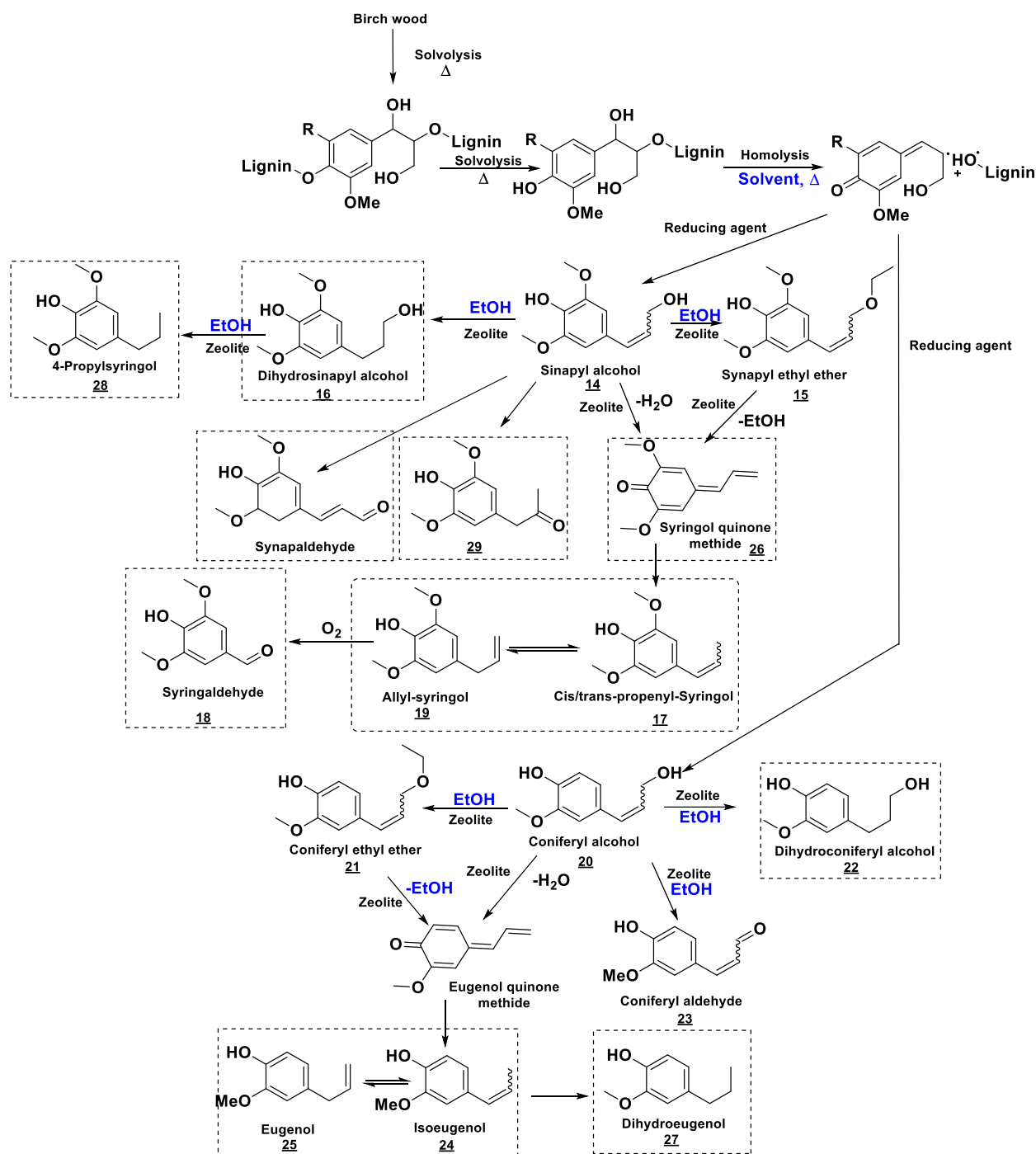
As mentioned above, during organosolv pulping, the β -O-4' bonds in lignin are reductively cleaved to a large extent by solvolysis. The released monomers mostly comprise allylic alcohols. Reactions with model compounds demonstrated that those molecules can be transformed into stable monomers inside the pores of zeolites. Reactions with carbohydrate model compounds (cellulose, xylose, and glucose; Table S5) demonstrated that the products of sugar dehydration are formed in the presence of zeolites, in agreement with previous reports.^[10] Thus, we envisioned that different platform molecules might be obtained in one single process from all three components of biomass if the organosolv pulping of lignocellulose was performed in the presence of protonic BETA zeolite. To investigate the feasibility of the method, we selected birch wood as a biomass source. Birch wood was treated under depolymerisation conditions in ethanol/water (9:1 v/v) at temperatures between 180°C and

220°C in the presence of BETA-1 zeolite.

After the reaction, the crude mixture was filtered and concentrated under vacuum. The bio-oil was then extracted with EtOAc/H₂O to separate the monophenolic compounds from the products derived from the carbohydrates. Various syringyl and coniferyl derivatives from lignin were obtained, as described in Scheme 5. The structures of the main products (14–29) support the hypothesis in which the major pathway for lignin depolymerisation is lignin solvolysis and the release of allylic alcohols. These allylic alcohols are converted at a later stage inside the pores of the zeolite into stable products via elimination, reduction, and isomerisation reactions.

Furfural, ethylfurfural, ethyl-levulinate, levulinic acid, and ethyl

ether of 5-HMF along with small amounts of ethyl glucosides were the main products derived from carbohydrates (Scheme 6). Under the optimised reaction conditions, the yield of quantified aromatic monomers from lignin was calculated to be 20 wt% (21 Cmol%), accounting for the lignin content (Table 3). This corresponds to 44% of the theoretical maximum yield, demonstrating that the developed methodology is applicable to biomass and has advantages over previously reported methods for acid-catalysed pulping, which produced monomer yields ranging from 2 to 10 wt%.^[4a, 6] Although the reaction with model compound **1** resulted in a higher yield of monomers in isopropanol, when the reaction with birch wood was performed in isopropanol, no improvement in monomer yield was observed. We assume that due to the slow

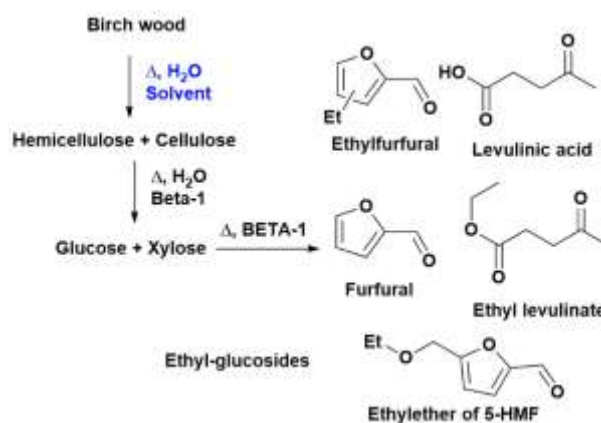


Scheme 5. Proposed scheme for lignin depolymerisation and allyl alcohol conversion and stabilisation in the presence of BETA-1 zeolite.

Table 3. Yields of lignin monomers and furfural from the organosolv pulping of birch wood in the presence of BETA-1 zeolite.

Entry	Catalyst	T, °C	Yield (14–29), wt%	Furfural-ethylfurfural, wt%
1	BETA-1	180	4.4	2.4
2	BETA-1	200	7.9	12.7
3 ^a	BETA-1	200	13.1	10.5
4	BETA-1	220	16.9	9.4
5 ^b	BETA-1	200	4.5	6.1
6 ^c	BETA-1	200	6.3	14.3
7 ^d	BETA-1	220	20	16.5
8 ^{a,e}	BETA-1	220	17.8	-

Reaction conditions: 50 mg catalyst, 200 mg wood, 4.5 mL EtOH, 0.5 mL H₂O, *t* = 2 h. Yield calculated as: mass of products/mass of lignin, and mass of furfural/mass of (cellulose + hemicellulose). ^a 100 mg wood, 25 mg catalyst. ^b 4.75 mL EtOH, 0.25 mL H₂O. ^c 4 mL EtOH, 1 mL H₂O. ^d 100 mg wood, 25 mg catalyst. ^e i-PrOH.



Scheme 6. Hemicellulose and cellulose depolymerisation in the presence of BETA-1 zeolite.

release of allylic alcohols during the organosolv pulping of wood, the released monomers can be converted into stable products at a sufficient rate in ethanol. The yield of furfural/ethylfurfural was 52 mol%, accounting for the hemicellulose content. The combined yield of ethyl-levulinate, levulinic acid, and the ethyl ether of 5-HMF was 21 mol%, accounting for the cellulose content, in

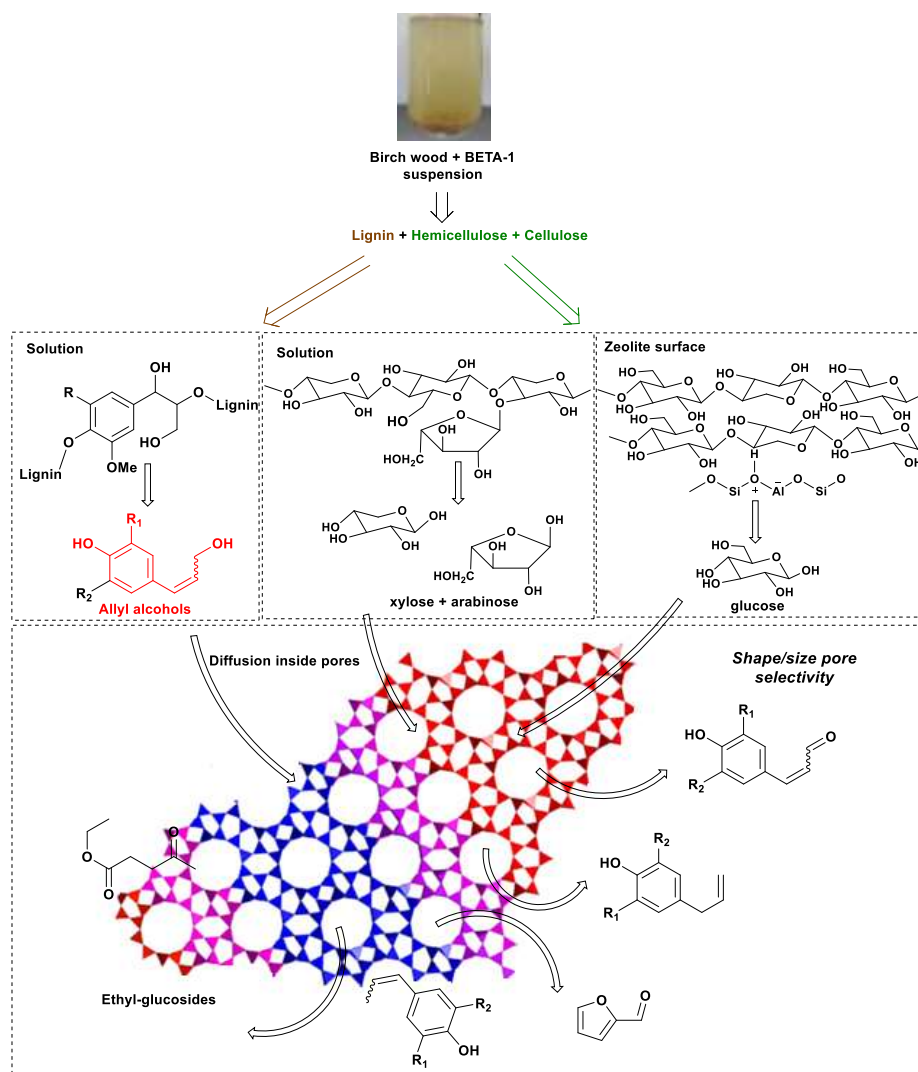


Figure 4. Schematic representation of the locations of the transformation of biomass components during zeolite-catalysed pulping.

addition to 55 mol% of solid pulp. The total yield of value-added products derived from the carbohydrate part of wood was 27 wt% (35 mol%), accounting for the contents of cellulose and hemicellulose (SI, Table S6). Given that the designed process does not require any pretreatment of biomass, the obtained yields of carbohydrate-derived products are satisfying. Reaction in the absence of the BETA zeolite catalyst at 220°C resulted in formation of allylic ethers in significantly lower yield (1.2 wt%, Figure S5).

Based on the results with model compounds and birch wood, we propose the following pathway for the overall process (Figure 4). The fractionation of wood begins with the solvolytic cleavage of ether and ester bonds within the lignin–carbohydrate complex (LCC). Oligomeric and polymeric fragments of lignin are released into solution and undergo reductive cleavage facilitated by reducing sugars or solvent, resulting in the formation of allylic alcohols.^[8b] The allylic alcohols diffuse inside the pores of zeolites and are transformed primarily into stable products such as coniferyl and syringyl derivatives (see the experimental results summarised in the Table 3). Ethanol was shown to be a good reducing agent under the developed reaction conditions. From the results given in Table 3, we can conclude that the addition of water is required, presumably to promote the cleavage of LCC. However, excess water might lead to the deactivation of the catalyst or side reactions involving monomers. The optimal ethanol/water ratio was determined to be 9/1 (v/v).

We suggest that the pores of BETA zeolite minimise but do not fully prevent the condensation reactions because these reactions require a transition state with large molecular dimensions to be accommodated and stabilised. We assume that the pore size of the catalyst lowers the probability of the substrate reaching the catalytic centre. Thus, the bimolecular reactions are hindered to a greater extent than the monomolecular reactions.

In the presence of BETA-1, hemicellulose and cellulose are fractionated under the conditions of organosolv pulping into C-5 and C-6 sugars, which are primarily transformed into furfural, ethylfurfural, the ethyl ether of 5-HMF, levulinic acid, and ethyllevulinate. While glucose is well known to form predominantly 5-HMF under acidic conditions, BETA-zeolites were recently reported to convert glucose into furfural via retro-aldol reaction with good selectivity.^[10] In this case, the solvent plays a crucial role in the selectivity of this process. In the present study, the best yield of furfural was achieved in dioxane, in agreement with past reports, while other products (LA, 5-HMF, etc.) were formed in larger quantities when ethanol was used as the solvent (SI, Table S5).

Conclusion

The current work demonstrates a novel approach for minimising recondensation reactions during the zeolite-assisted pulping of biomass. The approach is based on tuning the pore size of the zeolite to hinder bimolecular condensation and favour monomolecular reactions. This additive-free and transition metal-free methodology was successfully applied to woody biomass. Studies with model compounds revealed that the reaction pathway involves the reductive dehydration (elimination) of allylic alcohols inside the zeolite pores. The monomer yield (20 wt%) was superior to those previously reported for the acid-catalysed pulping of wood in the absence of metals (2–10 wt%).^[4a, 6] In our developed process, hemicellulose and cellulose are simultaneously depolymerised, and the released carbohydrates are transformed into platform chemicals over the acid active sites

of the zeolite. The findings enable further development of novel catalytic fractionation methodologies based on inexpensive acid catalysis. Ongoing work is focused on optimising the reaction system and the reaction conditions to maximise the yields of monophenolic compounds and carbohydrate derivatives.

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