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Lewis acid-catalyzed depolymerization of soda lignin in supercritical ethanol/water mixtures



Burcu Güvenatam^a, Erik H.J. Heeres^b, Evgeny A. Pidko^{a,c}, Emiel J.M. Hensen^{a,*}

^a Laboratory of Inorganic Materials Chemistry, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Institute for Technology and Management, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

^c Institute for Complex Molecular Systems, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT

The depolymerization of lignin model compounds and soda lignin by super Lewis acidic metal triflates has been investigated in a mixture of ethanol and water at 400 °C. The strong Lewis acids convert representative model compounds for the structure-forming linkages in lignin, namely α -O-4, 5-O-4 (C–O–C ether bridge), and α -1 (methylene bridge). Only the 5–5' C–C linkage in biphenyl was unaffected under the given reaction conditions. Full conversion of soda lignin was achieved without char formation. Lignin was converted into a wide range of aliphatic and aromatic hydrocarbons. Ethanol was involved in the alkylation of the lignin depolymerization products. These alkylation reactions increased the product yield by inhibiting repolymerization of the products. The resulting organic phase consisted of aliphatic hydrocarbons (paraffins and olefins), aromatic hydrocarbons (extensively alkylated non-oxygenated mono-aromatics, mainly alkylbenzenes as well as mono-aromatic oxygenates, mainly phenolics), condensation products (mainly naphthalenes) and saturated oxygenates (ketones and carboxylic acids). Although complete product analysis was not possible, the data suggest that the dominant fraction of lignin was converted into monomeric units with a small fraction with molecular weights up to 650 g/mol.

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1. Introduction

Lignin is one of the main constituents of abundant lignocellulosic biomass. This cheap and renewable feedstock has the potential to serve as a source of hydrocarbons for the production of liquid fuels and chemicals [1,2]. However, efficient conversion of lignin into value-added chemicals is challenging because of the high structural heterogeneity of lignin biopolymers and their recalcitrance to depolymerization.

In addition to conventional routes employing transition metal and Brønsted acid catalysts [3,4], reaction pathways catalyzed by Lewis acids are gaining increasing attention as promising and sustainable alternatives for the efficient depolymerization and deoxygenation of biomass constituents [5–7]. In particular, metal triflates can act as strong water-tolerant Lewis acids [7,8]. They retain substantial Lewis acidity not only in organic solvents but also in water. The use of water instead of organic solvents helps

to realize greener biomass conversion processes. An advantage of triflate catalysts is that $M(OTf)_n$ salts are typically only stable in water below 200 °C [7,8]. On the other hand, in some cases they have successfully been recovered from the reaction mixtures and reused without loss of activity [8]. The review of Kobayashi et al. discusses promising catalytic performance of rare-earth triflates in promoting a wide range of important organic reactions such as nucleophilic addition for C–C bond formation (aldol condensation, allylation, cyanation, Michael addition), cyclization (Diels–Alder reactions) and Friedel–Crafts acylation and alkylation [8]. It has also been reported that La, Ln, Yb and Sc triflates are effective catalysts in the Friedel–Crafts acylation and alkylation of aromatic derivatives using alcohols under mild conditions ($T < 100$ °C) [8,9]. These reactions require the use of an electrophile (e.g. alkyl halides, olefins), an aromatic nucleophile and Lewis or Brønsted acids [9]. The use of $M(OTf)_n$ salts (M = metal) in such processes provided good reaction rates and high selectivity towards the desired products at mild reaction conditions [7,8]. $Al(OTf)_3$ has also been reported to be effective to catalyze epoxide ring opening reactions at room temperature in polar solvents such as ethanol [10].

* Corresponding author. Tel.: +31 40 2475178.

E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).

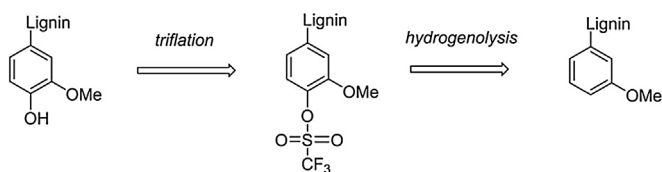


Fig. 1. Conceptual mechanism of triflate-assisted hydrogenolysis of lignin. Adopted from [23].

In previous studies, the use of triflic acid has also been investigated for comparison purposes against metal triflate catalysts. Significant differences have been found between the catalytic performances of metal triflates and triflic acid (TfOH); TfOH was less active for reactions such as Friedel–Craft alkylation, ring-opening of epoxides and cyclization of unsaturated alcohols [9–12].

The choice of the solvent plays an important role in determining the ability of a Lewis acidic salts to depolymerize lignin. In particular, previous studies evidence a very poor performance of metal acetates, chlorides and triflates when lignin upgrading is carried out in supercritical water [13,14]. Reactions in alcohol solvents and, in particular, in ethanol lead to a much deeper lignin depolymerization [13,15,16]. In catalysis by Lewis acids such as $\text{Al}(\text{OTf})_3$, the addition of small amounts of water to the organic solvent can result in significant improvements of the overall performance. For example, $\text{M}(\text{OTf})_n$ -catalyzed organic transformations can proceed via Lewis acid-assisted Brønsted acidity in the presence of water; the Brønsted acidity derives then from water [12]. The co-catalytic role of water likely helps to stabilize cationic intermediates. When water is added to organic solvents, the term “on water” has been frequently used in the literature. We speculate that carrying out biomass conversion reactions in ethanol/water mixtures might provide an alternative for aqueous phase reforming (APR) of biomass derived-products such as ethanol, sorbitol, glucose, glycerol to generate hydrogen and other products, for which also sometimes acidity is required [17,18]. $\text{M}(\text{OTf})_n$ salts are potential catalysts for such reactions. Previous studies evidence a beneficial effect of the use of water–ethanol [19–21] and water–methanol [22] media for the conversion of lignin. Besides the enhanced solubility of lignin in water–organic solvent mixtures, [19], such solvent systems effectively suppress char formation compared to the situation when the reactions are carried out in water.

In spite of the potential of the catalytic chemistry of super Lewis acidic metal triflate salts ($\text{M}(\text{OTf})_n$; $\text{M} = \text{Al}, \text{Cu}, \text{Ni}, \text{Sc}$ etc.) described above, only very few studies have used metal triflates as catalysts for the conversion of lignin. Hu et al. studied the triflate-assisted hydrogenolysis reaction for the hydrodeoxygenation of phenolics as lignin model compounds [23]. Fig. 1 shows that triflation of lignin by triflate anhydride $(\text{CF}_3\text{SO}_2)_2\text{O}$ proceeds in a similar manner as the acetylation of lignin by acetic anhydride. The reaction is promoted by the exchange of the hydroxyl group of phenol by the strongly electron-withdrawing $-\text{OTf}$ group [23,24]. To selectively cleave the resulting aryl– OTf bonds by hydrogen transfer, coordination to Pd^{2+} was required. In this example, triethylammonium formate (HCO_2NH_4) was used as the hydrogen donor. As a result of hydrogenolysis of the aryl– OTf bond, deoxygenated products were obtained. Similar approaches have been applied to the waste from the pulp and paper industry to reduce the strength of paper. This can make hydroxyl sites of cellulose more accessible for further processing [23]. Recently, Yang et al. investigated the catalytic effect of such water-tolerant Lewis acids as indium triflate, scandium triflate, ytterbium triflate, and indium chloride on the hydrolysis of lignin model compounds in aqueous solutions [14]. In the presence of $\text{In}(\text{OTf})_3$ a complete conversion of benzylphenyl

ether was achieved already at 225 °C after 3 h reaction, whereas the hydrolysis of more stable model compounds such as guaiacol and diphenyl ether required much higher reaction temperatures [14].

In this study, we discuss the use of Lewis acid triflate catalysts in ethanol/water solvent mixtures for the depolymerization of lignin. We first evaluated the performance of $\text{Al}(\text{OTf})_3$ for the conversion of model compounds such as phenol, benzyl phenyl ether, diphenyl ether, diphenyl methane and biphenyl in ethanol/water mixtures. We found that ethanol is also converted into a wide range of liquid hydrocarbons products as well as H_2 . With this knowledge, we also examined the conversion of soda lignin by metal triflates. The results of these reactivity studies are compared to those of our earlier study on the use of $\text{M}(\text{OTf})_n$ salts in which ethanol was the solvent [13].

2. Experimental methods

2.1. Materials

De-ionized water and/or absolute ethanol (Sigma–Aldrich, $\geq 99.8\%$) were used as reaction solvents. Aluminum (III) chloride hexahydrate (Fluka, $\geq 99.0\%$), aluminum (III) triflate (Aldrich, 99.9%), copper (II) triflate (Aldrich, 98%), nickel (II) triflate (Aldrich, 96%), scandium (III) triflate (Aldrich, 99%) were used as received. N-decane (Aldrich, anhydrous, $\geq 99\%$) and di-n-butyl ether (Aldrich, anhydrous, 99.3%) were used as external standards during GC analysis. Protobind 1000 lignin, which is obtained from wheat straw by soda pulping, was used as received from GreenValue (Switzerland).

The chemicals were diluted in tetrahydrofuran (Aldrich, anhydrous, $\geq 99.9\%$) 10 times prior to GC \times GC analysis. Chloroform-D (Cambridge Isotope Laboratories Inc, D, 99.8% stabilized with silver foil) was used as a solvent in ^1H - ^{13}C HSQC NMR analysis.

2.2. Catalytic activity measurements

All the experiments were performed in stainless-steel batch reactors with an internal volume of 13 mL. The reactors were filled with either 6.5 mL of anhydrous ethanol or 3.5 mL ethanol/3 mL water. In a typical run, a solution of 0.025 mol/L Lewis acidic salt containing 150 mg lignin was loaded into the reactor. For model experiments, 150 mg of a model compound was used. The reactors were sealed by Swagelok O-rings. The reactors were loaded under ambient atmosphere. The reactions were carried out at 400 °C with a reaction time of 4 h by placing the reactors in a pre-heated fluidized sand bath that allowed for rapid heating to the desired reaction temperature. The estimated autogeneous pressure under the reaction conditions in water–ethanol solvent system was between 375 and 400 bars. In our system, 10 parallel reactions could be run at the same time. After the reaction was completed, the reactors were quenched in an ice bath. After cooling, reactors were opened and the reaction solution was collected. When lignin residue was present, the solids were separated from the liquid products. The liquid phase consisted of two layers: an organic layer and an aqueous layer. The aqueous and organic layers were separated by decantation and separately weighed. Further analyses of the liquid organic phase were carried out by GC/MS-FID, GC \times GC, GPC and MALDI-TOF-MS and ^1H - ^{13}C HSQC NMR analysis methods.

The yields of organic products were calculated as:

$$\begin{aligned} \text{Yield of product}_i(\text{in mg}) &= \text{wt. of organic phase} \\ &\quad \times \text{Conc. of product}_i(\text{calc. from GC} \\ &\quad \times \text{GC – FID}) \end{aligned} \quad (1)$$

The selectivities of organic products were calculated according to:

Selectivity of product_i

$$= \frac{\text{yield of product}_i (\text{calc. from GC} \times \text{GC} - \text{FID})}{\text{total yield of all identified products (calc. from GC} \times \text{GC} - \text{FID})} \times 100 \quad (2)$$

2.3. Product analysis

2.3.1. Gas chromatography (GC) analysis:

For the identification and quantification of the products, GC/MS-FID analyses were performed on a Shimadzu GC/MS-QP2010 SE series. The GC was equipped with a Restek RTX-1701 capillary column (60 × 0.25 mm i.d. and 0.25 μm film thickness). The column flow was split in a 1:10 volume ratio to the MS and FID. The injector temperature was set at 250 °C. The oven temperature was kept at 45 °C for 4 min, followed by heating to 280 °C at a rate of 4 °C/min and then held at 280 °C for 5 min. Identification of products was done using the NIST11 and NIST11s libraries.

For product quantification, GC × GC analysis was performed on a Interscience Trace GC × GC equipped with a cryogenic trap system and two columns: a 30 m × 0.25 mm i.d. and a 0.25 μm film of Rtx-1701 capillary column connected by a meltfit to a 120 cm × 0.15 mm i.d. and a 0.15 μm film Rxi-5Sil MS column. An FID detector was used. A dual jet modulator was applied using carbon dioxide to trap the samples. Helium was used as the carrier gas (continuous flow 0.6 mL/min). The injector temperature and FID temperature were set at 250 °C. The oven temperature was kept at 40 °C for 5 min then heated up to 250 °C at a rate of 3 °C/min. The pressure was set at 0.7 bar at 40 °C. The modulation time was 6 s. Before GC × GC analyses, the organic samples were diluted with tetrahydrofuran (THF); an amount of 1000 ppm di-n-butyl ether (DBE) was added as an external standard.

For gas phase analysis, reactions were conducted in a 100 mL Parr stainless steel stirred high-pressure autoclave. Gaseous products were analyzed by an Interscience Compact GC system. Molsieve 5 Å and Porabond Q columns were coupled with a thermal conductivity detector (TCD) and Al₂O₃/KCl column with a flame ionization detector (FID).

2.3.2. Gel permeation chromatography (GPC) analysis:

GPC analysis was performed on a Shimadzu apparatus equipped with two columns connected in series (Mixed-C and Mixed-D, polymer Laboratories) and a UV/vis detector at 254 nm. The column was calibrated with polystyrene standards. Analyses were carried out at 25 °C using tetrahydrofuran (THF) as eluent at a flow rate of 1 mL/min. Samples were dissolved with the concentration of 2 mg/mL and filtered using a 0.45 mm filter membrane prior to injection.

2.3.3. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF-MS) analysis:

The MALDI-TOF-MS measurements were performed with an Autoflex Speed (Bruker) instrument equipped with a 355 nm Nd:YAG smartbeam laser with maximum repetition rate of 1000 Hz, capable of executing both linear and reflector modes. 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) was used as the matrix. The accelerating voltage was held at 19 kV and the delay time at 130 ns for all experiments. Mass spectra were acquired in the reflector positive ion mode by summing spectra from 500 random laser shots at an acquisition

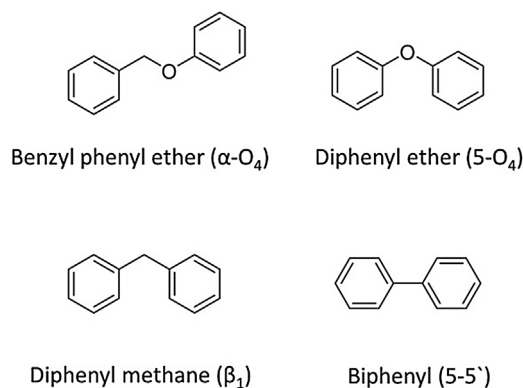


Fig. 2. Model compounds commonly used to represent the main type of linkages present in lignin.

rate of 100 Hz. Samples were dissolved in THF with a concentration of 1.5 mg/mL prior to analysis.

2.3.4. ¹H-¹³C HSQC nuclear magnetic resonance (NMR) spectrometry analysis:

All NMR spectra were recorded using a Varian Inova 500 MHz spectrometer. Approximately 0.3 mL of reaction sample was dissolved in 0.4 mL chloroform-D. ¹H-¹³C HSQC NMR spectra were obtained using the gHSQCAD program. Normally, eight scans, 2 s relaxation delay, and 256 t₁ increments were used. Data processing was performed using the MestReNova software.

3. Results and discussion

3.1. Conversion of model compounds in ethanol/water mixtures

We first studied the conversion of model compounds such as phenol, benzyl phenyl ether (BPE), diphenyl ether (DPE), diphenyl methane (DPM) and biphenyl in the presence of Al(OTf)₃ at 400 °C in the ethanol/water mixtures (Fig. 2). Representative reaction products are summarized in Fig. S1 and they included alkylated benzenes, phenols and diaromatic compounds.

The products detected by GC × GC analysis from a blank experiment to study the conversion of ethanol in the presence of water with the Al(OTf)₃ catalyst (Table 1) included aliphatic hydrocarbons (mainly paraffines and olefins, some cyclics), non-oxygenated mono-aromatics (alkylbenzenes), naphthalenes and saturated mono-oxygenates (ketones and carboxylic acids). We already discussed possible mechanisms of ethanol conversion into these products in our earlier study [13]. Given the wide range of products from ethanol, it was not possible to accurately determine selectivities in the catalytic experiments using the model compounds. Therefore, we limit ourselves to discuss the conversion of the model compound and discuss the products in terms of product classes and differences seen in the GC analyses as compared with the blank experiment.

The monomeric model compound phenol was fully converted. The main products were alkylphenols. This is apparent from the increased selectivity of phenolics compared with the blank experiment. About 70% of phenol was converted into alkylphenols by ring alkylation. Besides ethyl, also propyl, butyl and other sidechains were detected. Di-aromatics and naphthalenes were formed in relatively small amounts and they are formed by condensation reactions. Naphthalenes formation can be due to ring closure reaction of butyl-substituted aromatics. Butyl substituents on the aromatic rings were frequently observed in the product mixture. We also observed alkylbenzenes, alkylated naphthenes (cycloalkanes), and di-aromatics. Their presence shows that deoxygenation

Table 1
Conversion of representative model compounds in the presence of Al(OTf)₃ in ethanol/water mixture at 400 °C (reaction time: 4 h)¹.

Substrate	X (%)	Amount of products (mg)							
		Aliphatics			Aromatics			Mono-aromatic oxygenates	Saturated oxygenates
					Mono-aromatics	Di-aromatics	Naphthalenes	Phenolics	Ketones
Blank ²	–	560	184	–	33	–	–	51	8
Phenol	100	647	109	30	50	109	–	40	10
Benzyl phenyl ether	100	654	146	39	49	59	–	20	10
Diphenyl ether	70	652	113	28	95	19	–	29	10
Diphenyl methane	100	641	126	48	68	68	–	19	–
Biphenyl	58	665	105	86	76	665	Trace	19	Trace

¹75 mg of Al(OTf)₃ and 150 mg of substrate were used in 3.5/3 mL ethanol/water mixture.

²Blank experiment without model compound.

and hydrogenation reactions occur under these reaction conditions. Based on the product distribution, the rate of aromatic ring alkylation was higher than the rates of deoxygenation and hydrogenation. The presence of phenol also seems to have an effect on the conversion of ethanol, as less aromatics and more aliphatics were produced.

BPE was also completely converted under the same conditions. The main products were alkylphenols and alkylbenzenes. The products were similar with the products from phenol. In comparison, less alkylphenols and more mono-aromatics were obtained. This is because the cleavage of the α-O-4 bond in BPE yields phenol and toluene as products [6]. The conversion of DPE was not complete. This is most likely due to the lower reactivity of the 5-O-4 ether bond in DPE as compared to the α-O-4 linkage in BPE [6,13,14]. Compared with phenol and BPE, higher amounts of naphthalenes and lower amounts of alkylphenols were formed during DPE conversion (Table 1). Interestingly, DPM was fully converted to mainly monomeric products and naphthalenes. The cleavage of the α-1 (aryl-aryl) bond in DPM is generally considered to be more difficult than the cleavage of carbon-oxygen bonds. It was previously reported that oxidation of the C-C bond by water helps to cleave this bond [25]. We speculate that in the present experiments this oxidation reaction is co-catalyzed by water. The oxidation of the α-1 bond will facilitate the subsequent hydrogenolysis of the C-C bond. Different from the α-1 type (alkyl-aryl) C-C bond, the rate of the cleavage of the 5-5' (aryl-aryl) C-C bond in biphenyl was negligible under the given reaction conditions. Although the aryl-aryl bond in biphenyl was not cleaved, the biphenyl conversion was substantial due to alkylation of the aromatic rings.

In summary, triflate-assisted hydrogenolysis of lignin model compounds in ethanol/water mixtures at high temperatures resulted in complete cleavage of α-O-4 (aryl-alkyl) type ether and α-1 (aryl-aryl) type C-C bonds, partial conversion of 5-O-4 type ether bonds and no cleavage of 5-5' (aryl-aryl) C-C bonds. Alkylation of the aromatic rings by ethanol was extensive. Under these reaction conditions, ethanol reacts to a wide range of compounds, including mainly aliphatics and some aromatics.

3.2. Lignin conversion by Lewis acid catalysts

Before investigating the conversion of lignin by Lewis acid Al salts, we first compared the conversion of ethanol by Al(OTf)₃ in pure ethanol [13] and the ethanol/water mixture at 400 °C. The reaction mixture was composed of an organic phase and an aqueous phase. The low polarity of the organic phase allowed its separation by decantation. Substantial amounts of water were formed, which is mainly due to the extensive deoxygenation of the products from ethanol conversion.

Table 2 shows that the dominant products in the organic phase were aliphatic hydrocarbons. The aliphatic product fraction contains highly branched hydrocarbons and included paraffins and

olefins. By GC analysis, hydrocarbons with up to 30 carbon atoms were observed. The amount of mono-aromatics in the product mixture was higher in ethanol/water than in pure ethanol (Fig. 3, Table 2). In the presence of water, also naphthalenes were formed. These findings suggest that cyclization reactions catalyzed by the Brønsted acidity from water in the ethanol/water mixture contributed to aromatics formation.

Table 2 also reports the reaction data for the conversion of soda lignin in ethanol [13] and ethanol/water by Al(OTf)₃ under the same reaction conditions. The color of the organic phase was dark, indicating that oligomers were still present. A detailed analysis of the respective higher molecular weight compounds was carried out by using the MALDI-TOF-MS method, for which results are discussed below. In contrast to the experiment in pure ethanol, no solid residue was left after reaction in the ethanol/water mixture. These results point to the high degree of depolymerization of the starting lignin in ethanol/water. As before, it was not possible to

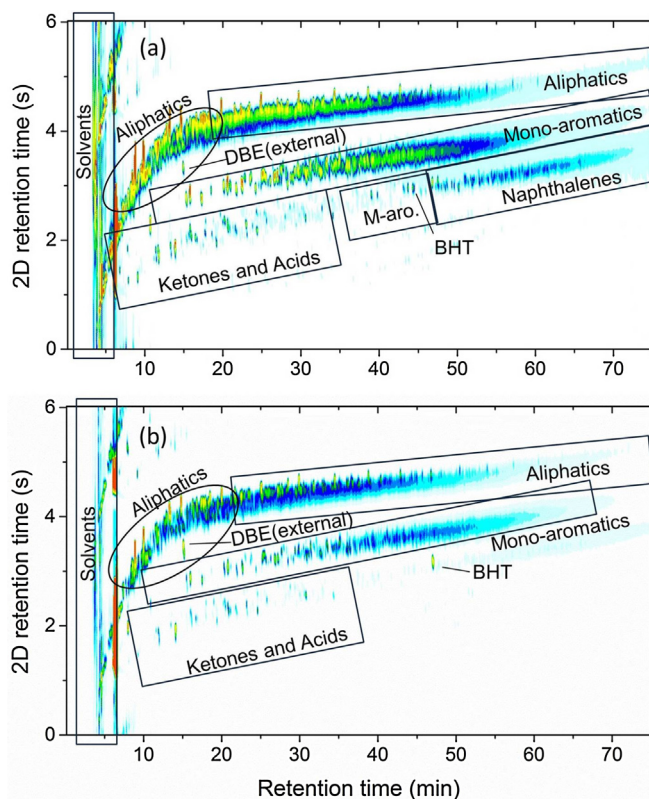


Fig. 3. GC × GC chromatograms of organic phase obtained from Al(OTf)₃-catalyzed conversion of ethanol at 400 °C a) in the presence and b) in the absence of water¹ (reaction time: 4 h).

¹The data is taken from our earlier study (Ref. [13]).

Table 2
Yields of organic products obtained from ethanol and lignin conversion by using Lewis acid Al salts in ethanol and ethanol/water at 400 °C (reaction time: 4 h)¹.

Catalyst	Solvent	Lignin initial weight, mg	Weight of organic products, mg (selectivities, wt.%)										Total yield (from GC), mg	Total weight of organic phase, mg
			Aliphatics			Aromatics		Mono-aromatic oxygenates		Saturated oxygenates		Carboxylic acids		
			Aliphatics	Mono-Aromatics	Naphthalenes	Phenols	Guaiacols	Ketones						
Al(OTf) ₃	Ethanol ²	-	497 (89)	44 (8)	-	-	-	11 (2)	5 (1)	557	633			
Al(OTf) ₃	Ethanol/water	-	560 (67)	184 (22)	33 (4)	-	50 (6)	9 (1)	836	862				
Al(OTf) ₃	Ethanol ²	150	491 (75)	104 (16)	6 (1)	13 (2)	26 (4)	13 (2)	653	710				
Al(OTf) ₃	Ethanol/water	150	697 (67)	187 (18)	52 (5)	21 (2)	52 (5)	21 (2)	1,041	1,122				
AlCl ₃	Ethanol/water	150	239 (57)	148 (34)	8 (2)	8 (2)	17 (4)	4 (1)	424	589				

¹0.025 mol/L of Lewis acidic salt was used in either 6.5 mL of ethanol or ethanol/water (3.5/3 mL ethanol/water) solvent.

²The data is taken from our earlier study (Ref. [13]).

distinguish between the products from lignin depolymerization and ethanol conversion. Comparing the reaction results in pure ethanol with and without lignin, we observe that the amount of monomeric products from lignin is lower than the starting amount of lignin. This is consistent with the observation that solids were left after the reaction in pure ethanol [13]. The reaction products were mainly aromatics and phenols.

In a separate experiment, we carried out a lignin conversion reaction in a larger autoclave and analyzed the gas cap by gas chromatography. In this way, we found that C₂H₆, C₂H₄, CO₂, CO and H₂ were the main gaseous products. The formation of these products shows that reforming reactions of ethanol took place. We expect that hydrogen necessary for lignin depolymerization and deoxygenation reactions were obtained upon reforming reactions of ethanol. In the mini-reactors used for the regular experiments, we could not quantify these gaseous products.

Aqueous phase formed upon the conversion of soda lignin in water-ethanol mixture at 400 °C after 4 h was also analyzed by GC/MS (Fig. S2). The main products found in the aqueous phase were ethylene oxide, carboxylic acids (acetic, propanoic, butanoic, pentanoic acids), acetone, acetaldehyde, ethyl acetate, n-propanol, butanone and n-butanol. These products were formed by the conversion of ethanol [13] and were therefore excluded from the calculations of the total organic yields.

In ethanol-water, the increase in product yield in the presence of lignin was higher than the amount of starting lignin (Table 2). This suggests that lignin depolymerization was complete in this case, consistent with the finding that no solids were left. As will be shown below, oligomers were present in addition to monomers (see below). Notably, when the reaction was carried out in the ethanol-water mixture with AlCl₃ as the catalyst, the product yield was much lower than in the blank and lignin conversion experiments with Al(OTf)₃. This underlines the importance of the triflate anion in lignin and ethanol conversion.

The GC × GC chromatograms of the organic phase obtained from the lignin conversion experiments with AlCl₃ and Al(OTf)₃ catalysts in ethanol-water are shown in Fig. 4. The data clearly point out the higher product yield for the Al(OTf)₃ catalyzed experiment. The dominant products were aliphatics. This fraction also included some naphthenes, which could not be separated from the paraffins and olefins by the GC × GC analysis. All aromatic products were extensively alkylated. The most common aromatic products are shown in Fig. 5. Alkylphenols were the main oxygenated mono-aromatics in the product mixture. Condensation of aromatic monomers, likely due to dehydrogenation and cyclization of alkyl substituted aromatics, resulted in naphthalenes and indanes. These products were also found to be alkylated. Alkylated biphenyls and pyrenes were also detected in small amounts. Also cyclopentane and cyclohexane rings, which were typically alkylated were observed. Small amounts of alkylated saturated mono-oxygenates were also present among the products.

The significant catalytic difference between Al(OTf)₃ and AlCl₃ Lewis acid has been reported before in the context of the cycloisomerization of unsaturated alcohols. In contrast to Al(OTf)₃, AlCl₃ and TfOH were not active in this reaction [11]. Al(OTf)₃ complexes with the alcohol group and not with the C=C double bond of the unsaturated alcohol. This leads to regioselective catalytic activation of unsaturated alcohols by Al(OTf)₃. The term “combined acidic system” [26] refers to the enhancement of the Brønsted acidity of the hydroxyl protons of unsaturated alcohols by Al(OTf)₃. The increased acidity of the hydroxyl protons facilitated the activation of the double bonds relevant to cycloisomerization. As lignin contains oxygen-containing functional groups (carbonyl, ethoxide, ether groups) as well as C=C double bonds, Al(OTf)₃ might facilitate a similar kind of chemistry, activating the linkages within lignin.

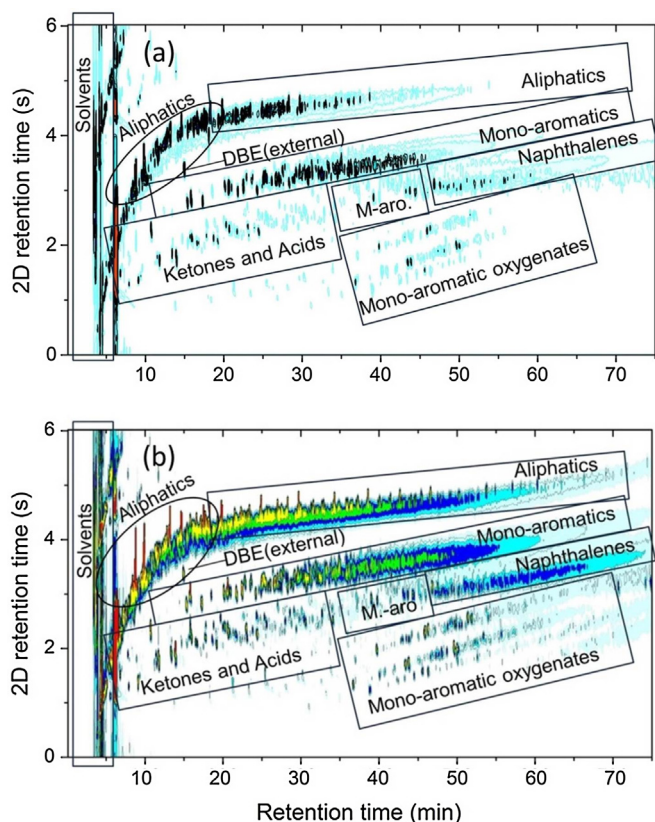


Fig. 4. GC \times GC chromatograms of organic phases obtained from the conversion of 150 mg soda lignin in the ethanol/water mixture at 400 °C in the presence of (a) AlCl_3 and (b) $\text{Al}(\text{OTf})_3$ (reaction time: 4 h).

Besides, this chemistry may also play a role in the conversion of ethanol.

3.3. Influence of catalyst loading

We also investigated the influence of the catalyst loading on the conversion of lignin in ethanol/water mixture using the $\text{Al}(\text{OTf})_3$ catalyst. When relatively small amounts of catalysts were used (8 and 25 mg), solid residue was observed in the reactor; at higher

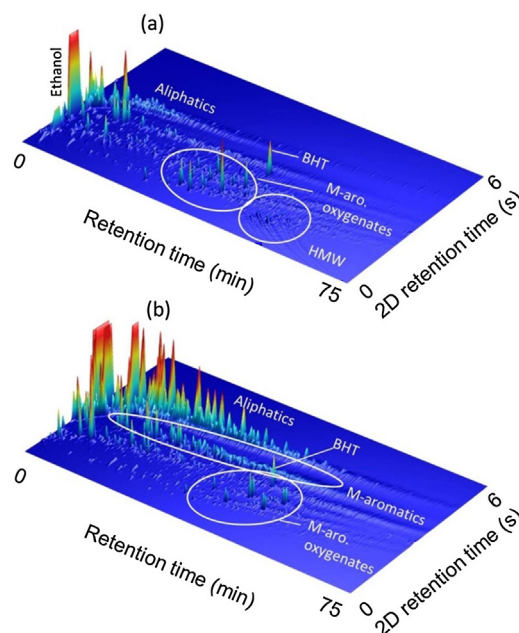


Fig. 6. GC \times GC chromatograms of organic phase obtained from lignin conversion in the presence of a) 8 mg, b) 50 mg of $\text{Al}(\text{OTf})_3$ in ethanol/water at 400 °C (reaction time: 4 h).¹
¹M.-aro.: mono-aromatics, HMW: higher molecular weight products, BHT: butylated hydroxytoluene (used as stabilizer).

catalysts loading (50 and 75 mg), no lignin residue was observed anymore after reaction. Representative GC \times GC chromatograms of the organic phase products from experiments using 8 mg and 50 mg of catalyst are compared in Fig. 6. The total organics yield increased with increasing catalyst loading (Table 3). With 8 mg catalyst, the GC \times GC chromatogram contains peaks due to higher molecular weight products and mono-aromatic oxygenates. With 50 mg catalyst, the contribution of these higher molecular weight products was much lower. The data in Table 3 shows that increasing catalyst loading led to increased yields of aliphatics, mono-aromatics and naphthalenes as well as ketones and carboxylic acids. The yield of phenols and guaiacols were not influenced significantly by the changes in catalyst loading.

Fig. 7a compares the gel permeation chromatograms (GPC) of the organic phases obtained in ethanol–water at different

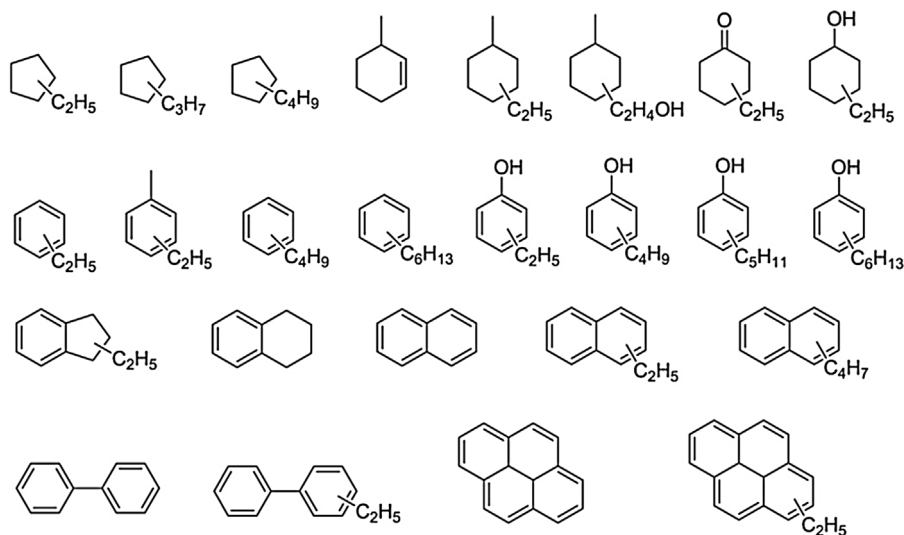


Fig. 5. Representative structures obtained from lignin conversion in the presence of metal triflate salts in the ethanol/water mixture at 400 °C (reaction time: 4 h).

Table 3
Effect of catalyst loading on the yields of organic products obtained from lignin conversion in the presence of Al(OTf)₃ in ethanol/water at 400 °C (reaction time of 4 h)¹.

Lignin weight, mg	Catalyst weight, mg	Weight of organic products, mg (selectivities, wt.%)								Total yield, mg
		Aliphatics	Aromatics		Mono-aromatic oxygenates		Saturated oxygenates			
			Mono-aromatics	Naphthalenes	Phenols	Guaiacols	Ketones	Carboxylic acids		
150	75	697 (67)	187 (18)	52 (5)	21 (2)	11 (1)	52 (5)	21 (2)	1,041	
150	50	577 (70)	150 (18)	43 (5)	16 (2)	7 (1)	33 (4)	4 (<1)	830	
150	25	482 (79)	63 (10)	21 (3)	21 (3)	6 (1)	19 (3)	Trace	612	
150	8	48 (43)	14 (13)	6 (5)	21 (19)	7 (6)	16 (14)	Trace	112	

¹Experiments were carried out in 3.5/3 mL ethanol/water mixture.

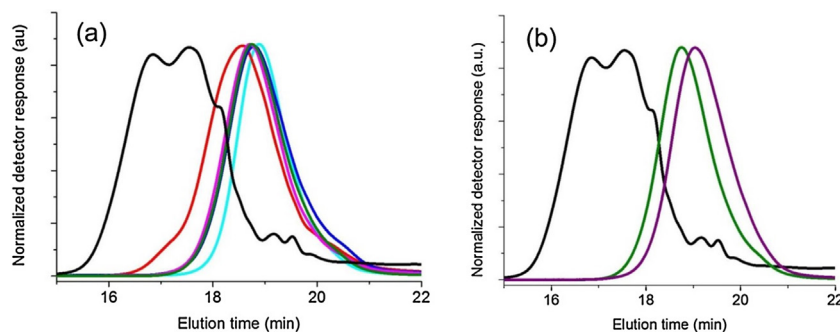


Fig. 7. Comparison of GP chromatograms of organic phase obtained from a) (light blue): ethanol conversion in the presence of 75 mg Al(OTf)₃ in ethanol/water; lignin conversion in the presence of (red): 8 mg, (dark blue): 25 mg, (pink): 50 mg, b) (green): 75 mg of Al(OTf)₃, (purple): 21 mg of AlCl₃ in ethanol/water at 400 °C (reaction time: 4 h); (black): ethanol soluble fraction of soda lignin sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

catalyst loadings. The molecular weight data derived from these chromatograms are given in Table 4. As a reference, the ethanol-soluble fraction of soda lignin was used. The corresponding chromatogram shows the high molecular weight of the soda lignin ($\overline{M}_w = 1144$ g/mol) with a tail into the low-molecular weight regime. Compared with the lignin reference, only the mixture obtained at 8 mg catalyst loading contains a clear feature of high-molecular weight fragments. \overline{M}_w of this mixture is 434 g/mol. The average molecular weight is mainly determined by the ethanol conversion products. However, \overline{M}_w is significantly higher than that of the organic products obtained in the same solvent without lignin ($\overline{M}_w = 205$ g/mol), implying that the average molecular weight values are strongly influenced by the presence of oligomers. With increasing catalyst loading, the \overline{M}_w decreases and the high-molecular weight tail in the GP chromatogram disappears. At the higher catalyst loadings, the chromatograms overlap and do not

change anymore. This can indicate that almost all lignin has been depolymerized into monomeric fragments. On the other hand, the average molecular weight is still higher than the average molecular weight of the blank experiment without lignin. Based on the current data, we cannot conclude whether the shift to high-molecular weight is due to an influence of lignin on ethanol conversion or the incomplete depolymerization of oligomers. In any case, the results confirm that with increasing catalyst loading the depolymerization degree of lignin strongly increased.

Fig. 7b compares the GP chromatograms of the organic phase formed upon the reaction in the presence of Al(OTf)₃ and AlCl₃ from lignin in ethanol/water. With AlCl₃ as the catalyst, lignin/ethanol conversion resulted in a strong shift of the peak in GP chromatograms towards lower molecular weights (Fig. 7b) in agreement with the lower efficiency of lignin depolymerization. In addition, ethanol condensation reactions were less extensive in

Table 4
GPC analysis results of organic phase obtained from lignin conversion in the presence of Al(OTf)₃ in ethanol/water at 400 °C (reaction time: 4 h)¹.

Lignin weight, mg	Solvent type	Catalyst weight, mg	Substrate/catalyst weight ratio	Average molecular weights		
				\overline{M}_n	\overline{M}_w	\overline{M}_z
Lignin ²	–	–	–	535	1,144	1,986
–	Ethanol/water	75	–	144	205	267
150	Ethanol/water	75	2	152	243	347
150	Ethanol/water	50	3	174	300	435
150	Ethanol/water	25	6	156	271	405
150	Ethanol/water	8	20	205	434	782

¹(\overline{M}_n): number-average molecular weight, (\overline{M}_w): weight-average molecular weight, (\overline{M}_z): z-average molecular weight. Weight average distributions were calculated as follows: $\overline{M}_n = \sum N_i M_i / \sum N_i$, $\overline{M}_w = \sum N_i M_i^2 / \sum N_i M_i$, $\overline{M}_z = \sum N_i M_i^3 / \sum N_i M_i^2$.

²A reference sample was obtained by dissolving soda lignin in ethanol at 80 °C and filtration; the ethanol-soluble fraction was analyzed by GPC.

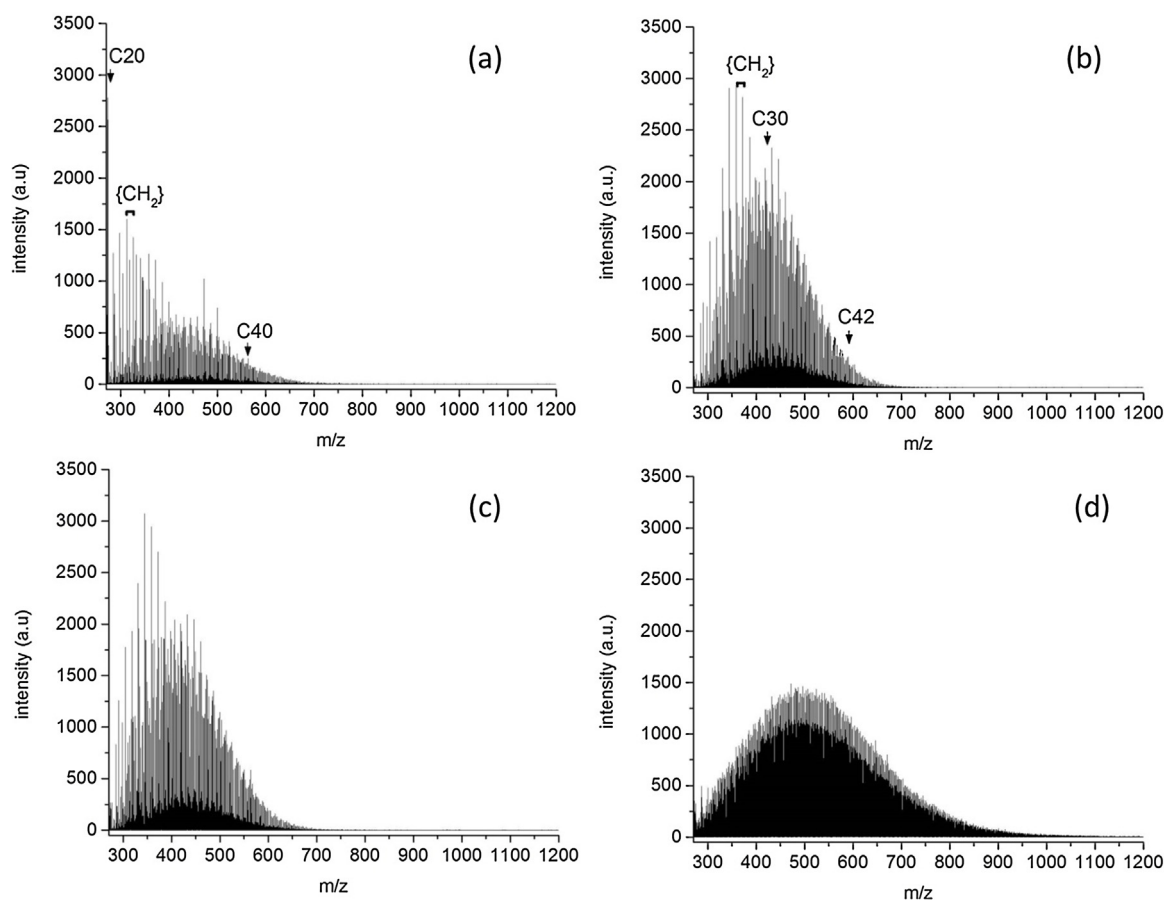
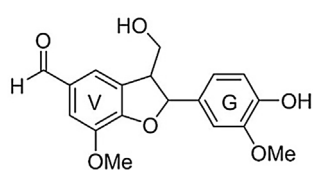
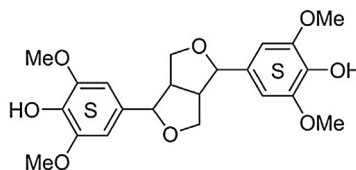


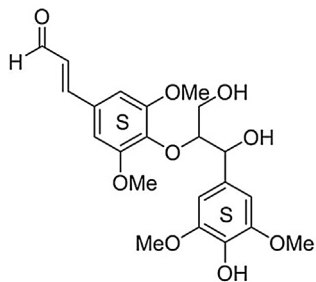
Fig. 8. MALDI-TOF-MS spectra of organic phase obtained from the reaction in ethanol/water mixture at 400 °C (a): using 75 mg of $\text{Al}(\text{OTf})_3$ in the absence of soda lignin, (b and c): using 75 mg and (d): using 8 mg of $\text{Al}(\text{OTf})_3$ in the presence of soda lignin (reaction time: 4 h).



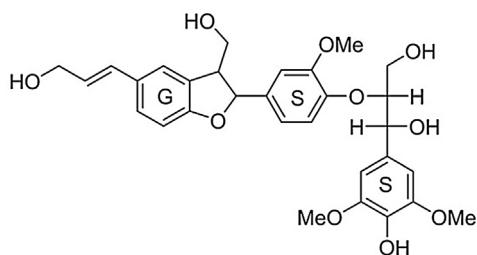
Compound 1, G(8-5)V⁺
MW=330 g/mol



Compound 2, S(8-8)S
MW=418 g/mol



Compound 3, S(8-O-4)S⁺
MW=434 g/mol



Compound 4, S(t8-O-4)S(8-5)G
MW=614 g/mol

Fig. 9. Representative oligolignol units [29].

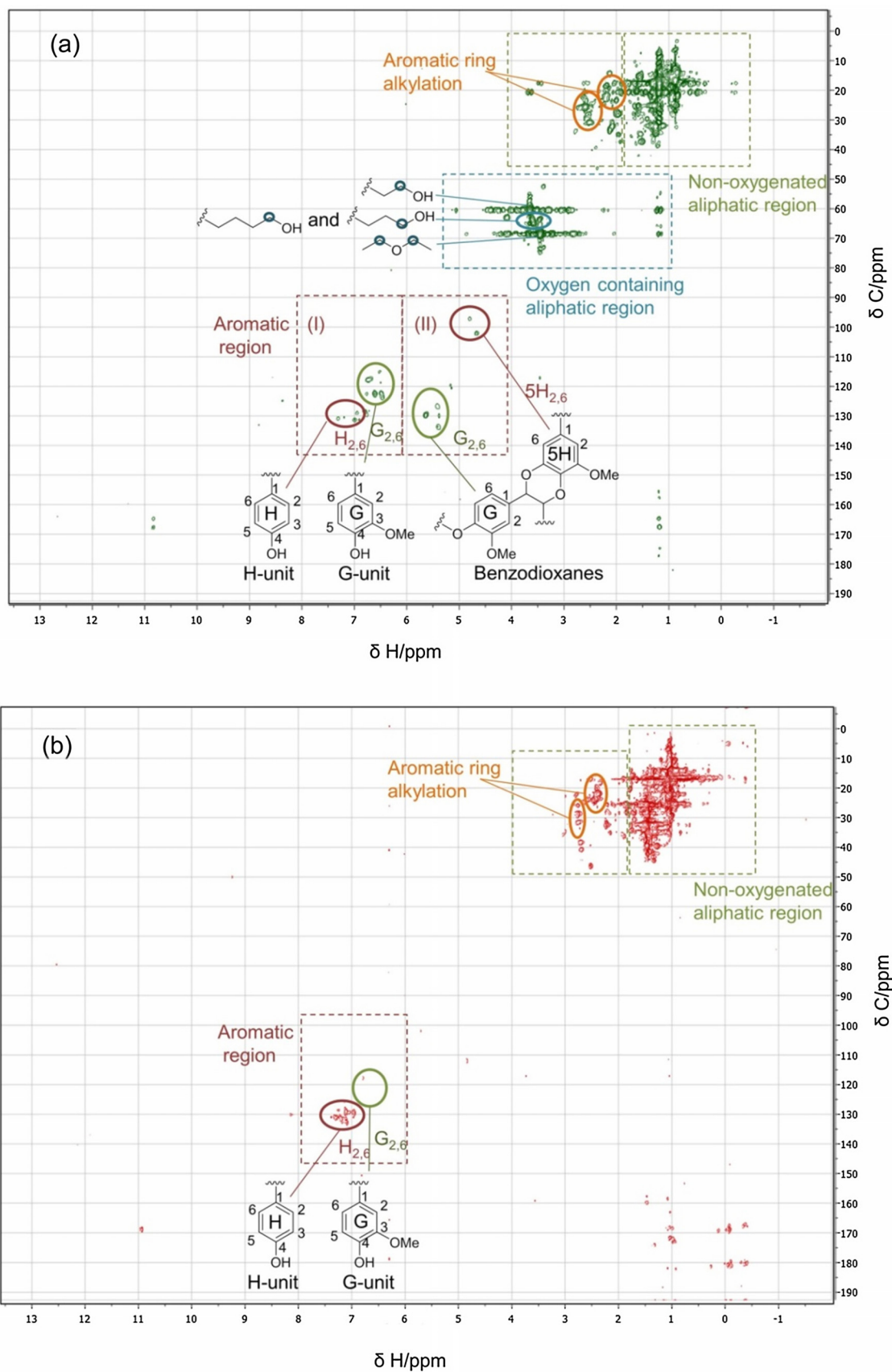


Fig. 10. ^1H - ^{13}C HSQC NMR spectra of the organic phase obtained from the reactions in ethanol/water mixture at 400°C using a) 8 mg (green) and b) 75 mg (red) of $\text{Al}(\text{OTf})_3$ in the presence of soda lignin (reaction time: 4 h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 5
Yields of organic products obtained from the conversion of ethanol in the presence of metal triflate salts in ethanol/water at 400 °C (reaction time: 4 h)¹.

Catalyst	Lignin initial weight, mg	Weight of organic products, mg (selectivities, wt.%)					Total yield (from GC), mg
		Aliphatics	Aromatics		Saturated oxygenates		
			Mono-aromatics	Naphthalenes	Ketones	Carboxylic acids	
Al(OTf) ₃	–	560 (67)	184 (22)	33 (4)	51 (6)	8 (1)	836
Ni(OTf) ₂	–	631 (82)	108 (14)	Trace	31 (4)	Trace	770
Cu(OTf) ₂	–	630 (79)	104 (13)	24 (3)	40 (5)	Trace	798
Sc(OTf) ₃	–	570 (73)	123 (16)	24 (3)	55 (7)	8 (1)	780

¹0.025 mol/L of Lewis acidic salt was used in 3.5/3 mL ethanol/water mixture.

this case due to the lower catalytic performance of AlCl₃ compared with Al(OTf)₃, further contributing to the clear shift of the product distribution to low molecular weights.

MALDI-TOF-MS analysis was used to determine the molecular mass distribution of the heavy fragments in the organic phase. The MALDI-TOF spectra depicted in Fig. 8 compare the absolute molecular mass distribution of the organic products obtained in the absence (Fig. 8a) and presence of lignin (Fig. 8b–d) in the ethanol–water mixture. Two spectra obtained from two separate lignin depolymerization reactions under the same conditions (Fig. 8b and c) show the good reproducibility of the reaction.

Fig. 8a shows that the heavy products from ethanol conversion in an experiment with high catalyst loading (75 mg) have molecular weights between 280 and 400 g/mol. The MALDI-TOF-MS analysis starts at 280 g/mol. The formation of heavy products is in good agreement with the observation of hydrocarbons formation with up to 30 carbon atoms. The tail up to 650 g/mol corresponds to hydrocarbons containing up to 40 carbon atoms. The individual components of similar intensity in the MALDI-TOF spectra are separated by 14 mass units, reflecting the broad range of hydrocarbons present in the mixture. This suggests that ethanol conversion by Al(OTf)₃ does not proceed via conventional Guerbet-type chemistry in which even-numbered hydrocarbons are the predominant products [16]. The organic phase derived from a similar experiment in the presence of lignin (Fig. 8b and c) contained a substantially larger amount of products in the 300–500 g/mol mass range. The products were most likely derived from lignin. Considering that the common lignin constituents such as phenylpropane guaiacol and phenylpropane syringol have molecular weights in the 166–197 g/mol range [27], these findings show that lignin depolymerization also resulted in oligomeric fragments containing two or three aromatic units. In a previous study [28], the products from soda hardwood lignin determined by MALDI-TOF with typical masses of 397, 429,

447, and 481 g/mol were confirmed to be dimers; a product with a mass of 615 g/mol was a trimer. Despite this broad molecular weight distribution, all of the compounds were soluble in ethanol. No solid lignin residue was obtained in the experiment with high catalyst loading (75 mg).

In the experiment with a lower amount of catalyst (8 mg), the molecular weight distribution of the resulting organic phase extended up to almost 900 g/mol (Fig. 8d). This together with the observation that a substantial amount of lignin residue was observed after the reaction indicates that the depolymerization degree of the lignin was lower. The higher degree of depolymerization with 75 mg of catalyst compared with 8 mg catalyst did not only lead to the formation of products with lower molecular weight, but also to a smaller number of compounds. Semi-quantitative comparison of GC × GC data of the C₂₀₊ fraction with the MALDI-TOF-MS data indicates that the absolute amount of high-molecular weight products is less than 5% of the total product yields reported in Table 2. This also applies to the contribution of lignin oligomers in the lignin conversion experiments. We further analyzed the MS spectra in Fig. 8d to identify the presence of common lignin oligomers/sub-units [29] in the product mixture obtained at the lowest catalyst loading (8 mg). Examples of dimeric and trimeric lignol compounds with molecular masses of 330, 418, 434 and 614 g/mol that were observed by MALDI-TOF-MS are shown in Fig. 9.

The organic phases obtained at low (8 mg) and high (75 mg) catalyst loadings were further analyzed by ¹H-¹³C HSQC NMR. The resulting HSQC spectra are shown in Fig. 10a and b, respectively. The spectra clearly show the presence of substantial amount of aliphatic products. At low catalyst loading, the HSQC spectrum contains features due to carbon atoms close to ether and alcohol groups. These features are absent in the mixtures obtained at high catalyst loading. The difference is consistent with the presence of

Table 6
Yields of organic products obtained from lignin conversion by using different metal triflate salts in ethanol/water at 400 °C (reaction time of 4 h)¹.

Catalyst	Lignin initial weight, mg	Weight of organic products, mg (selectivities, wt.%)						Total yield (from GC), mg	
		Aliphatics	Aromatics		Mono-aromatic oxygenates		Saturated oxygenates		
			Mono-aromatics	Naphthalenes	Phenols	Guaiacols	Ketones		Carboxylic acids
Al(OTf) ₃	150	697 (67)	187 (18)	52 (5)	21 (2)	11 (1)	52 (5)	21 (2)	1,041
Ni(OTf) ₂	150	669 (73)	128 (14)	37 (4)	18 (2)	9 (1)	55 (6)	Trace	916
Cu(OTf) ₂	150	699 (75)	121 (13)	37 (4)	19 (2)	Trace	47 (5)	9 (1)	932
Sc(OTf) ₃	150	731 (74)	138 (14)	40 (4)	20 (2)	Trace	49 (5)	10 (1)	988

¹0.025 mol/L of Lewis acidic salt was used in ethanol/water (3.5/3 mL ethanol/water) solvent.

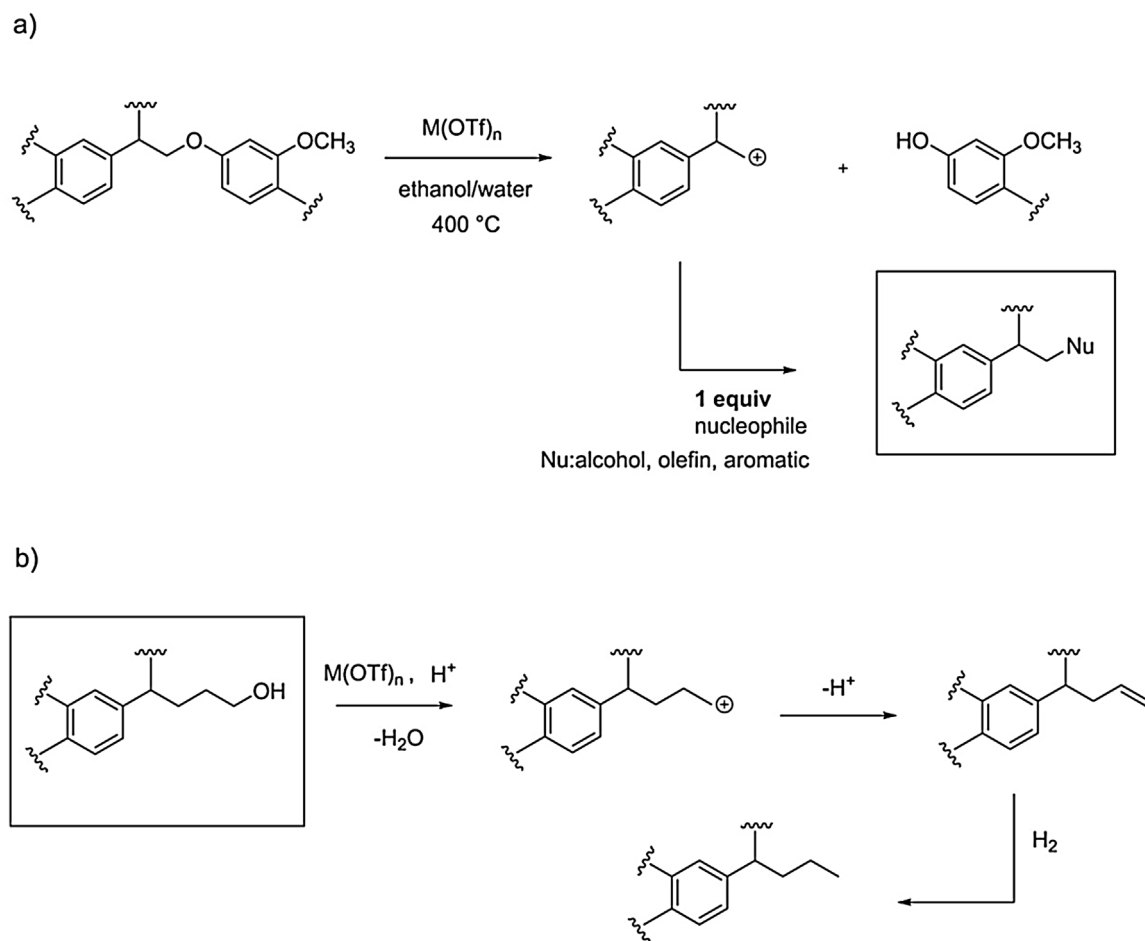


Fig. 11. Possible cleavage of representative lignin functionality in the presence of metal triflates in ethanol/water at 400 °C (adapted from [9,31]) for the a) formation of aryl alcohols, b) formation of aryl alkenes and aryl alkanes.

ethanol, propanol, butanol, diethyl ether in the gas chromatograms of the organic phase obtained in the low catalyst loading experiment. The HSQC spectra also contain evidence for the presence of alkyl groups connected to aromatic rings [16]. These groups are already present in the products obtained at low catalyst loading. In the aromatic region, signals that according to literature [30] can be assigned to p-hydroxyphenyl (H), guaiacyl (G) and 5-hydroxyguaiacyl (5H) units were observed. Guaiacyl units (aromatic region I) and benzodioxanes (aromatic region II) were seen at low catalyst loading. The presence of the dilignol unit benzodioxane in aromatic region II is in line with the MALDI-TOF results of the same experiment (Fig. 8d). These structures were not visible anymore at high catalyst loading. In the aromatic region, one also observes the increase of the amount of aromatics, which could be either phenols or benzenes, in line with the GC \times GC analysis.

3.4. The effect of the cation on the conversion of lignin and ethanol

We further investigated the influence of the cation on ethanol conversion and lignin depolymerization by using triflate salts of Ni^{2+} , Cu^{2+} and Sc^{3+} in comparison with Al^{3+} in ethanol/water mixture. In all catalytic reactions, ethanol was converted to mainly higher aliphatic and aromatic hydrocarbons as discussed earlier in this chapter for $\text{Al}(\text{OTf})_3$ salt.

Organic phases obtained upon conversion of ethanol were further analyzed by GC \times GC. The products were similar as observed

during ethanol conversion with $\text{Al}(\text{OTf})_3$ (Table 5). The majority of the ethanol products were non-oxygenated compounds, evidencing again the high degree of deoxygenation by using the $\text{M}(\text{OTf})_n$ catalysts at 400 °C in the ethanol/water mixture. This was also clear from the substantial amounts of water formation in all $\text{M}(\text{OTf})_n$ -catalyzed reactions. Only small differences in the product selectivities were observed for the different $\text{M}(\text{OTf})_n$ salts. While the yield of alkylated mono-aromatics increased with Sc and Al triflates, Cu and Ni triflates mainly promoted formation of aliphatic hydrocarbons (Table 5). With $\text{Ni}(\text{OTf})_2$, no naphthalenes were formed. For all catalytic reactions carried out in the presence of lignin, there was no solid residue left. As in the conversion of ethanol, there were minor differences between the catalytic results of the different $\text{M}(\text{OTf})_n$ catalysts. With $\text{Al}(\text{OTf})_3$, the mono-aromatics yield was slightly higher than other $\text{M}(\text{OTf})_n$ catalysts (Table 6). This is in line with the results of ethanol conversion reactions without lignin. Also, total yields of organic products were high with $\text{Al}(\text{OTf})_3$. From the comparison of the total organics yields between experiments with and without lignin, one can conclude that Al and Sc triflates were more active in ethanol conversion than the other triflates; it is reasonable to conclude that they are also more active in catalyzing alkylation.

Summarizing, the influence of the cation type was negligible under these reaction conditions. Nevertheless, the anionic part had the strongest effect on catalysis as discussed earlier. It should be stressed that the metal cations are needed to initiate hydrolysis reactions [23].

3.5. Proposed reaction mechanisms

A possible mechanism for the cleavage of a representative functionality of lignin by triflate-assisted hydrogenolysis in ethanol/water is given in Fig. 11.

We propose that the $M(\text{OTf})_n$ catalyst can coordinate to hydroxyl, carboxyl, ether and carbonyl groups of lignin. The strong electron withdrawing ability of $M(\text{OTf})_n$ results in oxygen removal (Fig. 1) and subsequent carbocation formation [9]. The important catalytic step is the generation of the organic cation (Fig. 11a). The cation will react with various nucleophiles (Nu) where Nu-H can be an alcohol, olefin or aromatic specie [9,31]. Also, the reactivity of the nucleophile towards the cation under reaction conditions is important. Extensive alkylation of activated species in ethanol/water at 400 °C indicates that ethanol reacted with the organic cations forming aryl-alcohols (Fig. 11a). Aryl-alcohols will then be dehydrated to form aryl-alkenes, which later can be hydrogenated to aryl-alkanes (Fig. 11b).

4. Conclusion

Triflate-assisted hydrogenolysis in ethanol/water mixture using metal triflates resulted in complete conversion of a soda lignin at 400 °C without formation of char or insoluble residue. The resulting organic phase contained aromatic and aliphatic hydrocarbons and higher molecular weight products (with masses up to 600 g/mol) derived from lignin and a relatively small amount of oxygenated aromatics. Combined results of GC × GC, GC-FID/MS, GPC and MALDI-TOF-MS indicates that most of the lignin was converted into monomeric units under optimized reaction conditions using $\text{Al}(\text{OTf})_3$ as catalyst. In addition, ethanol was partially converted into a wide range of products including aliphatics, aromatics, ketones and acids. ^1H - ^{13}C HSQC NMR results point out the strong catalytic effect of triflate salts on deoxygenation of ethanol and its conversion products. Similarly, triflation of oxygen-containing functionalities of lignin led to deoxygenation. The resulting carbocations are stabilized by alkylation reactions with ethanol. These alkylation reactions will reduce repolymerization rates and, in this way, prevent char formation. These results are in good accordance with the complete conversion of model compounds containing α -O-4, 5-O-4 and α -1 bonds in ethanol/water with the $\text{Al}(\text{OTf})_3$ catalyst. The 5-5' type C-C bond found in biphenyl that does not contain an oxygen atom prone to attack by triflate cannot be converted in this way. This result may suggest that the high-molecular weight fragments contain a significant amount of such carbon-carbon bonds.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2015.08.039>.

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