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Lewis-acid catalyzed depolymerization of Protobind lignin in supercritical water and ethanol

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 use of metal acetates, metal chlorides and metal triflates as Lewis acid catalysts for the depolymerization of soda lignin under supercritical conditions was investigated. The reactions were carried out at 400 °C in water and ethanol. Lignin conversion in supercritical water led to formation of insoluble char and resulted in low yields of monomeric products. When the reaction was performed in supercritical ethanol, char formation was inhibited and higher yields of low molecular-weight organic products were obtained. The ethanol solvent was also converted in two ways. Firstly, the lignin depolymerization products were alkylated by ethanol. Secondly, ethanol was converted into a range of higher hydrocarbons including paraffins and olefins. Possible mechanisms of the lignin and ethanol conversion reactions are discussed.

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1. Introduction

Lignin is attractive as a renewable source of aromatics [1,2]. The cleavage of the different types of linkages in lignin is particularly challenging, making it difficult to obtain aromatics in reasonable yield. To develop an economically viable route for the upgrading of lignin into fuels and chemicals, efficient catalysts need to be identified. Among the many approaches, also the use of base [3–8] and acid catalysts [9–16] for lignin depolymerization has been addressed. For example, Labidi and co-workers recently reported about base-catalyzed depolymerization of various types of lignin in water [4,5]. Depolymerization of organosolv lignin in aqueous NaOH at 320 °C and 250 bar yielded about 11 wt% oxygen-containing aromatic products such as phenols, catechols and guaiacols. The main disadvantage of base catalysts is the extensive repolymerization of the products into insoluble char [3–8]. To prevent condensation reactions, the use of additives such as boric acid and phenol has been explored [3,5]. For instance, char formation can be suppressed by the addition of phenol at 300 °C [5]. Boric acid, however, promoted formation of condensation products, mainly di-aromatic species, in water [3]. Base catalysis was also explored in combination with organic solvents such as

alcohols (methanol, ethanol, propanol and butanol) and acetone [7,8]. In ethanol, the base-catalyzed depolymerization of organosolv-derived lignin at 290 °C resulted in high conversions with only 7 wt% ether insolubles [7]. This high lignin conversion could only be reached when large amounts of strong bases such as CsOH, KOH, and NaOH were used.

Brønsted acid catalysts, extensively used in oil refineries, have also been considered for the conversion of biomass [9–11]. For example, amorphous silica-alumina [9] and zeolites [10,11] have been evaluated as catalysts for lignin depolymerization. An early study showed that hydrocracking of Alcell lignin in tetralin by NiW supported on silica-alumina at 400 °C in 30 min resulted in a lignin conversion of 25 wt% and 5 wt% dichloromethane-solubles [9]. Catalytic fast pyrolysis has also been investigated as a technology to upgrade lignin. The use of ZSM-5, BEA, mordenite, and USY (ultrastabilized Y) zeolites provided high aromatic yields [10]. For instance, USY zeolite yielded 75 wt% liquids of which about half were aromatics [11].

So far, few studies have investigated the role of Lewis acid catalysts for the depolymerization of lignin. Davoudzadeh et al. studied the degradation of Kraft lignin in tetralin by the Lewis acid BF₃ [12]. The reaction was carried out in the presence of phenol as the proton donor. The yield of distillable products was found to be 25 wt% at 155 °C and atmospheric pressure. During the liquefaction of Kraft lignin in methanol, ZnCl₂ increased char formation at relatively low temperatures (250–350 °C) [13]. At higher

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

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

temperatures (400–420 °C), the use of ZnCl₂ or FeCl₃ led to 24 wt% monomeric products, mainly phenolics and cresols [14]. In another study, the use of FeCl₃ and NiCl₂ salts in water afforded 18 wt% ether solubles (mainly phenolics) from Alcell lignin at 300 °C [15]. Iron-based catalysts such as Fe-sulfides and Fe-sulfate, which were earlier employed in the liquefaction of coal, have also been used for the conversion of lignin [16]. Recently, such iron-based catalysts have again been used for the conversion of lignin [7]. In ethanol, a maximum oil yield of 63 wt% was obtained at 350 °C using Fe-sulfate in an atmosphere of 5 bar H₂. Under these conditions, no deoxygenation of the products was observed.

In a recent study, we explored the use of Lewis acid salts for the decomposition of dimer compounds that contain representative α -O-4, 5-O-4, β -1 (methylene bridges) and 5-5' linkages present in lignin [17]. We showed that the yield of monomeric products was higher in ethanol than in water. This is due to the extensive alkylation of the mono-aromatic products that inhibits their condensation into larger products. The highest yields of deoxygenated mono-aromatics were obtained using Lewis acid catalysts at 400 °C in supercritical ethanol. The preferred Lewis acid catalysts were Fe, Cu, Ni and Al chlorides. In the present study, metal chlorides (Fe⁺², Co⁺², Cu⁺², Ni⁺² and Al⁺³), acetates (Fe⁺², Co⁺², Cu⁺², Ni⁺²) and triflates (Cu⁺², Ni⁺², Al⁺³ and Sc⁺³) were used as catalysts for the conversion of Protobind lignin. The reactions were carried out in water and ethanol under supercritical conditions at 400 °C.

2. Experimental

2.1. Materials

Protobind 1000 lignin, which is obtained from wheat straw by soda pulping, was used as received from GreenValue (Switzerland). Deionized water with a pH value of 5.5 and absolute ethanol (Sigma Aldrich, $\geq 99.8\%$) was used as reaction solvents. Iron(II) acetate (Aldrich, 95%), copper(II) acetate (Aldrich, powder, 98%), cobalt(II) acetate tetrahydrate (Merck, $\geq 98.0\%$), nickel(II) acetate tetrahydrate (Aldrich, 98%), iron (II) chloride tetrahydrate (Aldrich, $\geq 99.0\%$), copper(II) chloride dihydrate (Aldrich, $\geq 99.0\%$), cobalt(II) chloride (Aldrich, anhydrous, $\geq 98.0\%$), nickel(II) chloride (Aldrich, anhydrous, 98%), aluminum(III) chloride hexahydrate (Fluka, $\geq 99.0\%$), scandium(III) triflate (Aldrich, 99%), aluminum(III) triflate (Aldrich, 99.9%), copper(II) triflate (Aldrich, 98%), nickel(II) triflate (Aldrich, 96%) were used without further purification. Ethyl acetate (VWR, 99.5%) was used as the extraction solvent. n-Decane (Aldrich, anhydrous, $\geq 99\%$) and di-n-butyl ether (Aldrich, anhydrous, 99.3%) were used as external standards during GC analysis. Samples were diluted by tetrahydrofuran (Aldrich, anhydrous, $\geq 99.9\%$) ten times prior to GC $\times$ GC analysis and thirty times prior to GPC analysis.

2.2. Catalytic activity measurements

All the experiments were performed in stainless-steel batch reactors with an internal volume of 13 mL. Reactions were carried out at 400 °C with a reaction time of 4 h. The reactors were filled with either 8 mL of water or 6.5 mL of anhydrous ethanol. In a typical run, 150 mg of lignin and 0.025 mol/L of Lewis acidic salt were loaded to each reactor. The reactors were sealed by the use of Swagelok o-rings. Reactions were carried out by placing the reactors in a preheated fluidized sand bath that allowed for rapid heating to the desired reaction temperature. No additional gas was used and reactions took place under autonomous pressure developed under these conditions.

In our system, ten parallel reactions could be run simultaneously. After the reaction was completed, the reactors were quenched in an ice bath. When char was formed or lignin residue

remained, the solids were separated from the liquid products by filtration. For the experiments in water, the organics were extracted by adding ethyl acetate in a 1:1 volume ratio with water. For the experiments in ethanol, the liquid products were collected after filtration and weighed. In case metal chlorides and triflates were the catalysts, the liquid phase consisted of two layers—an organic and an aqueous layer. The aqueous and organic layers were separated by decantation. The liquid organic phases were further analyzed by GC/MS-FID, GC $\times$ GC and GPC methods.

2.3. Product analysis

Gas Chromatography (GC) analysis—For the identification and quantification of the reaction 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 $\times$ 0.25 mm i.d. and 0.25 μ m 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 in ethanol-mediated reactions, GC $\times$ GC analysis was performed on an Interscience Trace GC $\times$ GC equipped with a cryogenic trap system and two columns: a 30 m $\times$ 0.25 mm i.d. and a 0.25 μ m film of RTX-1701 capillary column connected by a meltfit to a 120 cm $\times$ 0.15 mm i.d. and a 0.15 μ m 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 the carrier gas at a flow rate of 0.6 mL/min. The injector and FID temperatures were set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes 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.

To perform a qualitative analysis of the gas-phase products, ethanol conversion was carried out in a 100 mL Parr stainless steel stirred high-pressure autoclave. Upon the completion of the reaction, the autoclave was cooled to room temperature and the built-up pressure was released by collecting the gaseous products in a separate stainless steel vessel. The products were then analyzed with Interscience Compact GC. Molsieve 5 Å and Porabond Q columns were coupled with a thermal conductivity detector (TCD), and the Al₂O₃/KCl column with a flame ionization detector (FID).

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.

3. Results and discussion

3.1. Lignin conversion in sc-water and sc-ethanol

Table 1 shows that the hydrothermal conversion of Protobind lignin resulted in very low yields of low-molecular weight organic products. The main product was a black-colored char residue, which was insoluble in water and THF. The total organics yields for the catalytic reactions were around 6–8 wt% (Table 1). The yield in the blank reaction was higher. The monomers were grouped into mono-aromatics, mono-aromatic oxygenates (phenolics, catechols and guaiacols), saturated mono-oxygenates (ketones, carboxylic acids) and non-oxygenated mono-cyclic products (cyclopentanes

Table 1

Product distribution for the depolymerization of Protobind lignin in the presence of Lewis acids in water at 400 °C (reaction time: 4 h).

Catalyst	Yield of organic products (wt%)					Total yield (wt%)
	Mono-aromatics	Mono-aromatic oxygenates		Saturated products		
		Phenolics	Catechols	Ketones and carboxylic acids	Non-oxygenated mono-cyclics	
Blank	0.4	5.5	2.0	1.1	0.4	9.4
FeCl ₂	0.5	2.0	3.1	0.7	0.5	6.9
CuCl ₂	0.6	1.6	3.1	0.7	0.5	6.5
CoCl ₂	0.5	1.3	3.1	0.9	0.5	6.3
NiCl ₂	0.5	1.2	3.1	0.9	0.5	6.2
AlCl ₃	0.5	1.2	3.1	0.9	0.5	6.2
Fe(OAc) ₂	0.5	2.8	3.4	0.7	0.3	7.7
Cu(OAc) ₂	0.4	2.4	3.5	1.0	0.3	7.6
Co(OAc) ₂	0.5	2.5	3.3	1.5	0.3	7.9
Ni(OAc) ₂	0.4	2.3	3.3	0.8	0.3	7.1
Sc(OTf) ₃	0.1	0.9	0.5	–	0.2	1.8

and cyclohexanes). In all experiments, the main monomeric products were mono-aromatic oxygenates (phenolics and catechols), obtained in yields ranging from 4.3 to 7.5 wt%. The product mixture also contained a small amount of ketones, with cyclopentanones predominating. We speculate that these compounds derive from the small amount of residual carbohydrates in the parent lignin [18]. Previous studies have shown that cyclopentanones can be formed in water via rearrangement of furfurals obtained during sugar dehydration [19]. When Sc(OTf)₃ was the catalyst, the total organics yield was the lowest (1.8 wt%). The activity order observed in these experiments indicates that Lewis acids negatively affect lignin conversion in sc-water.

The product mixtures from the blank reaction and the reaction with Sc(OTf)₃ were also analyzed by GC × GC (Fig. 1). This method distinguishes mono-cyclics (hydrocarbons), mono-aromatics, mono-aromatic oxygenates (phenolics, catechols, guaiacols), ketones, carboxylic acids, di-aromatics and high molecular-weight (HMW) components. It can be seen that the use of Sc(OTf)₃ resulted in a much broader range of HMW components compared with the blank reaction. Di-aromatics with carbon-carbon linkages dominated among the condensation products.

Summarizing, the use of Lewis acids in sc-water is not suitable for the upgrading of lignin. Mostly, insoluble char was obtained. A small amount of monomeric products obtained after extraction, mainly consisted of oxygenates. The monomers yield was higher without catalyst than in the presence of Lewis acids.

Reaction of lignin in sc-ethanol resulted in a wide range of products, which were analyzed in detail by GC/MS-FID and GC × GC methods. GC detectable products included aliphatic hydrocarbons (paraffins, olefins, saturated cyclics), aromatic hydrocarbons (alkyl-benzenes and naphthalenes), mono-aromatic oxygenates (phenols and guaiacols) and saturated oxygenates (ketones and carboxylic acids). These products derived from conversion of lignin as well as ethanol. Representative GC × GC chromatograms are shown in Fig. 2. In the blank reaction, the total organics yield was 42 mg (Table 2). Although there was no char formation, some insoluble lignin residue was obtained. The main products were ketones and aliphatics (Fig. 2a) with selectivities of 67 and 18 wt%, respectively. The aliphatic hydrocarbons mainly consisted of cyclic and linear hydrocarbon products (alkanes and alkenes) with chain lengths up to six carbon atoms. In addition, carboxylic acids were obtained with a selectivity of 7 wt%. The yield of mono-aromatics and alkylated phenols was very low (~3 mg). As shown in Table 3, the average molecular weight (*M_w*) of depolymerized lignin was ca. 425 g/mol. This value was lower than the *M_w* (1144 g/mol) of the ethanol-soluble fraction of Protobind lignin. Thus, lignin conversion in sc-ethanol resulted in relatively high-molecular weight fragments in the absence of catalyst.

Fig. 1. GC × GC chromatograms of organic products formed upon the conversion of Protobind Lignin in sc-water at 400 °C: (a) Sc(OTf)₃-catalyzed, (b) blank reactions (reaction time: 4 h). (1): Mono-cyclic saturated hydrocarbons, (2): higher molecular weight components.

Using M(OAc)_n, the total organics yields increased almost one order of magnitude compared with the blank reaction (Table 2). The highest yield was 463 mg for Cu(OAc)₂. Similar with the blank reaction, the main products were ketones and carboxylic acids (Fig. 2b). In addition, aliphatic hydrocarbons (alkanes and alkenes) were also detected in GC × GC analysis (Fig. 2b). They were formed via coupling reactions of ethanol with yields ranging between 66 and 88 mg. Formation of mono-aromatic oxygenates (mainly alkyl phenolics and trace amounts of guaiacols) was favored for Cu(OAc)₂ and Co(OAc)₂ with ~18 mg yields. Mono-aromatics yields ranged between 8 and 24 mg. Using M(OAc)_n, the *M_w* of the product mixtures was in the 400–470 g/mol range (Table 3), close

Fig. 2. GC $\times$ GC chromatogram of organic products formed upon the conversion of Protobind Lignin in supercritical ethanol (a) blank, and in the presence of (b) $\text{Co}(\text{OAc})_2$, (c) CuCl_2 , (d) $\text{Al}(\text{OTf})_3$ at 400 °C (reaction time: 4 h).

to value for the blank reaction. Clearly, $\text{M}(\text{OAc})_n$ did not promote depolymerization of lignin beyond the degree obtained in the blank reaction.

MCl_n catalyzed the conversion of ethanol into higher hydrocarbons, mainly paraffins (Fig. 2c). This result shows that extensive deoxygenation reactions took place. This was also evident from the formation of significant amounts of water. It also led to phase separation. The organic phase was collected by decanting. The resulting bio-oil contained products from lignin as well as from ethanol conversion. The total organics yields were slightly lower for MCl_n than for $\text{M}(\text{OAc})_n$ catalysts. Among the chlorides, the highest yield of 368 mg was obtained for CuCl_2 . Compared with

$\text{M}(\text{OAc})_n$, the yields of ketones and carboxylic acids were lower, and those of alkylated mono-aromatics were higher (Table 2). In addition, in the presence of MCl_n , alkylated mono-aromatic species were formed. The highest mono-aromatic yield of 81 mg was obtained with CuCl_2 as the catalyst. Trace amount of naphthalenes were formed, most likely due to the condensation of mono-aromatics. The amount of naphthalenes was higher in the presence of CuCl_2 . In addition, yields of mono-aromatic oxygenates (alkyl-phenolics and guaiacols) was below 15 mg. The $\overline{M}_w$ varied in the range 227–354 g/mol, which demonstrates that the degree of lignin depolymerization was higher for MCl_n than for $\text{M}(\text{OAc})_n$.

Table 2

Yields of organic products from Protobind lignin depolymerization in the presence of Lewis acids in ethanol at 400 °C (reaction time: 4 h).

Catalyst	Weight of organic oil, mg (selectivities, wt%)							Total weight of organic oil (mg)
	Aliphatics	Aromatics		Mono-aromatic oxygenates		Other oxygenates		
		Mono-aromatics	Naphthalenes	Phenolics	Guaiacols	Ketones	Acids	
Blank	8 (18)	1 (3)	–	1 (3)	<1 (2)	28 (67)	3 (7)	42
Fe(OAc) ₂	66 (22)	8 (3)	–	10 (3)	1 (<1)	123 (41)	89 (30)	297
Cu(OAc) ₂	88 (19)	19 (4)	–	14 (3)	5 (1)	273 (59)	65 (14)	463
Co(OAc) ₂	73 (21)	24 (7)	–	14 (4)	3 (1)	203 (58)	35 (10)	352
Ni(OAc) ₂	66 (22)	18 (6)	–	6 (2)	–	187 (62)	24 (8)	301
FeCl ₂	139 (50)	47 (17)	3 (1)	11 (4)	3 (1)	42 (15)	33 (12)	278
CuCl ₂	184 (50)	81 (22)	11 (3)	11 (3)	4 (1)	40 (11)	37 (10)	368
CoCl ₂	83 (48)	33 (19)	2 (1)	7 (4)	3 (2)	29 (17)	16 (9)	173
NiCl ₂	112 (48)	35 (15)	2 (1)	9 (4)	5 (2)	52 (22)	19 (8)	234
AlCl ₃	160 (49)	69 (21)	3 (1)	3 (1)	7 (2)	49 (15)	36 (11)	327
Cu(OTf) ₂	269 (67)	64 (16)	<4 (<1)	4 (1)	4 (1)	48 (12)	12 (3)	402
Ni(OTf) ₂	364 (67)	92 (17)	5 (1)	11 (2)	5 (1)	43 (8)	22 (4)	543
Al(OTf) ₃	491 (75)	104 (16)	<6 (<1)	13 (2)	–	26 (4)	13 (2)	653

Table 3

Molecular weight distribution of organic fractions from Protobind lignin depolymerization in the presence of Lewis acids in ethanol at 400 °C (reaction time: 4 h).

Catalyst	GPC analysis		
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
Lignin ^a	535	1144	1986
Blank	216	425	774
Fe(OAc) ₂	198	404	636
Cu(OAc) ₂	213	417	686
Co(OAc) ₂	251	471	783
Ni(OAc) ₂	259	455	701
FeCl ₂	208	345	555
CuCl ₂	177	300	509
CoCl ₂	205	344	560
NiCl ₂	209	354	575
AlCl ₃	125	227	408
Al(OTf) ₃	155	268	411
Ni(OTf) ₂	173	285	419
Cu(OTf) ₂	150	257	397

^a Reference sample obtained by solubilization of Protobind lignin in ethanol at 80 °C followed by filtration; the ethanol-soluble fraction was analyzed by GPC.

The $\overline{M}_w$ was around 270 g/mol for the bio-oil obtained using M(OTf)_n catalysts. The degree of lignin depolymerization was higher than in experiments with MCl_n catalysts (Table 3). The total organics yields were approximately two times higher for Ni(OTf)₂ and Al(OTf)₃ than for MCl_n (Table 2). The products were alkylated mono-aromatics, naphthalenes and alkylated mono-aromatic oxygenates (phenols and guaiacols) (Fig. 2d). In the presence of M(OTf)_n catalysts, depolymerization products were alkylated by ethanol. The highest yield for alkylated mono-aromatics (104 mg) was obtained with Al(OTf)₃. Similar to MCl_n, yields of mono-aromatic oxygenates were low, which points to the high deoxygenation activity in the presence of M(OTf)_n. Alkylation and formation of higher hydrocarbons from ethanol led to the formation of significant amounts of water. The strong Lewis acid M(OTf)_n catalysts strongly promoted ethanol conversion into higher paraffins and olefins (Fig. 2d). Aliphatic hydrocarbons were the main products with selectivities of ~70%. Al(OTf)₃ was the most active catalyst for the formation of aliphatics. The ketones and carboxylic acids yields were substantially lower (Table 2) compared with the experiments using M(OAc)_n.

Summarizing, condensation and repolymerization reactions proceeded at much lower rates in sc-ethanol than in sc-water. A significant reduction in the average molecular weight of the starting Protobind lignin was achieved. The degree of depolymerization increased with increasing Lewis acidity of the catalyst. Under these reaction conditions, ethanol was found to react into a wide range of aliphatic products. In addition, ethanol was also involved in the alkylation of aromatic products obtained from lignin depolymerization reactions. MCl_n and M(OTf)_n were more active in the conversion of ethanol than M(OAc)_n. Comparing the results obtained in water and ethanol, we can conclude that ethanol is preferred for the Lewis-acid catalyzed depolymerization of lignin.

3.2. Ethanol conversion by Al(OTf)₃

In an attempt to qualitatively distinguish the products of the conversion of the ethanol solvent from products originating from

Fig. 3. GC × GC chromatogram of organic products formed upon the conversion of ethanol at 400 °C in the presence of Al(OTf)₃ (reaction time: 4 h).

lignin, the conversion of ethanol by Al(OTf)₃ was analyzed in detail. Table 4 shows that the total organics yield from ethanol conversion after 4 h reaction at 400 °C was 11 wt% (557 mg). This yield was lower than the yield (653 mg) when Protobind lignin was present under otherwise similar conditions. The GC × GC chromatogram of the organic products is shown in Fig. 3. The reaction yielded a wide range of aliphatic hydrocarbons and alkylated mono-aromatics (Table 4). Aliphatic products included highly branched hydrocarbons containing up to 30 C atoms. This aliphatic product fraction contained predominantly paraffins and a small amount of olefins. These findings suggest that carbon-carbon coupling reactions take place at high rate and that they lead to removal of oxygen. The composition of the gas-phase was qualitatively analyzed in a separate experiment. The conversion of ethanol was accompanied by the formation of various gaseous products including H₂, CO, CO₂, CH₄ as well as C₂–C₄ alkanes and alkenes. We propose that these products are formed via cracking, decarboxylation, decarbonylation, dehydration and reforming reactions. Such decomposition paths provide molecular H₂ necessary for both the formation of saturated hydrocarbons and to promote hydrogenolysis and deoxygenation of lignin towards mono-aromatic products discussed in the previous section. Nevertheless, the direct hydrogen transfer paths utilizing ethanol as H₂-donor cannot be excluded.

About 8 wt% (44 mg) of the organic products corresponded to completely deoxygenated mono-aromatics. The conversion of paraffins to aromatics at elevated temperatures in the condensed phase has been reported previously [20]. This shows that not all the aromatics in the lignin conversion reactions in sc-ethanol derived from lignin.

One of the possible carbon-carbon coupling reactions for alcohols is the Guerbet reaction [21–25]. Such reactions involve alcohol dehydrogenation to form an aldehyde or ketone intermediate, aldol condensation of the aldehyde or ketone intermediates to form C–C bonds, and hydrogenation of the resulting unsaturated product [21]. Typically, bases [21–25] such as MgO, K₂CO₃, copper chromite and Mg/Al/Cu mixed oxides, and additives such as NaOCH₃ [25] are employed as catalysts for the Guerbet reaction. The products of the Guerbet reaction of ethanol are typically higher alcohols. Given the nature of the catalysts employed in this study and the reaction products, we conclude that Guerbet chemistry is most likely

Table 4

Yields of organic products from ethanol conversion in the presence of Al(OTf)₃ at 400 °C (reaction time: 4 h).

Catalyst	Weight of organic oil, mg (oil yield, wt%)					Weight of organic oil, mg (Total organics yield, wt%)
	Aliphatics	Mono-aromatics	Phenolics	Ketones	Acids	
Al(OTf) ₃	497 (9.7%)	44 (0.9%)	trace	11 (0.2%)	5 (0.1%)	557 (11%)

not involved in the formation of the hydrocarbon products from ethanol. Instead, we surmise that strong Lewis acids dehydrate the alcohols as a first step towards their conversion. Brønsted as well as Lewis acid catalysts can dehydrate ethanol [20,26–34]. So far, zeolites [27,28,31] and alumina [32,33] have been used to dehydrate ethanol to ethylene. Compared to Brønsted acid zeolites, the acid sites on alumina required higher reaction temperatures and led to lower ethylene yield [35].

Two competitive paths are involved in the dehydration of ethanol [33], namely intramolecular dehydration to ethylene (Eq. (1)) and intermolecular dehydration to diethyl ether (Eq. (2))

While diethyl ether formation will be favored at lower temperature, the product selectivity will shift to ethylene at higher temperatures [31]. Acetaldehyde can also be formed as a side-product [31]. As shown before [17], diethyl ether, acetaldehyde and butenes were the initial products of ethanol conversion at temperatures in the 300–350 °C range in the presence of Lewis acids. Oligomerization of the resulting olefins can be promoted by strong Lewis acids. Short-chain olefin oligomerization is a commercial process to produce gasoline, middle distillates and lubricant oils [27–30,36]. Although other catalysts are currently implemented, initially AlCl_3 was used as the catalyst for such oligomerization reactions [36].

We propose the following reaction mechanism for Lewis acid-catalyzed ethanol conversion (Fig. 4). The initial step is the acid catalyzed dehydration of ethanol to ethylene or diethyl ether (Fig. 4a) [35]. Coupling reactions of short-chain olefins such as ethylene, propylene and butenes resulted in higher aliphatic hydrocarbons (Fig. 4b). Lewis acid salts such as AlCl_3 and BF_3 have been previously explored as catalysts for the cationic oligomerization of α -olefins [37]. The resulting olefins can be hydrogenated

to paraffins, likely via hydrogen transfer reactions or involving hydrogen obtained due to ethanol decomposition. Ethanol decomposition might be thermal or catalytic [38]. Hydrogen transfer reactions might explain the formation of aromatics next to alkanes.

The carbenium ions involving in the oligomerization reaction can also be involved in the activation of C–H bonds in superacidic media [27,39]. They are electrophilic enough to abstract a hydride anion from linear and cyclic alkanes [39]. These intermediates can also be stabilized forming branched alkanes and alkenes (Fig. 4b). It should also be mentioned that AlCl_3 has been used for the isomerization of *n*-alkanes at temperatures as low as 150 °C [36]. Accordingly, we expect that MCl_n and $\text{M}(\text{OTf})_n$ can catalyze isomerization reactions via hydride shift reactions at 400 °C. We did not observe the formation of higher alcohols in the present study. Even if they were formed, they will be rapidly dehydrated to alkenes. This is supported by the presence of butenes in the product mixture.

Aromatics can be obtained by the cyclization of olefins, a reaction that is well known in the field of zeolite catalysis [20,27]. In such chemistry, cyclization involves transfer hydrogenation reactions between olefins and low carbon number alkanes such as propane and butane [20]. Another mechanism is Diels-Alder reaction [40,41] upon which cyclization can occur in the presence of Lewis acid catalysts (Fig. 4c). As given in Fig. 4d, cyclic carbocations can be aromatized under acidic conditions via hydride transfer reactions [20]. AlCl_3 is also known as a catalyst for alkylation of aromatics, e.g. for the production of ethyl benzene via Friedel-Crafts reactions [35]. This explains the extensive alkylation of aromatics in our study. Thermal cracking of long-chain aliphatic hydrocarbons might also be involved in the reaction mechanism. This will promote formation of methane, ethane, ethylene and propylene [20]. To summarize, ethanol conversion to higher aliphatic hydrocarbons and alkylated mono-aromatics was favorable in the presence of the super Lewis acid catalyst $\text{Al}(\text{OTf})_3$ at 400 °C.

Fig. 4. Proposed reaction mechanism for ethanol conversion. Adopted from Refs. [20,27,39].

4. Conclusion

We show that Lewis acid metal salts can be used to depolymerize lignin in sc-ethanol at 400 °C. In sc-water, the use of Lewis acids mainly led to condensation reactions of the products obtained from Protobind lignin. Char was the main product in this case and monomeric yields were very low. In sc-ethanol, depolymerization of lignin led to much higher organic yields. The degree of depolymerization of lignin increased going from metal acetates to metal chlorides to metal triflates. The choice of the metal cation had comparatively little influence on the product distribution. Ethanol was converted to higher alkanes, alkenes and a small amount of aromatics, most likely via Lewis acid catalyzed dehydration, oligomerization and hydrogen transfer reactions. In addition, the aromatics obtained by thermal cracking of lignin were alkylated.

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References

- [1] Z. Strassberger, S. Tanase, G. Rothenberg, *RSC Adv.* 4 (2014) 25310–25318.
- [2] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, *Renew. Sust. Energ. Rev.* 21 (2013) 506–523.
- [3] V.M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li, J.A. Lercher, *Chem. Eur. J.* 17 (2011) 5939–5948.
- [4] X. Erdocia, R. Prado, M.À. Corcuera, J. Labidi, *Biomass Bioenerg.* 66 (2014) 379–386.
- [5] A. Toledano, L. Serrano, J. Labidi, *Fuel* 116 (2014) 617–624.
- [6] V. Roberts, S. Fendt, A.A. Lemonidou, X. Li, J.A. Lercher, *Appl. Catal. B* 95 (2010) 71–77.
- [7] J.E. Miller, L. Evans, A. Littlewolf, D.E. Trudell, *Fuel* 78 (1999) 1363–1366.
- [8] T. Ogi, S. Yokoyama, *Sekiyu Gakkaishi-JPI* 36 (1993) 73–84.
- [9] R.W. Thring, J. Breau, *Fuel* 75 (1996) 795–800.
- [10] Y. Yu, X. Li, L. Su, Y. Zhang, Y. Wang, H. Zhang, *Appl. Catal., A* 447–448 (2012) 115–123.
- [11] Z. Ma, E. Troussard, J.A. van Bokhoven, *Appl. Catal., A* 423–424 (2012) 130–136.
- [12] F. Davoudzadeh, B. Smith, E. Avni, R.W. Coughlin, *Holzforschung* 39 (1985) 159–166.
- [13] A. Vuori, M. Niemela, *Holzforschung* 42 (1988) 327–334.
- [14] T. Sugita, Y. Tsuji, H. Mori, *Chem. Express* 3 (1988) 507–510.
- [15] M.M. Hepditch, R.W. Thring, *Can. J. Chem. Eng.* 78 (2000) 226–231.
- [16] C. Xu, T. Etcheverry, *Fuel* 87 (2008) 335–345.
- [17] B. Güvenatam (2015), Catalytic pathways for lignin depolymerization, Ph.D. thesis, Eindhoven University of Technology, ISBN: 978-90-386-3844-7.
- [18] X. Huang, T.I. Korányi, M.D. Boot, E.J.M. Hensen, *ChemSusChem* 8 (2014) 2276–2288.
- [19] M. Hronec, K. Fulajtarová, T. Liptaj, *Appl. Catal., A* 437–438 (2012) 104–111.
- [20] D. Seddon, *Catal. Today* 6 (1990) 351–372.
- [21] T.W. Birkby, J.T. Kozłowski, R.J. Davis, *J. Catal.* 298 (2013) 130–137.
- [22] C. Carlini, M. Marchionna, M. Novello, A.M.R. Galletti, G. Sbrana, F. Basile, A. Vaccari, *J. Mol. Catal. A: Chem.* 232 (2005) 13–20.
- [23] M.N. Dvornikoff, M.W. Farrar, *J. Org. Chem.* 22 (1957) 540–542.
- [24] M.J.L. Gines, E. Iglesias, *J. Catal.* 176 (1998) 155–172.
- [25] C. Carlini, M.D. Girolamo, A. Macinai, M. Marchionna, M. Novello, A.M.R. Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* 200 (2003) 137–146.
- [26] I. Takahara, M. Saito, M. Inaba, K. Murata, *Catal. Lett.* 105 (2005) 249–252.
- [27] M. Guisnet, N.S. Gnep, F. Alario, *Appl. Catal., A* 89 (1992) 1–30.
- [28] C.T. O'Connor, M. Kojima, *Catal. Today* 6 (1990) 329–349.
- [29] G.N. Long, R.J. Pellet, J.A. Rabo, U.S. Patent 4 528 414, 1985.
- [30] R. Bauer, P.W. Glockner, W. Keim, H. van Zwet, H. Chung, Shell Oil Co., U.S. Patent 3 644 563, 1972.
- [31] X. Zhang, R. Wang, X. Yang, F. Zhang, *Microporous Mesoporous Mater.* 116 (2008) 210–215.
- [32] T.K. Phung, A. Lagazzo, M.A.R. Crespo, V.S. Escribano, G. Busca, *J. Catal.* 311 (2014) 102–113.
- [33] G. Chen, S. Li, F. Jiao, Q. Yuan, *Catal. Today* 125 (2007) 111–119.
- [34] J. Bedia, R. Barrionuevo, J. Rodríguez-Mirasol, T. Cordero, *Appl. Catal., B* 103 (2011) 302–310.
- [35] H. Xin, X. Li, Y. Fang, X. Yi, W. Hu, Y. Chu, F. Zhang, A. Zheng, H. Zhang, X. Li, *J. Catal.* 312 (2014) 204–215.
- [36] A. Corma, H. Garcia, *Chem. Rev.* 103 (2003) 4307–4365.
- [37] J. Skupińska, *Chem. Rev.* 91 (1991) 613–648.
- [38] C.L. Kibby, W.K. Hall, *J. Catal.* 31 (1973) 65–73.
- [39] G.A. Olah, G.K. Surya Prakash, Á. Molnár, J. Sommer, *Superacid-catalyzed reactions, Superacid Chemistry*, second ed., John Wiley & Sons, Inc., Hoboken, NJ, USA, 2009, pp. 501–756.
- [40] M.J.S. Dewar, A.B. Pierini, *J. Am. Chem. Soc.* 106 (1984) 203–208.
- [41] S. Kobayashi, M. Sugiura, H. Kitagawa, W.W.-L. Lam, *Chem. Rev.* 102 (2002) 2227–2302.