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Ethanol: A Promising Green Solvent for the Deconstruction of Lignocellulose

Kubilay Tekin,[a] Naijia Hao,[b] Selhan Karagoz,[c] and Arthur J. Ragauskas*[bde]

Abstract: Growing energy demand and the need to reduce environmental impact, increase energy security, and rural economic development has encouraged the development of sustainable renewable fuels. Non-food lignocellulosic biomass is a suitable source for sustainable energy because the biomass feedstocks are low cost, abundant, and carbon neutral. Recent thermochemical conversion studies are frequently directed at converting biomass to high quality liquid fuel precursors or chemicals in a single step. Supercritical ethanol has been selected as a promising solvent medium to deconstruct lignocellulosic biomass since the ethanol has extraordinary solubility towards lignocellulosic biomass and can be resourced from cellulosic ethanol facilities. This review provides critical insight into both catalytic and non-catalytic strategies of lignocellulose deconstruction. In this context, the supercritical ethanol deconstruction pathways are thoroughly reviewed; gas chromatography coupled with mass spectrometry (GC-MS), one-dimensional and two-dimensional nuclear magnetic resonance spectrometry (NMR), and elemental analysis strategies towards liquid biomass deconstruction products are critically presented. This review aims to provide readers a broad and accurate roadmap of this novel biomass to biofuel conversion techniques.

Introduction

Ethanol has been widely applied as a viable solvent for the decomposition of lignocellulosic biomass over the last few decades and is classified as an environmentally preferable green solvent as it is produced by fermenting renewable sources including sugars, starches and lignocellulosics.[1] In comparison with other solvents, ethanol is a relatively low-cost solvent and readily available when incorporated into a second-generation cellulosic ethanol production facility. Substitution of organic solvents with an environmentally favorable solvent for the deconstruction of lignocellulosic biomass is indeed of importance in terms of green chemistry and sustainability. Ethanol has a pronounced enhancement of solubility at the supercritical state, which makes an excellent reaction medium for the decomposition of lignocellulose.[2] The critical temperature and pressure for ethanol are as follows: Tc = 240.9 °C, Pc = 6.14 MPa. Furthermore, supercritical ethanol (Sc-EtOH) is less corrosive and more reactive when compared with supercritical water (SCW).[2] Various solvents including alcohols (methanol, ethanol, isopropyl alcohol), polyols (ethylene glycol, glycerol), cyclic ethers (tetrahydrofuran, dioxane), ketones (acetone, methyl isobutyl ketone), and water can be used for the thermochemical processing of lignocellulose. Low boiling point alcohols (e.g., methanol, ethanol, isopropanol) are most common solvents used in the thermochemical processing of lignocellulose due to their ease of recovery and low cost.[3] Although alcohols such ethanol, methanol, and isopropyl alcohol have similar solvent properties such as solvent strengths, dielectric constants, critical points, and hydrogen donation abilities, ethanol has come to the forefront among others due to its non-toxic property. The depolymerization of lignocellulosic biomass in Sc-EtOH benefits from its hydrogen donation ability, high heat transfer efficiency, and it hinders the re-polymerization of unstable fragments of biomass which results in less char formation.[4] The three main components of lignocellulosics are lignin, cellulose, and hemicellulose and Figure 1 presents the typical structures of these components. Most of the studies dealing with biochemical conversion of lignocellulosic biomass mainly focus on the utilization of the carbohydrate components of lignocellulosics to produce liquid fuels.[5] The lignin portion is often considered as a low-value product, which interferes with enzymatic hydrolysis and the fermentation processes. Thus, several chemical and/or mechanical pretreatment methods have been applied to minimize lignin in lignocellulosics prior to a biological conversion. A successful alternative process involves catalytic reductive fractionation of lignocellulose in which lignin is solvolytically extracted and simultaneously depolymerized via hydrogenolysis. The products are a lignin-derived oil and a carbohydrate pulp.[6] Although effective removal of lignin is possible in the catalytic reductive fractionation process, utilization of the entire lignocellulosic biomass is important in terms of economic and environmental point of view. For select bioresources, direct conversion of lignocellulosic without fractionation to biofuels and/or value-added chemicals using an environmentally friendly solvent such as ethanol looks as a promising approach. Studies regarding the decomposition of lignocellulosic biomass in subcritical/supercritical EtOH without and with catalysts has

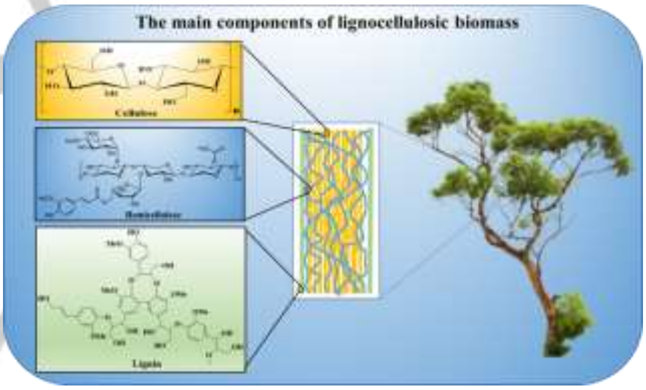

Figure 1. The main components of lignocellulosic biomass.

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become a research focus area and herein, non-catalytic and catalytic decomposition of lignocellulosic biomass and its components in ethanol processing are reviewed. The importance of green solvents in the chemical process as well as lignin utilization using supercritical solvents are well documented in the literature.[7] The present paper exclusively focuses on the deconstruction of lignocellulose as well as its components in ethanol.

Non-catalytic deconstruction of lignin

Lignin is a natural polymer that is composed of phenylpropane units including sinapyl, coniferyl, or *p*-coumaryl alcohol linked through aryl ether bonds (i.e., *α*-O-4-aryl ether, *β*-O-4-aryl ether), and carbon-carbon bonds (i.e., 5-5-biphenyl, *β* -1-(1,2-diarylpropane), *β*-5-phenylcoumaran, and *β*-*β*-(resinol)).These lignin inter-unit linkages are illustrated in Figure 2.[8] Lignin, the most significant non-carbohydrate component in biomass, is found in most terrestrial plants with a content of 15~40%.[9] Wood contains lignin in an approximate range of 25–35%.[10] The composition and amount of lignin in softwood, hardwood, and even in different parts from the same plant is dissimilar.[11] Nonetheless, it is well recognized as a significant future source of renewable oxygenated aromatic hydrocarbons.[12]

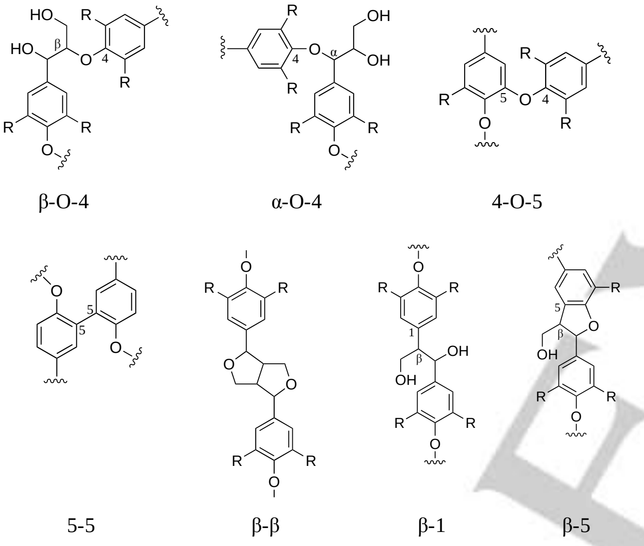

Figure 2. Examples of the most dominant lignin linkages in lignin[8]

Lignin has a rigid and amorphous structure and it is difficult to decompose upon thermal treatment in the absence of oxygen with thermal degradation studies reporting a broad decomposition range between 350 to 600 ºC.[13] Thermal degradation of lignin yields aromatic oxygenates that are being actively investigated as a feedstock for chemical industry or blending with conventional transportation fuels.[14] Jet fuel, a type of aviation fuel, is composed of mixtures of naphtha (C_5–C_{15}) and kerosene (C_9–C_{16}) components; lignin-derived bio-oil has a high potential to meet the requirements of the carbon chain length of jet fuel.[14] Degradation of lignin in Sc-EtOH produces mainly monomeric phenols. Figure 3 presents examples of the monomeric phenols formed from ethanol processing.

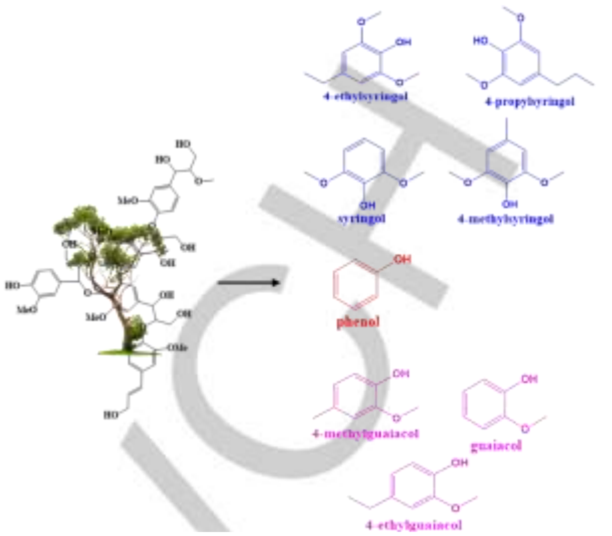

Figure 3. Monomeric phenols from degradation of lignin in ethanol.

Table 1 summarizes the published research efforts regarding both non-catalytic and catalytic conversion of lignin in ethanol. Kim et al. investigated the depolymerization of organosolv lignin produced from poplar wood varying several parameters including temperature (200, 275, and 350 °C), residence time (20, 40, and 60 min), lignin/solvent ratios (50, 100, and 150 g/mL) with an initial hydrogen gas pressures of 2 or 3 MPa.[15] The highest bio-oil yield (94.9 wt%) was obtained at the lowest reaction temperature (200 °C) with a residence time of 20 min and solvent ratio of 100 ml /g lignin, the highest amounts of monomeric phenols were obtained at 350 °C and 40 min and 100 mL/ g lignin (Table 1, entry 1). Depolymerization of Protobind lignin in ethanol was carried out at 200, 250 and 280 °C with residence times of 15, 30 and 45 min under autogenic pressures.[16] The highest bio-oil yield (~81 wt%) was obtained at 200 °C for all tested residence times (Table 1, entry 2), the higher reaction temperature resulted in a decrease in bio-oils. The liquefaction of laboratory prepared lignin from the hydrolysis of red pine sawdust using concentrated sulfuric acid was carried out in EtOH at 293, 300, 333 and 350 °C with a fixed residence time (30 min).[17] The highest bio-oil yield was approximately 30 wt% and obtained at 293 °C (Table 1, entry 3). The bio-oil yield was ~ 25 wt% at 300 °C / 333 °C and lower than the yield of ~30 wt% at 293 °C. The lowest bio-oil yield (~ 23 wt%) was obtained at the highest temperature of 350 °C. Although high yields of bio-oils from ethanol processing of lignocellulose can be accomplished at 200 °C, these bio-oils are mainly composed of oligomer-rich components rather than a monomer-rich fraction at this temperature. The bio-oil yield from the liquefaction of poplar wood derived organosolv lignin does not change significantly between 265 and 350 °C in ethanol whereas the monomeric products increase with increasing the temperature when at relatively short residence times are employed (15-45 min).[15] At the temperatures higher than 350 °C, a great deal of reactive free radicals can be formed in the reaction medium; these free radicals from monomeric lignin fragments come together to form oligomers/polymers which results in an increased amount of char formation. In contrast to aforementioned studies, Nielsen and co-workers found the optimum temperature for the liquefaction of lignin from wheat straw was 400 °C for the highest bio-oil yield.[18]

Table 1. Summary of non-catalytic and catalytic degradation of lignin in ethanol (* operating pressure)

Entry	Feedstock	T (°C)	t (min)	P_{int} (MPa)	Catalyst	Key Findings	References
1	Organosolv lignin	200-350	30-60	2-3 (H_2)	-	[f1]	[15]
2	Protobind lignin	200-280	15-45	-	-	[f2]	[16]
3	Lab prepared lignin using conc. H_2SO_4	293-350	30	2 (N_2)	-	[f3]	[17]
4	Lab prepared lignin from wheat straw	250-450	0-480	-	-	[f4]	[18]
5	Alkali lignin	180-300	60-480	7.2*	10% NaOH	[f5]	[4b]
6	Organosolv lignin	290	0-60	-	Metal hydroxides and metal carbonate	[f6]	[21]
7	Kraft lignin / Organosolv lignin	350	30-180	0.1 (N_2) or 0.3 (H_2)	10 wt% catalyst: MgO loaded different supports (i.e., carbon, Al_2O_3, and ZrO_2), Ru/C, and physical mixtures of Ru/C and MgO.	[f7]	[22]
8	Alkali lignin	300-400	60	11.6-13.2*	Sulfated ZrO_2, sulfated ZrO_2 supported Al_2O_3, and synthesized high-silica zeolites in H form and a commercial zeolite catalyst	[f8]	[23]
9	Concentrated sulfuric acid hydrolysis lignin (CSAHL) / Kraft lignin	350	0-60	21.7-35.1	Formic acid to lignin ratio: 1.5	[f9]	[26]
10	Alkali lignin	440	300	N/A	Metal supported zeolites (Co, Ni, and Cu in loadings 5, 10 and 30 wt% and the Si/Al_2 ratio of ZSM-5 (30, 50, 80 and 200)).	[f10]	[29]
11	Alkali lignin	180-300	0-480	N/A	Raney/Ni or Rh/C catalyst	[f11]	[31]

[f1] The highest bio-oil yield was ~95 wt%.

[f2] The highest bio-oil yield was ~81 wt%.

[f3] The highest bio-oil yield was ~30 wt%.

[f4] The highest bio-oil yield was ~40 wt%.

[f5] The highest bio-oil yield was ~67wt%. Higher temperature resulted in higher relative yields of phenols.

[f6] The lignin conversion was ~93% and obtained with the use of 7.8 meq KOH. The studies with model compounds showed that EtOH-derived products incorpareted into bio-oils.

[f7] The use of co-catalyst incresaed monomeric phenols. By replacing N_2 with H_2, the moleculer weight (Mw) of bio-oil decreased and monomeric phenols yield increased. Under identical conditions, bio-oil from organosolv lignin had a higher yield of aromatic monomers and lower Mw in comparison with Kraft lignin in the catalytic runs (with Ru/C and MgO/ZrO_2 catalyst).

[f8] All catalysts gave higher conversion than that of the non-catalytic run. The highest bio-oil yield was 62.5 wt% and obtained with sulfated ZrO_2 catalyst. Ethanol itself degraded without and with the use of catalyst.

[f9] The conversion and bio-oil yeilds were 99% and 90 wt% for KL and 92 % and 85 wt% for CSAHL. The compounds in the bio-oil were mainly phenols, esters, furans, alcohols, and traces of aliphatic hydrocarbons.

[f10] The highest monoaromatic yield (98.2 wt%) was and obtained with the use of 10 wt% Cu loaded on ZSM-5 with a Si/Al_2 ratio of 30.

[f11] The highest bio-oil yield of ~75wt% was obtained with Raney-Ni catalyst. The use of either Raney/Ni or Rh/C catalyst increased the relative content of phenols.

The authors used lignin which was acid insoluble and obtained from wheat straw via enzymatic hydrolysis. The lignin was processed at 250-450 °C, and residence time (0-8 h). The maximum bio-oil yield from lignin was approximately 40 wt% which was obtained at a temperature of 400 °C with a residence time of 4 h (Table 1, entry 4). Notably, the optimum temperature for high bio-oil yields depends strongly on the type of lignin employed. The differences in starting lignin structure have significant effects on the yields of bio-oils and the products of lignin subcritical/supercritical ethanol processing. Park et al. investigated the relationship between the lignin depolymerization behavior and its structure.[19] Six types of lignin samples were obtained from oak and pine wood using three different delignification techniques (ethanosolv, formasolv, and Klason). As oak wood has a higher content of sinapyl alcohol units, ether linkages in the lignins derived from oak wood were found three times higher than that in the lignins derived from pinewood. The frequency of ether linkages in the lignin samples were as follows: formasolv > ethanolsolv > Klason. The lignin samples were treated in Sc-EtOH and formic acid at 250–350 °C. Depolymerization studies showed that both the plant source and lignin isolation method have effects on subsequent bio-oil yields upon Sc-EtOH treatment. At 350 °C, bio-oil yields higher than 81 wt% and lignin conversion higher than 95% were achieved regardless of the plant source. At a lower temperature, plant source may have a significant impact on bio-oil yields. For example, at 300 °C, oak wood derived formasolv lignin resulted in a bio-oil yield of 86.2 wt%, whereas oak wood derived Klason lignin resulted in a bio-oil yield of 27.9 wt% at the same condition.[19] Several factors, such as biomass type, initial hydrogen pressure, solvent to biomass ratio, reaction autogenous pressure, reaction time, temperature, and different products recovery procedure, may affect the bio-oil yields significantly.[20] Zeb et al. concluded that the high reaction pressure was a major factor towards the bio-oil yields by investigating the effect of solvent to biomass ratio (using two methods: i.e., fix biomass amount while changing solvent amount, fix solvent amount while changing biomass amount). Higher pressure from 22.7 MPa to 42.8 MPa enhanced the bio-oil yield by 110.31%. This finding could be attributed to that the ethanol acted as a hydrogen donating agent, a source of hydrogen, and an esterification agent during the ethanol processing of lignocellulose.[20b]

Catalytic deconstruction of lignin

Most recent Sc-EtOH studies have focused on the role of catalysts for the decomposition of lignin. The catalytic decomposition of lignin in ethanol significantly changes bio-oil compositions when it is compared to noncatalytic decomposition of lignin. Several homogenous and heterogeneous catalysts have been tested for the deconstruction of lignin in Sc-EtOH. Heterogeneous catalysts are more attractive than homogeneous catalysts for the decomposition of lignocellulosic materials in ethanol as they can be easily separated and re-used. However, a high catalyst to biomass ratio might be required for the efficient decomposition of lignocellulose in ethanol. Guo and co-workers investigated autocatalytic depolymerization of alkali wet straw lignin impregnated with NaOH in subcritical/supercritical EtOH (T=150-300 °C, t=1-8 h).[4b] The highest lignin conversion yield and bio-oil yield (obtained at the temperature of 240 °C and a residence time of 4 h with a pressure of 7.2 MPa) were 74.88% and 67.58%, respectively (Table 1, entry 5). Miller and co-workers investigated the depolymerization of Kraft- and organosolv-derived lignins in Sc-EtOH using various bases including KOH, NaOH, CsOH, LiOH, $Ca(OH)_2$, and Na_2CO_3 at 290 °C for 1h.[21] It was reported that stronger bases were found to be more effective for the deconstruction of lignin under Sc-EtOH conditions. In the case of KOH, the conversion of lignin was 93% (Table 1, entry 6).

The positive synergistic effect of co-catalyst (a combination of metal supported carbon and solid-base catalysts) to produce monophenol-rich bio-oil from lignin in ethanol was demonstrated by Limarta and co-workers.[22] Kraft lignin was depolymerized in ethanol at 350 °C for 60 min without and with catalysts (i.e., MgO/C, MgO/Al_2O_3, MgO/ZrO_2, Ru/C, Ru/C+MgO/C, $Ru/C+MgO/Al_2O_3$, and $Ru/C+MgO/ZrO_2$). The bio-oil yield from the non-catalytic was found to be 36.2 wt%. All tested catalysts produced more bio-oil than that of the non-catalytic run. Although the maximum bio-oil yield (88.1 wt%) was obtained with Ru/C, the use of co-catalyst (i.e., mixture of Ru/C and MgO/ZrO_2) increased the monomeric phenols (Table 1, entry 7). The phenolic monomer yield was 1.70 wt% in the non-catalytic run and the co-catalyst of Ru/C and MgO/ZrO_2 increased the phenolic monomer yield to 5.16 wt%.[22] It was suggested that ethanol acted as a nucleophilic reagent for C-O-C cleavage through alcoholysis reactions, while Ru/C and MgO are most responsible for the depolymerization of fragmented species into monomeric and smaller fragments. The above-mentioned lignin depolymerization reactions were solvolysis-based carried out under a nitrogen atmosphere. The authors also investigated lignin depolymerization through hydrogenolysis, the catalytic reactions using $Ru/C+MgO/ZrO_2$ were carried out at 350 °C for 60 min under H_2 atmosphere. The use of H_2 instead of N_2 led to the slight reduction of the bio-oil yield from 79.6 wt% to 76.9 wt% but molecular weight of bio-oil was decreased from 861 g/mol to 784 g/mol. This finding may suggest that the external hydrogen did not contribute to a larger degree of lignin depolymerization since ethanol may supply a sufficient amount of hydrogen at this reaction temperature 350 °C using Ru/C as a catalyst.

Kuznetsov and co-workers investigated the effects of sulfated ZrO_2, sulfated ZrO_2 supported Al_2O_3 catalysts, and acidic zeolite catalysts for the decomposition of alkali lignin from Aspen wood in ScEtOH at 350 and 400°C.[23] Alkali lignin was depolymerized without and with the use of sulfated ZrO_2, sulfated ZrO_2 supported Al_2O_3, and various laboratory synthesized high-silica zeolites [in H-form with Si/Al = 100 (HHSZ-100) and Si/Al = 30 (HHSZ-30)] and a commercial zeolite [with Si/Al = 4.9 (HY)] catalysts at 300, 350 and 400 °C and a residence time of 60 min. The tested catalysts gave higher conversion than that of the control trial with no catalyst. For example, at 350 °C, the conversion of the lignin reached ~60 wt% in the presence of ZrO_2-Al_2O_3 compared to ~53 wt% in the non-catalytic run. At 400 °C, the conversion of the lignin reached ~72 wt% in the presence of ZrO_2-Al_2O_3 under 26.0 MPa compared to ~49 wt% in the non-catalytic run. The highest bio-oil yield was 62.5 wt% employing the sulfated ZrO_2 catalyst (Table 1, entry 8). The yielded bio-oils contained a wide range of organic compounds including esters, ethers, phenols, aldehydes, ketones, alkanes, and alkenes. The relative yield of ethers significantly increased with all tested catalysts. Notably, ethanol itself was degraded without and with the use of a catalyst under the reaction conditions. However, the conversion of ethanol from the non-catalytic run was low and increased with the use of catalyst.[23] The primary product from ethanol conversion was 1,1-diethoxyethane for all tested catalysts. Under the high reaction temperatures (i.e., 300 and 350 °C), ZrO_2 containing catalysts resulted in higher yields of gas whereas the high temperatures did not show significantly changes of the gas formation in the presence of zeolites.

It is well known that formic acid generates *in-situ* hydrogen at elevated temperatures above 200 °C and its use in lignin solvolysis/hydrogenolysis reactions in ethanol yields higher bio-oils as the addition of formic acid suppress the formation of char, and hinders the recombination of reaction intermediates.[24] Notably, ethanol also acts as an effective hydrogen donor by hydride transfer of its α-hydrogen.[25] The combine effect of ethanol and formic acid enhances the yields of de-polymerized lignin. Riaz and co-workers demonstrated that the use of formic acid with lignin under Sc-EtOH conditions provided a high conversion (92%) and bio-oil yield (85 wt%) at 350 °C with a residence time of 30 min and a formic acid-to-lignin mass ratio of 1.5 (Table 1, entry 9).[26] The crude bio-oil contained phenols, esters, alcohols, and traces of aliphatic compounds. The relative content of the detectable hydrocarbons by gas chromatography coupled with mass spectrometry (GC-MS) changed depending on the reaction conditions employed (i.e., residence time, pressure, and catalyst to lignin ratio). Phenols and esters were dominant products in catalytic runs. For example, with a formic acid to lignin mass ratio of 0.5, the total percentage of phenols plus esters exceeded 47 wt%. Among the phenolic compounds, phenol was the major product but methyl, methoxy, and ethyl groups bonded to the aromatic ring were observed. The phenolic compounds with different substitution patterns are mainly formed from monomers lignin fragments under acid catalyzed ethanol processing conditions.[10] The formation of ethyl esters takes place under Sc-EtOH reaction conditions. Although the exact mechanism for the acid-catalyzed depolymerization of lignin in ethanol is not fully known, the cleavage of etheric bonds in lignin is considered to have an important effect on the product compositions. In most native lignocellulosics constituents, the amount of ether linked inter-unit linkages are much higher than carbon-carbon interunit linkages. For example, Evtuguin et al. reported that Eucalypt lignin showed abundance of β-O-4 linkage (0.56 per aromatic C_6), α-O-4 linkage (0.23 per aromatic C_6), and β-β linkage (0.13 per aromatic C_6).[27] These etheric bonds are less stable and readily ruptured under elevated Sc-EtOH conditions. The depolymerization of lignin in ethanol is enhanced with the use of an acidic catalyst leading to the rupture of ether and carbon-carbon bonds are cleaved producing monomeric and oligomeric reactive free radicals. Some of these radicals are stabilized by ethanol and subsequently quenched but repolymerization still occurs.[28] These possible two pathways competitively occur depending on operating conditions (i.e., temperature, residence time, catalyst amount, and strength of acid).

Zeolites, especially ZSM-5, catalyze aromatization and cracking reactions due to their ideal pore structure and acid sites for the reaction.[29] Jeong et al. examined the depolymerization of Protobind lignin in the presence of metal supported ZSM-5 catalysts (Co, Ni, and Cu) using ethanol as a solvent at 440 °C for 5 h.[30] The type of metal, as well as Si/Al_2 ratio, played a crucial role on the yields of monoaromatic products. The highest monoaromatic yield was 98.2 wt% obtained with the use of 10 wt% Cu loaded on ZSM-5 with a Si/Al_2 ratio of 30 (Table 1, entry 10). It was demonstrated that there is a linear correlation between the acid density of Cu/ZSM-5 with various Si/Al_2 ratios and the yield of monoaromatic compounds. The aluminum content of extra framework increased with decreasing in the Si/Al_2 ratio, which resulted in an increase of the acidity of the catalyst which increased the yield of monoaromatic under Sc-EtOH conditions. Selected monoaromatic compounds from catalytic runs were determined and were shown to be mainly composed of benzaldehyde, ethylbenzene, *m*-xylene, toluene together with some minor compounds such as o-cresol, 2-ethylphenol, and syringol.

Heterogeneous catalysts such as Raney Ni, Pd/C, Rh/C have been used for the lignin hydrogenation reactions and earlier studies were mainly aimed at the structural elucidation of the lignin.[31] Guo et al. carried out the depolymerization of alkali lignin from wheat straw in subcritical/supercritical EtOH using either Raney/Ni or Rh/C catalysts. The use of Raney/Ni or Rh/C catalysts increased bio-oils yields at all tested temperatures (180-300 °C) and residence times (1-8 h) compared to non-catalytic runs.[32] The use of either Raney/Ni or Rh/C catalysts promoted the hydrogenation of the fragmented intermediates, which inhibits repolymerization reactions. The highest bio-oil yield of ~75 wt% was obtained with Raney-Ni catalyst at 240 °C and a residence time of 4 h (Table 1, entry 11) compared to the yield of ~62 wt% in the non-catalytic run under the same reaction temperature and time. Analysis of the bio-oils detected the presence of esters, ketones, acids, and phenols. The use of either Raney/Ni or Rh/C catalyst increased the relative content of phenols under all tested temperature (i.e., 180, 240 and 300 °C) and residence times (i.e.,1, 4, and 8 h). For example, at 180 °C, the non-catalytic run resulted in a relative content of phenols of 14.85%, the use of Raney/Ni and Rh/C promoted the content of phenols to 27.88% and 29.60%, respectively. The use of the catalyst increased the amount of de-polymerized lignin, which resulted higher yields of phenolics as the phenol is the basic entity of lignin structure. Although the char yield decreased in the catalytic runs, char formation was observed in both non-catalytic and catalytic runs. Li's group at Tianjin University demonstrated that the Kraft lignin could be completely converted into bio-oil with the help of a molybdenum carbide catalyst at 280 °C for 6 h.[33] The bio-oil consisted of C_6–C_{10} esters, alcohols, arenes, phenols, and benzyl alcohols in remarkably high yield without any tar or char formation. Ethanol formed a complex on the surface of the catalyst which served as the active site and facilitated the formation of reactive intermediates, which then functionalized the lignin fragments formed during the Sc-EtOH reaction. The same group also investigated the decomposition of Kraft lignin over various molybdenum-based catalysts (i.e., MoO_3/Al_2O_3, Mo/Al_2O_3, Mo_2N/Al_2O_3, and α-MoC_{1-x}/AC) at 280 °C in Sc-EtOH for 6 h and an initial nitrogen pressure of 0.5 MPa.[34] It was demonstrated that Mo-based catalysts showed remarkable catalytic performance for the decomposition of lignin in Sc-EtOH producing promising overall yields of high-valued chemicals without tar and char formation. For example, the total depolymerized product yield was promoted to 1640 mg/g lignin using α-MoC_{1-x}/AC catalyst compared to a total depolymerized product yield 173 mg/g lignin in the non-catalytic run. The possible reaction pathway for the formation of C_6−C_{10} oxygenated compounds is shown in Figure 4.[34] The suggested reaction steps involve the formation of lignin fragments by the noncatalytic decomposition of the lignin and interactions of these fragments with the radicals generated from ethanol in the presence of Mo-based catalysts. It was also mentioned that ethanol itself was degraded and incorporated into the fragments from lignin that are present in the reaction medium during Sc-EtOH process. The authors investigated the conversion of EtOH with a selected catalyst (Mo/Al_2O_3) under same conditions and the results were compared with the processing of lignin and EtOH together with the catalyst. The compounds that are believed to be released from the degradation of EtOH in the presence of Mo/Al_2O_3 are shown in Table 2. The degradation of EtOH with Mo/Al_2O_3 produced mainly acetaldehyde, ethyl acetate, butanol, and 1,1-diethoxyethane with amounts of 879, 1615, 917, and 651 mg/g lignin, respectively. When a Sc-EtOH treatment was conducted with the catalyst and lignin, the product mixture contained acetaldehyde, ethyl acetate, butanol, and 2-butenol were the main compounds in the amounts of 566, 526, 982, and 410 mg/g of lignin applied, respectively.

Hensen's group at the Eindhoven University of Technology investigated transition metal (i.e., Ti, Mo, Nb, W) nitrides and TiO_2 catalyst for lignin depolymerization in Sc-EtOH at 300 and 340 °C for 1 h.[35] The highest THF soluble fraction (~61 wt%) was obtained with the use of W_2N (urea glass) at 340 °C for 1 h. The highest aromatic monomer yield was ~19 wt% and this was obtained with the use of TiN (urea glass). The products obtained with TiN were classified as hydrogenated cyclics, oxygen-free aromatics, and oxygen-containing aromatics. The metallic character of TiN facilitated hydrogen transfer reactions of the solvent, which were attributed to the presence of hydrogenated cyclics (mostly cyclohexenes). Of significance, alkylated aromatic products were obtained in bio-oils.

Studies regarding the use hydrotalcite-like catalyst (Cu–MgAlOx) for the depolymerization of lignin in Sc-EtOH has attracted much attention from the scientific community.[36] Hensen's group tested Cu-Mg-Al mixed oxide catalysts for the depolymerization of lignin in Sc-EtOH.[36d] They examined the depolymerization of lignin at the temperatures 300 and 380 °C and residence times of 4 and 8 h.[36d] The highest THF soluble fraction (bio-oil) was ~73 wt% obtained at 300 °C and 4 h. Formation of repolymerized products (solid residue containing char and catalyst) was a result of a balance among depolymerization, repolymerization, and alkylation (shown as Figure 5).[36c] C-alkylation and O-alkylation of the products were confirmed using model compounds (i.e., o-cresol, 2,4,6-trimethylphenol, and anisole) at 300 °C for 1 h over a CuMgAlOx catalyst. In a subsequent paper by the same group, the same catalyst (CuMgAlOx) was used, but the effect of Cu content and (Cu+Mg)/Al ratio on the product distribution from the decomposition of alkali lignin from the hydrolysis of wheat straw was investigated.[36a] The catalyst samples were denoted as CuxMgAl(y), where x referred to as the Cu content (by weight), and y was the atomic ratio of (Cu+Mg) /Al. The optimum catalyst,

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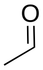
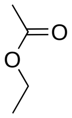
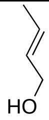
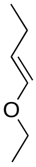
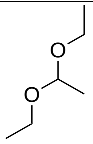
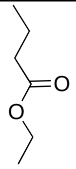
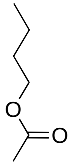
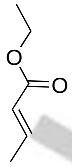
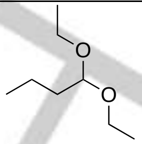
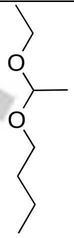
Table 2. Yields (mg/g of lignin) of the products from ethanol degradation without and with Kraft lignin added at 280 °C for 240 min over 0.5 g Mo/Al_2O_3 catalyst with initial 0.1 MPa of N_2 and 100 mL of ethanol.[33] Reprinted with permission from reference [33].

Aliphatics											
Without KL	879	1615	917	2	7	651	80	25	21	26	30
With KL	566	526	982	410	3	79	58	60	17	3	4

which has the highest total basic sites (0.35 mmol/CO_2), was found to be as $Cu_{20}MgAl_{(4)}$ and produced ~36 wt % monomers without formation of char at 340 °C for 4 h. Total basic sites of the tested catalyst strongly affected THF soluble yields, monomer yields and their contents at 340 °C for 4 h. All the tested catalysts produced high yields of C_{4+} alcohols and esters. It was mentioned that these products were formed via Guerbet-type reactions as well as esterification reactions. As shown in Figure 6, the Guerbet reaction is a condensation reaction of primary or secondary alcohols to the branched alcohols.[37] The higher the basicity of the catalyst gave higher amounts of alcohols and esters via Guerbet-type and esterification reactions.[36a, 38]

As mentioned above, alkylation reactions play an essential role for suppressing char formation. The authors used phenol as a model compound to determine the alkylation degree of phenol in ethanol at 340 °C for 4 h over the mixed oxide catalysts using HSQC NMR spectrometry as a semiquantitative analysis tool together with the GC-MS.[36a] The highest degree of alkylation for phenol was 8.1 and was obtained with Cu_{20}/γ-Al_2O_3. Alkylation from ethanol was also observed during the decomposition of lignin in Sc-EtOH using homogenous Lewis acids.[39] The studies above focused on either alkylated products and alkylation degree or ethanol self-degradation with catalysts under the conditions that lignin depolymerized.[34, 36a, 36d, 39] Reactions of ethanol via alkylation and esterification reactions were frequently determined using HSQC NMR data.[36a, 36c] In an earlier published work by Miller and co-workers (1999), the authors demonstrated the incorporation of EtOH-derived products into the bio-oil attributed to the presence of base catalysts using model compounds at 290 °C for 1 h in the presence of KOH.[21] The studies with model compounds (e.g., phenyl ether, phenol, catechols) showed that ethanol participated in the reactions of phenyl ethers and led to phenols and ethyl ethers that were subject to further reactions. Also, phenols and catechols were alkylated by ethanol or one of its products, then produced ethyl phenol and catechols. The experiments using alcohol and base demonstrated that ethanol was primarily converted into acetic acid and 1-butanol. As stated earlier, incorporation of ethanol into the products derived from lignin may also occur during non-catalytic Sc-EtOH processing, but this is limited.[18, 23, 40] The most important question is the amount of EtOH derived products, which were incorporated into bio-oils after Sc-EtOH processing of lignin. The preferred way to assess the amount of EtOH derived products is to determine the overall carbon balances as EtOH itself can transform into the bio-oil as well as gaseous products.[41] Carbon balances that exceed 100 % can provide an estimate on the quantity of EtOH-derived

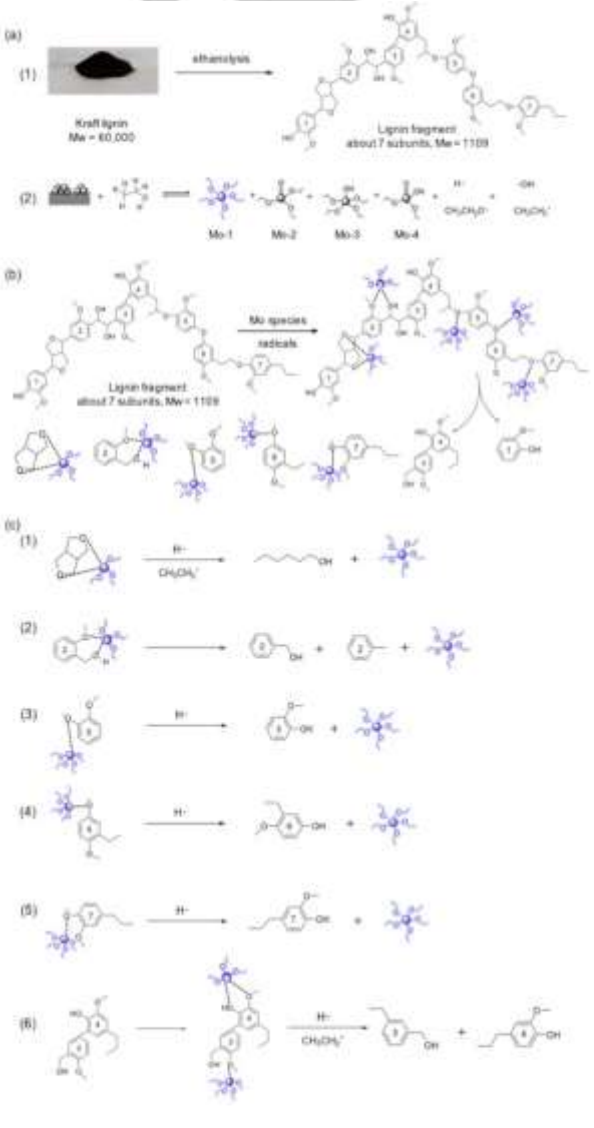


Figure 4. Possible Reaction Pathways of (a) Ethanolysis of Lignin and Formation of Active Mo Species and (b, c) Formation of the Final Products.[34] Reprinted with permission from reference [34].

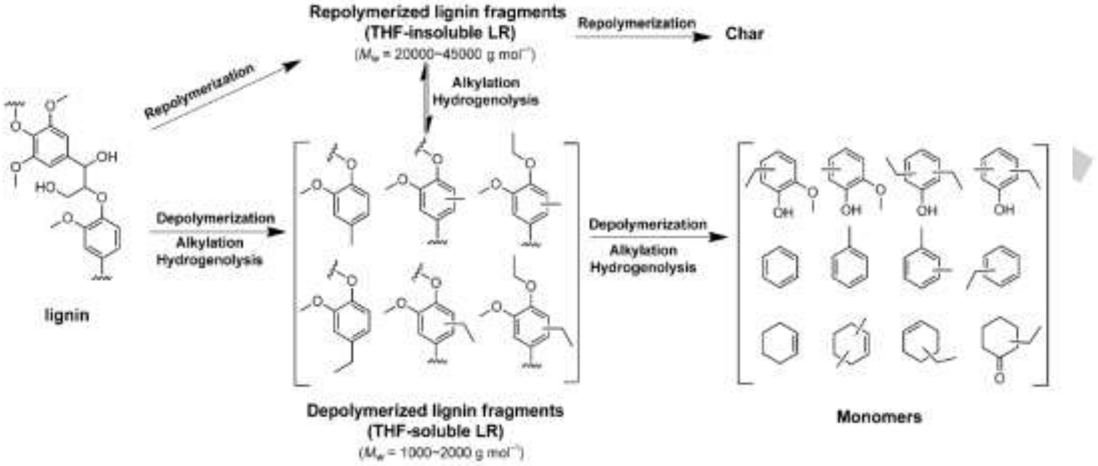


Figure 5. Possible reaction routes during lignin depolymerization in ethanol in the presence of catalyst.[36c] Reprinted with permission from reference [36c].

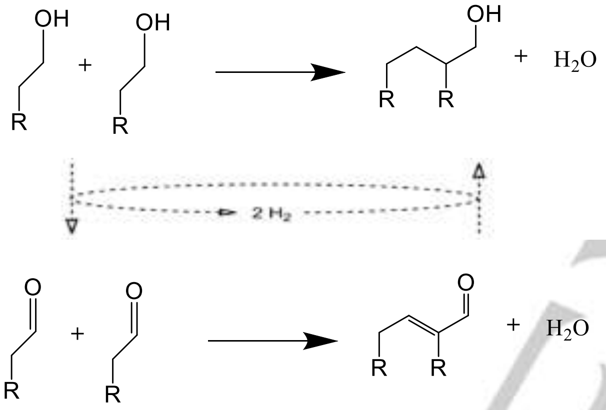


Figure 6. Schematic representation of the Guerbet reaction for primary alcohols.[37] Reprinted with permission from reference [37]

products incorporated into the bio-oils. In a very recent study, Hensen's group at the Eindhoven University of Technology estimated the amount of ethanol derived products in the bio-oils using carbon-14 dating analysis of the bio-oils.[36b] The carbon-14 dating technique can distinguish carbon from biomass and carbon from petroleum derived sources. Biomass includes a fixed amount of ^{14}C which is close of the ^{14}C content of atmospheric CO_2; on the other hand, fossil fuel derived ethanol contains only very small amounts of ^{14}C due to its radioactive decay (half-life of 5730 years). For this purpose, the authors carried out their experiments with ethanol derived from petroleum.[36b] The results demonstrated that the amount of incorporated carbon atoms from ethanol was 18% at 200 °C. Remarkably at 380 and 420 °C, the values were reported to be 60 and 61%, respectively. As expected, more degradation products from ethanol take place at higher reaction temperatures, which results in increased participation of fragments from ethanol into the bio-oil. The method used by Huang et al. is interesting as well as tedious. [36b] For future studies, it would be interesting to compare the results from carbon balance and the results from the ^{14}C technique for the estimation of ethanol derived carbon amounts attached into the bio-oils after the deconstruction of lignin in ethanol medium.

Deconstruction of cellulose in ethanol

In contrast to lignin subcritical/supercritical EtOH studies there are only a few studies which examine the reactivity of cellulose under these conditions. Brand and Kim reported the liquefaction of cellulose at the temperatures of 265, 280, 300, and 350 °C with ethanol under an initial nitrogen pressure of 2 MPa.[17] In case of cellulose, the bio-oil yield was only 1.6 wt% at 265 °C. It was raised to 48.4 wt% when the temperature was increased to 350 °C. The gas product mainly consisted of carbon monoxide (CO) and carbon dioxide (CO_2). Typically, the mole yield of CO was higher than the mole yield of CO_2 except at the temperature of 265 °C. For example, CO has a mole yield of 9.8 mol% whereas CO_2 has a mole yield of only 4.1 mol%. Except at the temperature of 265 °C, the mole yield of CO was higher than the mole yield of CO_2. The cracking of the glycosidic linkage of cellulose is believed to lead to the formation of CO. Trace amounts of C_2 gases (C_2H_4 and C_2H_6) were detected in gas phase from cellulose decomposition in ethanol. The compounds detected by GC-MS from the decomposition of cellulose in ethanol were esters, acids, furans, glucose, ethers, ketones, and cyclopentanones. At 350 °C, the total relative yield of esters was the highest and reached 37.46 wt%.[17] Ester compounds in bio-oils help to reduce some of the unwelcome properties of typical bio-oils such as high acidity, corrosiveness, and thermal instability.[17, 42] Hong-Xiu and co-workers carried out the decomposition of cellulose in ethanol at 320 °C for 60 min.[43] They investigated the effect of ethanol to cellulose ratio on the bio-oil yield and its composition. The highest conversion and bio-oil yield were approximately 86% and 55 wt%, respectively and this was obtained at the solvent to cellulose ratio of 10:7. The bio-oil is composed of ketones, acids, esters, alcohols, and furans. An increase in solvent to cellulose ratio increased the formed ketones.

The generally accepted mechanism for the cellulose decomposition with an acid catalyst in ethanol starts with the conversion of cellulose into ethyl glucosides followed by formation of furan intermediates via dehydration of ethyl glucosides units. Further decomposition of furans produces esters (as shown in Figure 7).[44] Sels' group at the University of Leuven converted cellulose into ethyl levulinate sulfonated hyperbranched poly(arylene oxindole)s catalyst (5-Cl-SHPAO) in ethanol at the temperatures of 150, 160, 170, 180 and 190 °C and for 2, 3, 4, 6, and 10 h.[45] The highest ethyl levulinate yields were 60 % obtained at 160 °C for 6 h with a complete conversion of cellulose. Notably, the formation of humins occurred as a side product which accounted for the major carbon loss in the reaction. It is probable that some furan intermediates from cellulose were transformed into humins. In a previous report, it was demonstrated that humins are produced from furan via primarily aldol addition and condensation reactions.[46] Huber's group at the University Wisconsin also proposed that humins could also be produced from oligosaccharide intermediates during aqueous phase acid-catalyzed decomposition of cellulose.[47] In another study, cellulose obtained from cotton was treated with hydrochloric acid either in ethanol or water at the temperatures of 45 and 65 °C for 1–5 h.[48] Soluble sugar contents were the highest at 65 °C for 5 h using ethanol as a solvent.

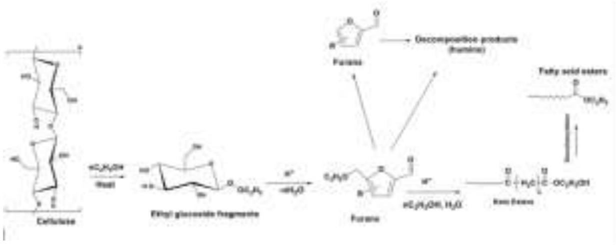


Figure 7. Acid-catalyzed decomposition of cellulose in ethanol.[43] Reprinted with permission from reference [44].

Deconstruction of lignocellulosic biomass in ethanol

Lignocellulosic biomass has been used as a raw material in biomass processing studies using ethanol as a supercritical solvent. Efficient conversion of lignocellulosic biomass into biofuels in ethanol remains a challenging process. Akalin et al. investigated the effects of process parameters on the bio-oil yield (wt%) and biomass conversion (%) produced from the liquefaction of the beech wood in ethanol media at different temperatures (from 265 to 320 °C), residences times (from 37 to 143 min) and biomass loadings (from 4 to 16 wt%).[49] The individual and interaction effects of process parameters were investigated statistically. The most significant factor on the bio-oil yield and biomass conversion was found to be the reaction temperature. The highest bio-oil yield from beech wood was obtained at 300 °C and it was about 40 wt% of the starting biomass (Table 3, entry1). Subsequently, the decomposition of Hawthorn stones (separated from the fruits) was carried out in ethanol at different temperatures (from 280 to 320 °C), residence times (60, 90 and 120 min) and biomass loading (~8-12 wt%).[50] The statistical investigation by a chemometric approach demonstrated that the most significant factor was the temperature which affected bio-oil yields as well as biomass conversions. The highest crude bio-oil yield was approximately 41 wt% (Table 3 entry 2). Another important study investigated effects of operating parameters (i.e., temperature, residence time, initial nitrogen pressure, biomass/solvent ratio) for the liquefaction of pine wood in ethanol. The tested temperatures, residence times, pressures, and biomass/solvent ratio were 280-400 °C, 0-240 min, 0.4-7.5 MPa, and 0.06-0.25 g/g, respectively.[51] Brand et al. demonstrated that the reaction temperature and residence time had pronounced effects on the bio-oil yields as well as biomass conversions from pine wood using ethanol as a solvent.[51] An increase of the temperature from 280 to 400 °C led to an increase in the bio-oil yield and the maximum bio-oil yield was observed to be 59.9 wt% at 400 °C (Table 3, entry 3). Biomass conversion also increased from ~34 to 98% with increasing the temperature from 280 to 400 °C. Almost 100% conversion of solid biomass into liquid and gaseous products was reported at 400 °C. Notably, 90% of beech wood decomposes in Sc-EtOH at 350 ºC with a residence time of 30 min.[52] A two-step process for the liquefaction of lignocellulosic biomass in ethanol has also been proposed.[53] Rice straw was first pretreated at 200 °C for 10 min with CO_2. After this first step, the slurry was then liquefied in ethanol at 275–345 °C for either 15 or 30 min. The highest biomass conversion and bio-oil yield was ~80 % and 48 wt %, respectively and obtained at 345 °C and 15 min residence time (Table 3, entry 4). In a subsequent work reported by Li et al., rice stalk was torrefied in a fixed-bed reactor at 200, 240, and 280 °C, respectively.[54] The torrefied rice stalk was depolymerized at 325 °C in ethanol for 60 min. The torrefaction process led to a decrease in bio-oil yields and biomass conversion. The increase in torrefaction temperature decreased bio-oil yield and increased solid residue yield. The highest biomass conversion and bio-oil yields were ~78% and ~55 wt% and obtained from non-torrefied rice stalk. However, the highest ester content and heating value were obtained with torrefied rice stalk at 200 °C (Table 3, entry 5).

All aforementioned studies demonstrated that the temperature is the most significant factor which affects bio-oil yields and biomass conversions. The second important parameter is the residence time. The initial pressures have little effect on the resulting bio-oils and biomass conversions. The type of biomass used is important for the determination of the optimal conditions for the highest bio-oil yields. Because, the yields are affected by the structure of the various biopolymers. It seems to be the temperature range from 300 - 400 C° is the optimum temperature for the liquefaction of lignocellulose in ethanol (Figure 8).[55]

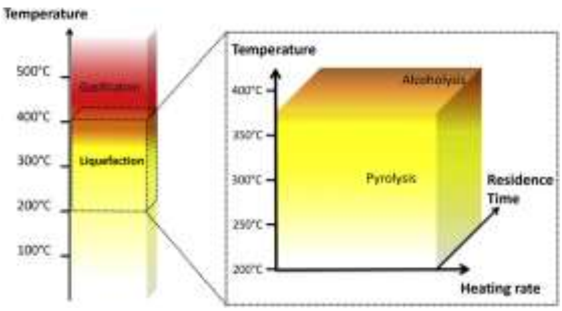


Figure 8. Liquefaction of lignocellulosic biomass in ethanol depending on the temperature, heating rate, and residence time.[55] Reprinted with permission from reference [55].

The use of homogeneous and heterogeneous catalysts also change optimum process conditions including temperature, time, initial pressure, biomass/solvent ratio for the highest crude

Table 3. Summary of non-catalytic and catalytic degradation of lignocellulosic biomass in ethanol (* operating pressure)

Entry	Feed	T (°C)	t (min)	P_{int} (MPa)	Catalyst	Key Findings	References
1	Beech wood	265-320	37-143	9-17* (purged with N_2)	-	[f1]	[48]
2	Hawthorn stones	280-320	60-120	1.0 (N_2)	-	[f2]	[49]
3	Pine wood	280-400	0-240	0.4-7.5 (N_2)	-	[f3]	[50]
4	Rice straw	275-345	15-30	N/A (purged with CO_2)	-	[f4]	[52]
5	Rice stalk	200-280 (Torre.) 325 (Rxn. Temp.)	60	14-15* (N_2)	-	[f5]	[53]
6	Pine wood	200-350	15-60	2-10 (H_2)	($FeSO_4$). $7H_2O$ and FeS	[f6]	[25]
7	Wood sawdust	300-400	40	2-10 (H_2)	[BMIM]Cl/$NiCl_2$	[f7]	[55]
8	Wood sawdust	320	40	2-6 (H_2)	MoO_2/SiO_2	[f8]	[56]

[f1] The highest biomass conversion and bio-oil yields were 88.5 % and 40.4 wt%.

[f2] The lowest and highest biomass conversion were ~55 and 83 %, respectively. The bio-oil yields were in the range from ~32 to ~41 wt%.

[f3] Biomass conversion were in the range ~34-98 1%. Bio-oil yield ranged from ~16 to 60 wt%.

[f4] In the first step, rice straw was pretreated at 200 °C for 10 min. In the second step, the temperature was raised to the desired temperature The highest biomass conversion and bio-oil yield was ~80 % and 48 wt% , respectively.

[f5] The highest biomass conversion and bio-oil yields were ~78% and ~55 wt% were obtained with non-torrefied rice stalk. The torrefaction process led to a decrease in biomass conversion and bio-oil yields but increased heating values of bio-oils.

[f6] The highest bio-oil yield was ~63 wt% and obtained with ($FeSO_4$). $7H_2O$ at 350 °C. Phenolic compounds were dominant regardless the type of catalyst.

[f7] Biomass conversion and bio-oil yields from the non-catalytic run were ~63 % and ~33 wt%, respectively. The biomass conversion was increased to ~70 % and the bio-oil yield was ~50 wt % with [BMIM]Cl/$NiCl_2$.

[f8] Biomass conversion and bio-oil yields were ~79 % and ~47 wt% in the non-catalytic run. Biomass conversion and bio-oil yields were ~90 % and ~72 wt% in the catalytic run.

bio-oil yield and biomass conversion. In earlier studies, various heterogeneous catalysts were tested for the conversion of lignocellulosic biomass in ethanol. Xu and Etcheverry investigated iron-based catalysts (FeS or $FeSO_4$) for the deconstruction of Jack pine powder in subcritical/supercritical EtOH.[25] The tested operating conditions were as follows: the temperature at between 200 and 350 ºC, initial hydrogen pressures at between 2.0 and 10.0 MPa, reaction times 15 and 60 min, 5 wt% of catalyst loading. The highest oil yield from the non-catalytic run was about 44 wt% at 350 ºC employing a residence time of 40 min and an initial hydrogen pressure of 2 MPa. The use of $FeSO_4$ increased the crude bio-oil yield to 63 wt% at 350 ºC and 40 min and an initial hydrogen pressure of 5 MPa (Table 3, entry 6). The use of catalyst decreased the heating values of crude oils. The heating values of crude bio-oil was 31.8 MJ/kg with no catalysts. It was 29.3 MJ/kg with $FeSO_4$ and 18.5 MJ/kg with FeS. Although iron based catalyst have ability to provide high bio-oil yields, they were unable to hydrodeoxygenate the resulting bio-oils. Thus, the low heating values obtained with the use of iron based catalysts in comparison with no catalyst. Phenolic compounds were dominant in all oils regardless of the type of catalyst or whether the catalyst was used or not. The use of high-pressure hydrogen and Sc-EtOH promoted the formation of long-chain alkanes. Recently, Liu and co-workers used a combination of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and nickel (II) chloride ($NiCl_2$) for the liquefaction of wood chips in ethanol.[56] The experiments were carried out at the temperature ranging from 300 to 400 ºC and initial hydrogen pressures varying from 2 to 10 MPa and a residence time of 40 min without and with co-catalyst (1.2 wt.% [BMIM]Cl and 300 µg/g $NiCl_2$). The bio-oil yield from the non-catalytic run was about 32.6 wt% and it was increased to 49.5 wt% using [BMIM]Cl/$NiCl_2$ catalyst (Table 3, entry 7). The identified compounds in light and heavy bio-oils from the liquefaction of wood chips were mainly composed of ester, phenols and carboxylic acids. No information was provided whether these compounds are generated from the catalytic or non-catalytic run. The same group synthesized silica-supported monoclinic molybdenum dioxide (MoO_2/SiO_2) catalyst for the liquefaction of wood in the form of sawdust in ethanol at 340 ºC for 40 min.[57] The crude bio-oil yield was 47 wt% at 320 °C for 40 min using an initial hydrogen pressure of 2 MPa. The use of the catalyst increased the bio-oil yield to ~60 wt% under same conditions (Table 3, entry 8). An increase of the initial pressure of hydrogen from 2 to 6 MPa, increased the crude bio-oil yield from ~60 to ~72 wt%. The metallic sites of MoO_2 can dissociate hydrogen and can produce active hydrogen atoms.[58] It is proposed that active hydrogen atoms aids to decompose lignocellulose in ethanol. Increasing the initial hydrogen pressure produce more active hydrogen which resulted in more bio-oil and less bio-char.[57] In a very recent study, Akalin et al. investigated the decomposition of beech wood was carried out in ethanol without with the use of hydrated cerium (III) chloride at 300 °C with residence times from 10 to 120 min.[44] The bio-oil yields from catalytic runs were higher than those of bio-oils from the non-catalytic runs under identical conditions. The highest bio-oil yield was ~48 wt% and obtained at 300 °C using 5 mmol of hydrated cerium (III) chloride at a residence time of 90 min in ethanol. In the non-catalytic run, phenols and esters were the dominant components in the bio-oil. With the use of the catalyst, the relative content of acids significantly increased and phenols decreased. It was proposed that condensation reactions were dominating for the long residence times, which affected the bio-oil compositions in the catalytic run.

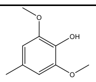
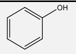
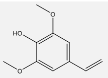
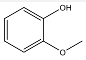
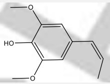
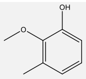
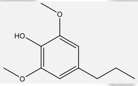
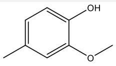
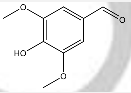
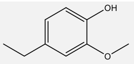
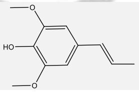
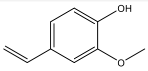
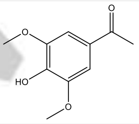
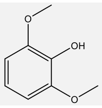
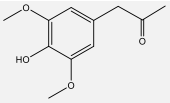
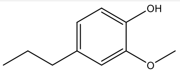
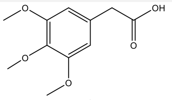
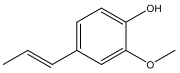
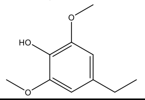
Characterizing bio-oils

Gas chromatography coupled with mass spectrometry (GC-MS) is a commonly used analytical technique for the qualitative and semi-quantitative analysis organic compounds in bio-oils from the liquefaction of lignocellulosic biomass in ethanol. A wide range of organic compounds in bio-oils arise from the decomposition of lignocellulosics or its lignin and cellulose components.

The detected monomeric compounds from the decomposition of lignin in ethanol are shown in Table 4.[15] The bio-oil from the decomposition of lignin in ethanol mainly contains monomeric phenols, acids, ketones and esters.[15, 32] The amount of each compound changes depending on the type of lignin employed as well as operating conditions. Notably, the use of catalyst has a significant effect on the composition of lignin-derived bio-oil and

10.1002/cssc.201801291

Table 4. The detected monomeric phenols from the decomposition of lignin in ethanol at 350 °C.[15]

Name of monomeric phenols	Structure	4-methylsyringol	
phenol		4-vinylsyringol	
guaiacol		cis-4-propenylsyringol	
3-methylguaiacol		4-propylsyringol	
4-methylguaiacol		syringaldehyde	
4-ethylguaiacol		trans-4-propenylsyringol	
4-vinylguaiacol		acetosyringone	
syringol		syringyl acetone	
4-propylguaiacol		3,4,5-trimethoxyphenylacetic acid	
isoeugenol		4-ethylsyringol	

may change the content and relative yield of organic compounds depending on the type and amount of catalyst. Figure 9 shows total ion chromatogram of bio-oil produced from concentrated sulfuric acid hydrolysis lignin (CSAHL) treated at 350 °C for 30 min with formic acid to lignin mass ratio of 1.5. The main compounds detected by GC-MS from the liquefaction of CSAHL in ethanol are esters, alcohols, ethers, ketones, acids, furans, cyclopentanones, and aromatic compounds.[26]

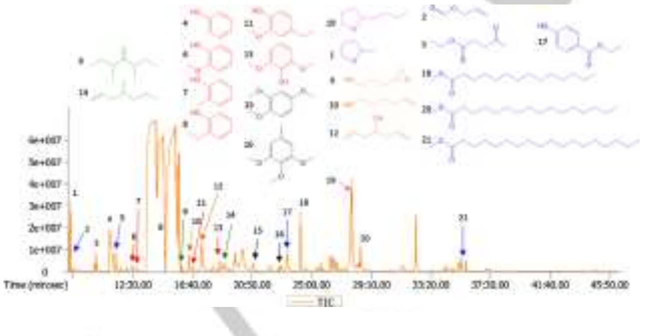


Figure 9. Total ion chromatogram of bio-oil produced after 30 min at 350 °C with a formic acid to lignin mass ratio of 1.5. The lignin source was CSAHL.[26] Reprinted with permission from reference [26].

GC-MS is an efficient analytical technology to identify the individual compound existing in bio-oils. Although GC-MS is being most commonly applied in the analysis of bio-oils, this technology still has challenges to accurately quantify all the compounds in the bio-oils. Usually the injector temperature for GC is set to around 250 °C, which means the chemical species with a high boiling point will not be able to enter the GC columns (e.g., phenolic oligomers). The absolute quantification of important individual compounds requires calibration curves obtained from internal standards of the chemical compounds of interest. This quantification method with internal standard can be expensive and time consuming; thus, most research efforts only calculate the relative percentage of chemical species (e.g., hydrocarbons, alcohols, esters) or an individual compound of interest based on the total identified compounds. To complement GC-MS and achieve a thorough analysis of the chemical components of the bio-oils, NMR has been widely employed in this research field.

Hydroxyl group containing compounds are major products from the decomposition of lignocellulose and hydroxyl groups critically influences the properties of the bio-oil. The phosphitylation of bio-oils with 2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP) followed by ^{31}P NMR analysis provides quantitative data on the hydroxyl groups content in bio-oils. Endo-N-hydroxy-5-norbornene-2,3-dicarboximide (NHND) is frequently used as an internal standard since the peak from this standard is well separated with signals from bio-oils. Figure 10 illustrates the derivatization reactions between TMDP and hydroxyl groups in bio-oils.[59] In Figure 10, phenolic OH include the non-condensed and condensed phenolic hydroxyl groups in bio-oils, respectively. The non-condensed phenolic structures which are capable of integration in a ^{31}P NMR spectra include guaiacyl, catechol, and *p*-hydroxyphenyl functional groups; syringyl group is usually overlapped with the condensed phenolic groups and cannot be well separated. The condensed phenolic OH structures include β-5, 4-O-5, and 5-5 C_5 substituted phenolic hydroxyl units. Table 5 summarizes the chemical shift assignment of the major hydroxyl functional groups detected in bio-oils.[59] Akalin et al. used hydrated cerium (III) as a catalyst to deconstruct beech wood in ethanol and applied ^{31}P NMR to determine the hydroxyl group contents in obtained bio-oils.[44] The deconstruction reactions were conducted with or without hydrated cerium (III) for 10, 60, and 120 min. For all the reaction times, catalytic obtained bio-oils contained at least 42% lower aliphatic OH content than the non-catalytic obtained bio-oils. Similarly, the involvement of the hydrated cerium (III) significantly reduced the phenolic contents in ethanol processed bio-oils, except that the β-5 and 5-5 units in the bio-oils obtained from a 10-min processing time. This finding by ^{31}P analysis suggested that the ethanol processing in a short time period may not have a significant effect on breaking down the C-C linkages in β-5 and 5-5 units. The reduced amount of the non-condensed phenolic structures (guaiacyl, catechol, *p*-hydroxyphenyl OH) along with the elemental analysis results of bio-oils (up to 50% reduction of the ratio O/C) in this study demonstrated that hydrated cerium (III) is a suitable catalyst for both the deconstruction and deoxygenation of biomass in ethanol.

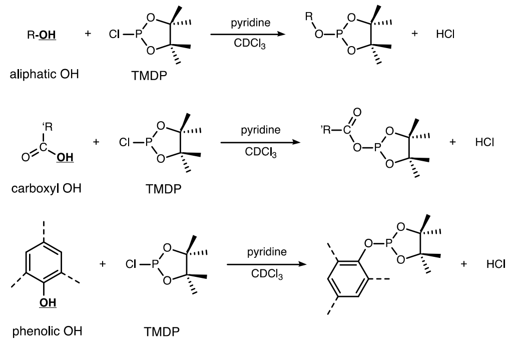


Figure 10. Derivatization reactions between hydroxyl groups in bio-oils and phosphorous reagent.[59]

Table 5. A typical chemical shift assignment of the hydroxyl groups in bio-oils. [59]

Hydroxyl functional groups		Integration region (ppm)
Internal standard (NHND)		152.8-151.0
Aliphatic OH		150.0-145.5
C_5 substituted condensed phenolic OH	β-5	144.7-142.8
	4-O-5	142.8-141.7
	5-5	141.7-140.2
Non-condensed phenolic OH	guaiacyl	140.2-139.0
	catechol	139.0-138.2
	p-hydroxyphenyl	138.2-137.3
Carboxylic acid OH		136.6-133.6

^1H-^{13}C HSQC NMR is another analytical technique employed to examine the products from ethanol processing of biomass. ^1H-^{13}C HSQC NMR benefits from its capability to detect the components of the whole fractions of the deconstructed products. HSQC spectra data are well separated which makes it possible to detect individual functional group in the complex products mixture. Huang et al. examined the role of the Cu-Mg-Al mixed oxide catalysts in the ethanol deconstruction of alkali lignin.[35a] HSQC NMR was used to analyze the tetrahydrofuran (THF) soluble residue lignin from the ethanol liquefaction reaction and the spectra data are shown in Figure 11.[35a] From the HSQC analysis of the residue lignins, there are two major findings. First, extensive signals from esters and alcohols exist in the spectra. These esters and alcohols may be formed from esterification and Guerbet reactions of aldehyde and hydroxyl groups with the Cu-Mg-Al mixed oxide catalysts. The occurring of these esterification and Guerbet reactions is also supported by the absence of aldehyde in the products detected by ^1H NMR in this work. Since aldehyde groups usually play an importance role in aldol condensation, which results in the re-polymerization and charring in the ethanol deconstruction reactions; esterification and Guerbet reactions triggered by the Cu-Mg-Al mixed oxide catalysts may be part of the reasons for the low char and higher aromatic monomers in the ethanol deconstructed products. The second finding is that there is a significant amount of C- or O- alkylated aromatic structures in the spectra. The alkylation reactions may reduce the reactivity of aromatic structures to be re-polymerized and condensed. In another word, the catalyst involved alkylation reactions may also contribute to the low char and higher aromatic monomers in the final products. Chen et al. used transition metal nitride catalyst to depolymerize lignin in ethanol and the HSQC analysis in their work also suggested that alkylation reactions occurring during the ethanol processing efficiently suppressed the re-polymerization and charring.[35] Elemental analysis is a useful technique to determine carbon, hydrogen and oxygen content of bio-oils produced from the decomposition of lignocellulose in ethanol. Previous studies regarding the decomposition of lignocellulose demonstrated that bio-oil contain more carbon and less hydrogen than that of raw biomass.[44, 60] Depending on the temperature and catalyst used, the carbon content can be increased and oxygen content decreased in comparison with the non-catalytic run, which corresponds to higher heating values.[17-18, 44] Heating values of bio-oils can be estimated from elemental composition of bio-oils using an empirical formula.[18, 44] Elemental analysis provides the atomic ratios of O/C and H/C in bio-oils. We can estimate the de-oxygenation degree in bio-oil from O/C atomic ratios. The previous studies demonstrated that the liquefaction of lignocellulose in ethanol resulting in lower O/C ratio in comparison with raw material. The O/C ratio of bio-oils changes depending on the operating conditions and can be significantly lowered using catalysts.[44, 61] The H/C ratio can provide clues regarding the aromatic content of bio-oils. If the H/C ratio of bio-oils and/or bio-chars is high, then the aromatic content is low.

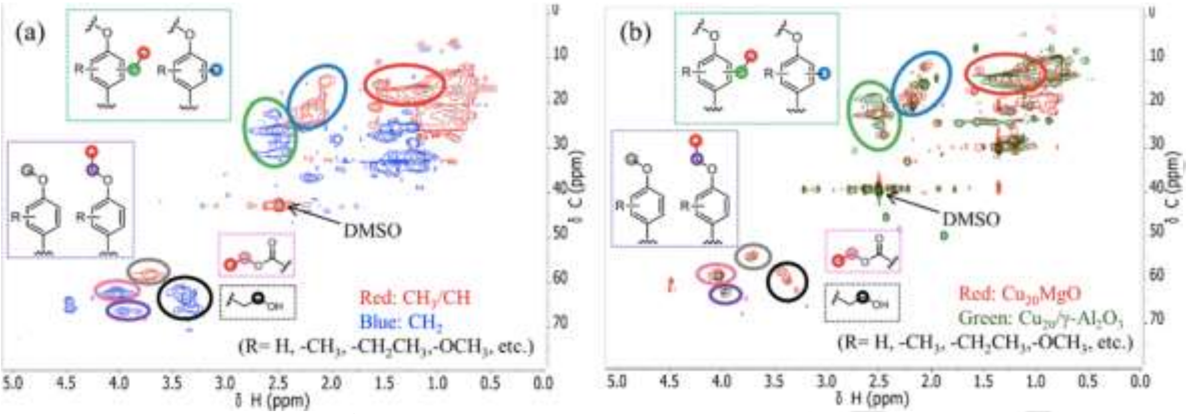


Figure 11. Side chain region from the ^1H-^{13}C HSQC NMR spectra of the residue lignin from the ethanol processing of alkali lignin at 340 °C for 4 h in a presence of: (a) $Cu_{20}MgAl_{(4)}$ * [*the subscript 20 denotes the weight percentage of Cu in the catalyst; (4) denotes the atomic ratio of the (Cu+Mg)/Al equals 4]; (b) Cu20MgO or Cu_{20}/γ-Al_2O_3.[36a] Reprinted with permission from reference [36a].

Conclusion and perspectives

The development of efficient lignocellulose conversion pathways to value added fuel range products and platform chemicals is a significant global challenge targeted at addressing future energy and sustainability challenges. The utility of the ethanol as a solvent media provides an environmental friendly approach to overcome the lignocellulose recalcitrance and obtain attractive depolymerized structures which are the precursors of fuel substituents and functionalized chemicals. The complex structures of the main constituents of lignocellulose offer a tremendous potential for desired sustainable production of fuels and chemicals. Both the fundamental understanding of the chemistry involved in supercritical and near supercritical ethanolysis reactions and creation of innovative biorefinery processing technologies in micro/large scales are desired for fully utilizing the potential of the lignocellulose constituent structures. Future studies in the field of deconstruction of lignocellulose to value added products include: 1) selectively convert biomass to a desired functionalized structures; 2) employing the whole biomass as a starting source; 3) developing economical viable catalysts suitable for the ethanolysis processing; 4) minimizing the condensation and re-polymerization reactions during deconstruction using ethanol; 5) deeper understanding of the mechanisms of the chemistry during the deconstruction reactions; 6) techno-economics analysis.

1) Current biomass deconstruction research works focus on two lignocellulose conversion strategies: convergent pathways to generate hydrocarbons as liquid transportation fuel precursors and divergent functionalization to produce chemical building blocks.[62] The convergent pathways usually require deoxygenation and hydrogenation to obtain saturated chains and deoxygenated aromatic structures. This pathway involving depolymerization, deoxygenation, and chain elongation is promising for reducing the fossil fuel dependence.[7a] Deconstruction of biomass in ethanol also contributes to the production of bulk chemicals (i.e., C2, C3, C4, and BTX) when followed with hydroprocessing steps.[63] Future research works may focus on finding pathways to deconstruct biomass in ethanol to chemical building blocks directly by keeping selected functional structures intact.

2) Using whole biomass as a feed material instead of pretreatment and separation of the three main constituents before deconstruction reactions in ethanol is of growing interest. For example, Sun et al. recently designed an integrated catalyst recycle system to obtain amines and alkanes precursors from the biomass deconstruction products in alcoholic solvent.[62] This concept of the full conversion of the whole biomass could be adopted in the future studies regarding catalytic biomass deconstruction reactions in ethanol.

3) Designing suitable catalysts for the deconstruction reactions in ethanol is a high priority and challenging target. The catalysts need to be environmentally free, noble metal free, low-cost and exhibit the ability to be recycled.[64] The suitability of the catalyst functioning in ethanol should be taken into consideration, e.g., the deconstruction of biomass in ethanol using Cu-Mg-Al catalyst successfully suppressed the undesired side reactions (i.e., char forming) and shift the reactions towards the depolymerization.

4) When deconstructing lignin in ethanol, the repolymerization and condensation of reactive fragments are significantly suppressing the yields of the monomers. Barret et al. used dimethyl carbonate as a co-solvent to successfully promote the yields of the stable depolymerized aromatic species when disassembling lignin in supercritical alcohol using Cu-Mg-Al catalyst.[65] The idea of using protection and stabilization reagents may inspire the future research works regarding deconstruction lignin in ethanol for higher yields of monomers.[66]

5) Deeper insight of the reaction mechanisms during lignocellulose deconstruction reactions in ethanol are needed. More complex model compounds of biomass constituents should be developed and applied in the mechanism studies.[64] In addition, advanced analysis techniques for analyzing the deconstruction products should also be applied in this research area including isotopic labeling and *in-situ* NMR techniques.[67]

6) Techno-economic analysis needs to be incorporated into future research studies regarding ethanol assisted biomass deconstruction. The direct conversion of lignocellulose to biofuels in ethanol is an attractive technology as much of ethanol can be recovered and reused in the process. Moreover, if all deconstructed products from lignocellulose, i.e., biofuels, biochars and gaseous are effectively used, it can lead to improved

capital effectiveness for the overall process. Nonetheless, as this technology begins to mature, TEA analysis of the overall process now needs to be assessed.

Dr. Arthur J. Ragauskas held the first Fulbright chair in Alternative Energy and is a Fellow of AAAS, IAWS and TAPPI. In 2014, he assumed a Governor's Chair for Biorefining based in the University of Tennessee's Department of Chemical and Biomolecular Engineering, with a complementary appointment in the UT Institute of Agriculture and serves in the US Energy and Environmental Science Directorate, Biosciences Division, and ORNL. His research program is directed at understanding and exploiting innovative sustainable bioresources. He is the recipient of the TAPPI Gunnar Nicholson Gold Medal Award, the ACS Affordable Green Chemistry award and AIChE Green Processing Award.

Keywords: Supercritical Ethanol Extraction • Biomass • Bio-oil

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