A Review of NMR Characterization of Pyrolysis Oils

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ABSTRACT

Pyrolysis of renewable biomass has been developed as a method to produce green fuels and chemicals in response to energy security concerns as well as to alleviate environmental issues incurred with fossil fuel usage. However, pyrolysis oils still have limited commercial application, mainly because unprocessed oils cannot be readily blended with current petroleum-based transportation fuels. To better understand these challenges, researchers have applied diverse characterization techniques in the development of bio-oil studies. In particular, nuclear magnetic resonance (NMR) is a key spectroscopic characterization method through analysis of bio-oil components. This review addresses the NMR strategies for pyrolysis oil characterization and critically discusses the applications of ^{1}H, ^{13}C, ^{31}P, ^{19}F, and two-dimensional (2-D NMR) analyses such as heteronuclear single quantum correlation (HSQC) in representative pyrolysis oil studies.

1. INTRODUCTION

Developing viable green energy technologies is imperative because of environmental issues related to fossil fuel usage.[1-3] Utilization of biomass has been introduced as a solution towards the development of sustainable and green energy platforms.[4] Lignocellulosic biomass is a complex composite primarily comprising three principle components: cellulose (35-50%), hemicellulose (20-35%), and lignin (10-25%).[5] Besides these three main components, biomass also has minor components including ash, protein, and other extractives, whose concentrations widely vary depending on the feedstocks. Lignocellulosic biomass is an attractive feedstock for biofuels because it is relatively inexpensive, abundant, avoids the “food or fuel” argument and is a renewable source of carbon. Typical bio-resources for biofuels include energy crops, such as switchgrass, miscanthus, poplar, and energy cane, or biomass residues from agriculture and forestry operations.[6] The U.S. Department of Energy and U.S. Department of Agriculture established a national goal that lignocellulosic biomass will supply 5% of the nation’s power by

2020 and 20% of its transportation fuels and 25% of its chemicals by 2030. This goal is approximately equivalent to 30% of the petroleum consumption in the year 2005.[7]

Biomass pyrolysis is a promising thermochemical conversion technology that involves irreversible thermochemical decomposition of lignocellulose in the absence of oxygen.[8] The complex polymer constituents of lignocellulose (i.e., lignin, cellulose, and hemicellulose) are depolymerized into smaller molecules upon thermal treatment. The pyrolysis products contain char, gas, and a pyrolysis oil. In particular, the pyrolysis oil has the potential to be blended in the transportation fuels even though it still has some challenges as a fuel, because of its physiochemical properties (which will be discussed in the following section).[9] In addition, a number of valuable chemicals such as methanol, phenol, catechol, carboxylic acid, and furfural, can be derived from pyrolysis oils.[10] Thus, understanding pyrolysis oil components is an essential part of pyrolysis research, which will provide a fundamental foundation from which future chemical upgrading of bio-oils can be developed.[11]

Various instrumental analytical techniques including gas chromatography (GC), liquid chromatography (LC), high-resolution mass spectrometry (HRMS), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and NMR were introduced for characterization of bio-oils in the previous studies.[12-16] One of the most comprehensive spectroscopic experiments suited for the comprehensive elucidation of bio-oil components is NMR spectroscopy. Various NMR experiments have been employed to better understand the components and structures of thermally generated bio-oils. ^{1}H and ^{13}C NMR have been widely used to investigate the structural hydrogen-carbon framework of bio-oils.[17] Moreover, selective analysis of the functional groups in the pyrolysis oils through other NMR analysis techniques allows a deep understanding the characteristics of pyrolysis oils. For instance, hydroxyl functional groups of bio-oils can be measured by phosphitylation followed by ^{31}P NMR.[18] Likewise, derivatization of bio-oils with 4-(tri-fluoromethyl)phenylhydrazine followed by ^{19}F NMR provides a quantitative and comprehensive understanding of carbonyl groups, which lead to corrosion and aging problems during upgrading.[19] 2D-NMR experiments, such as ^{1}H-^{13}C HSQC, are used to infer likely functional groups and substructures present in the oil by detecting one bond correlations between heteronuclear chemical shifts.[20] This review will point the importance of bio-oil characterization out and introduce applications of diverse NMR analysis methods including the ^{1}H, ^{13}C, ^{31}P, ^{19}F, and HSQC-NMR for the characterization. Moreover, potential applications of NMR techniques on bio-oils research are proposed.

2. CHALLENGES OF BIO-OILS AND UPGRADING METHODS

Pyrolysis oil, also known as bio-oil, is a dark-brown, free-flowing liquid product from biomass obtained using assorted pyrolysis processes. The oil is a very complex mixture containing phenolic compounds, carbohydrates, furans, ketones, aldehydes, carboxylic acids, and water.[8, 21] Although pyrolysis oil has considerable potential as an alternative fuel, it still has some technical barriers to be overcome. Characteristics of the bio-oil and challenges of its applications are summarized in Table 1.[8, 22-24] Polar oxygen-containing components (e.g., carboxylic acids, hydroxyl groups) cause bio-oils to be immiscible with non-polar transportation fuels. Water from feedstock participates in the pyrolysis reaction and affects the product yields and structures. The water contents of fast pyrolysis oils vary between 15 and 30 wt.%, and the presence of water lowers the oil's heating value and causes the delay problem in ignition engines.[24, 25] Corrosion problems of the bio-oils are primarily due to carboxylic acids and phenolic compounds, which cause storage and transportation problems.[26] Ortega et al.[27] and others[28-30] have investigated the aging process of bio-oils and have analyzed how their chemical and physical properties change during aging. Aging experiments resulted in the increase of viscosity, molecular weight, and non-volatile contents of bio-oil samples, because the etherification, esterification, and olefin condensation occurred during aging process.[30] For these reasons, upgrading is a necessary step to convert bio-oils into refinery products (e.g., gasoline, diesel, jet fuel, olefins). Bridgwater[31] and others[32-36] have discussed bio-oil upgrading methods. Typical upgrading methods and their characteristics are presented in Table 2.[31, 37-40] Aforementioned bio-oil upgrading methods are potential solutions for overcoming the challenges of bio-oil applications; however, these methods still need further developments. Structure characteristics of bio-oil products can reveal insight for subsequent upgrading methods; therefore, understanding and selecting a proper analysis method is as important as developing the upgrading methods.

3. NMR ANALYSIS OF BIO-OILS

Mullen et al.[17] discussed the characteristics of analytical techniques applied to bio-oils, including GC, high-performance liquid chromatography (HPLC), gel permeation chromatography (GPC), FT-IR, and NMR. Among the characterization methods mentioned above, NMR techniques have been widely used for the structural elucidation of bio-oils. Table 3 summarizes applications of NMR characterization of various bio-oil products reported over the past decade. Diverse NMR methods provided structural information of the bio-oil products and assisted understanding the effects of diverse pyrolysis processes and post-pyrolysis upgrading methods.

The main advantages of the application of NMR to the analysis of bio-oils are 1) the whole bio-oil can be dissolved in an appropriate solvent and information about the whole functional groups can be obtained, which does not depend on the volatility of the components in the bio-oils; and 2) the chemical-shift ranges for functional groups have been well studied, and quantitative analysis of functional groups can be achieved by integration of peaks based on the proposed chemical shift assignment ranges. For example, Joseph et al.[41] proposed revised chemical shift ranges for the assignment of ^{13}C NMR and ^{1}H NMR data and discussed uncertainties of the functional group assignments because of the OH contents in bio-oils, incomplete relaxation, and nuclear Overhauser effects by analyzing 54 pyrolysis oil model compounds. However, NMR analysis of bio-oils still has several limitations. It is challenging to integrate online NMR analysis into pyrolysis production lines and hence remains primarily a laboratory research tool. In addition, NMR analysis is well known to be an insensitive research tool and for bio-oils it is often difficult to identify individual compounds and better suited to analyze changes in functional group composition. Practically, researchers need to apply several characterization techniques together to fully analyze bio-oils, to get thorough understanding of bio-oil components. In the following sections, the chemical shift assignments and applications of various NMR analysis methods will be thoroughly discussed.

4. ^{1}H NMR ANALYSIS OF BIO-OILS

Proton NMR is widely applied in bio-oil characterization. The ^{1}H nucleus is abundant, thus proton NMR allows rapid detection with a high signal-to-noise (S/N) ratio. However, unambiguous assignment of the NMR chemical shifts caused by severe spectral overlapping makes this analysis challenging.[42] Joseph et al.[41] reported ^{1}H NMR signal overlapping from different bio-oil model compounds in DMSO-d_6. The proton shifts in non-conjugated alkenes (6.0-4.0 ppm) overlap those in aliphatic OH groups (6.5-4.0 ppm) and ether groups (5.5-3.0 ppm). The signals between 3.0 and 2.0 ppm can be assigned to both aliphatic protons and protons on carbons attached to a carbonyl group. Table 4 compares typical ^{1}H NMR chemical shift integration regions reported in the literature and proposes a revised integration region.[17, 41, 43, 44] Aldehydes and carboxylic acids are assigned in the downfield regions of 10.0-8.3 ppm. Aliphatic protons are assigned to 3.0-0.5 ppm; however, primary, secondary, and tertiary protons cannot be distinguished by ^{1}H NMR.[41] The chemical shift range of 8.3-5.7 ppm is assigned to aromatics and alkenes, and that of 5.7-3.0 ppm is assigned to protons on carbons α to an oxygen atom. These chemical shift ranges are not distinguished further because of severe overlaps in the ^{1}H NMR spectrum. Phenols and aliphatic hydroxyl groups are not specified in the revised chemical shift integration regions because hydroxyl protons shift widely in different solvents and concentrations because of strong hydrogen bonding in polar solvents. Figure 1 presents typical assignments of a ^{1}H NMR spectrum for bio-oil from pinewood.

^{1}H NMR has been used to elucidate the structures of bio-oils obtained under different pyrolysis conditions and upgrading methods as well as those of chemicals extracted from bio-oils. Tessarolo et al.[45] used ^{1}H NMR to analyze bio-oils from pine wood and sugarcane bagasse. The bio-oils were obtained from non-catalytic and ZSM-5-catalyzed pyrolysis at different temperatures (450 °C, 500 °C, and 550 °C). The ^{1}H NMR chemical shift integration ranges of all bio-oil samples are presented in Table 5.[45] The bio-oil from sugarcane bagasse pyrolyzed with ZSM-5 showed an increase of aromatic and conjugated alkene hydrogen contents (8.2-6.0 ppm) and a decrease of hydrogen contents from oxygen-containing groups (12.5-8.2 ppm, 6.0-3.0 ppm) compared to non-catalytic sugarcane bagasse bio-oil. The same ZSM-5 catalyst effect was observed on pine wood bio-oils, i.e., an increase of aromatic and conjugated alkene hydrogen contents and a decrease of hydrogen contents from oxygen-containing groups. However, pine wood bio-oil catalytically pyrolyzed at 500 °C contained more hydrogen from ethers (4.2-3.0

ppm) compared to the non-catalyzed pyrolysis oil. This unusual tendency was due to the spectral overlap between the water region (3.7-3.3 ppm) and hydrogens related to ethers (4.2-3.0 ppm). The spectral overlap of aliphatic hydrogens and hydrogens α to carbonyl groups in the region from 3.0 to 2.0 ppm made the quantification of aliphatic hydrogens difficult.

Tanneru and Steele performed catalytic deoxygenation to convert pretreated pine wood bio-oil into partially deoxygenated products in the presence of syngas.[46] The pretreatment was an oxidation step to convert aldehydes in the crude bio-oil to carboxylic acids, which are more conductive to catalytic hydrotreating. The partially deoxygenated product was then fully deoxygenated to hydrocarbons. Figure 2 presents the ^{1}H NMR spectra of a) oxidized bio-oil, b) partially deoxygenated bio-oil, c) fully deoxygenated bio-oil, and d) a commercial gasoline-jet fuel-diesel mixture. A comparison of Figure 2a with Figure 2b reveals that protons in the region 5.2-3.2 ppm (esters, ethers, lignin-derived methoxy phenols) were almost eliminated by partial deoxygenation. Partial deoxygenation also increased the aliphatic hydrocarbon content (1.8-0.8 ppm). A comparison of Figure 2b with Figure 2c indicates that the full deoxygenation reduced the content of phenols, substituted phenols, and aromatic compounds (7.5-5.0 ppm). Figure 2c and Figure 2d show that the fully deoxygenated product exhibited a spectrum similar to that of the commercial gasoline-jet fuel-diesel mixture.

Mancini et al.[47] used quantitative ^{1}H NMR to detect the selective production of (1*R*,5*S*)-1-hydroxy-3,6-dioxa-bicyclo[3.2.1]octan-2-one (LAC) in cellulose pyrolysis oils. LAC has the potential to be applied in the organic synthesis of tetrahydrofuran structures found in natural products.[48] Cellulose pyrolysis was performed using the catalysts aluminum-titanate (AlTi), montmorillonite K10 (MK10), Sn-MCM-41, or recycled Sn-MCM-41. The ^{1}H NMR spectra of the LAC enriched bio-oils and pure LAC are shown in Figure 3. The quantitative ^{1}H NMR detection of LAC in bio-oils was achieved using a NMR standard-addition method.[49] The quantitative ^{1}H NMR results showed that the LAC concentrations in bio-oils using Sn-MCM-41 and recycled Sn-MCM-41 were 27.6 wt.% and 26.8 wt.%, respectively. The ^{1}H NMR results indicated that catalyst Sn-MCM-41 exhibited high efficiency to achieve LAC selective production in cellulose pyrolysis process.

5. ^{13}C NMR ANALYSIS OF BIO-OILS

^{13}C NMR spectroscopy provides carbon information of bio-oil components. In comparison to an ^{1}H NMR spectrum, a ^{13}C NMR spectrum benefits from a broader chemical shift range, which means less spectral overlap.[50] The limitation of quantitative ^{13}C NMR is its low sensitivity and long experiment time due to the low natural abundance of ^{13}C nuclei. Table 6 compares two typical ^{13}C NMR chemical shift integration ranges measured in DMSO-d_6, as proposed by Ingram et al.[43] and Joseph et al.[41] Joseph et al. reported that primary carbons overlapped with secondary and tertiary carbons extensively in the region 34-24 ppm of ^{13}C NMR from bio-oil model compounds.[41] Thus, the alkyl region (54-0 ppm) could not be subdivided into primary, secondary, and tertiary carbons. Methoxy/hydroxyl groups and carbohydrates were assigned to 70-54 ppm and 103-70 ppm, respectively, which was slightly different from the assignments proposed by Ingram et al.[43] In the study of model compounds, aromatic and alkene carbons overlapped completely in the region 163-103 ppm. Moreover, carbonyl carbons were easily distinguished in the region of 215-163 ppm in the studies of both Ingram et al. and Joseph et al.[41, 43]

Tarves et al.[51] investigated the effects of reactive gas atmospheres on the properties of switchgrass bio-oils produced by microwave pyrolysis. Bio-oils produced under various gaseous atmospheres (CO, CH_4, and H_2) and a model pyrolysis gas mixture (PyGas) were analyzed by ^{13}C NMR spectroscopy and compared with bio-oils obtained under an N_2 atmosphere. Table 7 compares the ^{13}C NMR data of switchgrass bio-oils obtained by microwave pyrolysis under different gas atmospheres.[51] Compared to the bio-oils obtained under an N_2 atmosphere (control group), the oils produced under CO and H_2 atmospheres contained 18.6% and 27.6% greater concentrations of aliphatic compounds (55-0 ppm), respectively. The CO, H_2, and PyGas atmospheres also produced higher percentages of aromatic compounds (165-95 ppm) and lower percentages of ketones, aldehydes, acids, and esters (215-165 ppm). In addition, the oils obtained under reactive gas atmospheres (CO, CH_4, H_2, and PyGas) contained approximately half of the percentage of alcohols and carbohydrates (95-55 ppm) compared to the N_2 atmosphere control group. The ^{13}C NMR integration results indicated that the reactive gas atmospheres resulted in lower contents of oxygen-containing compounds and higher contents of deoxygenated products in bio-oils.

Mante et al.[52] hydrothermally treated fluid catalytic cracking (FCC) catalysts and ZSM-5 additives and studied the effects of the treatments on bio-oils obtained from catalytic pyrolysis of poplar wood by ^{13}C NMR analysis. One commercial FCC catalyst and two commercial ZSM-5 additives were tested in the study. Table 8 presents the ^{13}C NMR analysis results of bio-oils produced with various catalysts.[52] The ^{13}C NMR integration results indicated that the bio-oil obtained with silica sand via non-catalytic pyrolysis contained the highest amounts of oxygenated compounds (220-180, 180-160, 105-60, and 57-55 ppm). In general, the use of FCC catalysts and ZSM-5 additives decreased the concentrations of oxygenated compounds and increased the aromatic contents (160-105 ppm) in bio-oil products. A comparison of the products obtained using fresh FCC catalyst (FCC-1) with those obtained using FCC catalyst hydrothermally treated at 732 °C (FCC-2) revealed that the contents of oxygen-containing compounds in the regions of 220-160, 105-60, and 57-55 ppm decreased 47.2% with FCC-2. This result indicated that the selectivity and activity of the FCC catalyst was promoted upon steaming. Conversely, the FCC catalyst steamed at 788 °C (FCC-3) did not decrease the oxygen content of the products compared to those obtained with the fresh FCC catalyst (FCC-1), which suggested that the severe treatment temperature (788 °C) led to diminished effectiveness of the catalysts for deoxygenation reactions (e.g., demethoxylation, decarboxylation, and decarbonylation). In contrast to the ^{13}C NMR analysis results for the products obtained using the FCC catalyst, those for the bio-oil showed that steaming of the ZSM-5 additives did not substantially lower the oxygen content in bio-oils. For example, in the case of phosphorous-impregnated ZSM-5 additive steam treated at 732 °C (PZSM5-2), the methoxy carbons from lignin decomposition products (57-55 ppm) were decreased by 9.9% and the carbons in alcohols, ethers, anhydrosugars, and levoglucosan (105-60 ppm) were decreased by 17.1%; however, carbonyl groups (220-160 ppm) in the bio-oil increased by 43.7% compared to the product obtained using fresh phosphorous-impregnated ZSM-5 additives (PZSM5-1).

Liu et al.[53] reported a method to upgrade bio-oils using zero-valent metals at ambient temperature and pressure. The effects of zero-valent metals were investigated on both model compounds and a bio-oil from rice husk. Table 9 presents a comparison of the ^{13}C NMR integration results of the raw and upgraded bio-oils from rice husk. According to the ^{13}C NMR integration results, carbonyl groups (215-170 ppm) in the upgraded bio-oil decreased by 68.4% compared to their contents in the raw bio-oil. This significant change was accompanied by an increase of the contents of alcohols and ethers (90-50 ppm) in the upgraded bio-oil. Selective conversion of benzaldehyde, which was used as a model compound, into benzyl alcohol in the presence of zero-valent zinc powders was consistent with the results for bio-oils from rice husk.

Alwehaibi et al.[54] characterized the phenolic compounds of the bio-oil obtained from spruce wood and used the bio-oil and its subfractions to stabilize biodiesel against autoxidation. The ^{13}C NMR spectra of the crude bio-oil and its isolated extracts are shown in Figure 4.[54] As evident from the ^{13}C NMR spectra, multi-solvent extraction clearly separated the bio-oil into two major families: carbohydrates (95-55 ppm) in the water-soluble extract and phenolic compounds (165-95 ppm) in the phenolic extract. The sharp peak at approximately 56 ppm indicated that the majority of the phenolic compounds have a methoxy substitution.

Recently, researchers combined NMR spectroscopy with modeling techniques to predict the chemical properties of bio-oils. Strahan et al.[55] summarized the ^{13}C NMR data for 73 different samples, including 55 bio-oils, two commercial fuels, and 16 small-molecule standards. The bio-oils were produced from various feedstocks, pyrolysis processes, and post-pyrolysis treatments. Partial least squares (PLS) models were created to correlate the ^{13}C NMR data with the samples' other chemical properties including their phenol concentration, cresol concentration, total acid number, elemental composition, and higher heating value. The chemical properties were predicted from the models and compared with the experimental values. These models can provide researchers a method for estimating pyrolysis oil's chemical properties using only ^{13}C NMR.

6. ^{31}P NMR ANALYSIS OF BIO-OILS

^{31}P NMR method has attracted increasing interest in bio-oil characterizations in recent years. It involves phosphitylation of hydroxyl groups with a ^{31}P reagent followed by quantitative ^{31}P

NMR analysis. This method provides quantitative information about various hydroxyl functional groups in bio-oils and complements ^{1}H NMR and ^{13}C NMR analysis, especially in cases where there are strong signals overlapping and dynamic range problems in the ^{1}H NMR spectra or long relaxation time issues in the ^{13}C NMR experiments. Pu et al.[56] reviewed the applications of ^{31}P NMR in lignin and lignin-derived products and stated that 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) is the most common phosphitylating reagent for lignin and its derivatives. Wroblewski et al.[57] examined five trivalent ^{31}P reagents to derivatize organic model compounds including phenols, aliphatic acids, aromatic acids, aliphatic alcohols, amines, and thiols. TMDP has emerged as an optimum reagent because most hydroxyl groups containing compounds derivatized with this reagent showed non-overlapped chemical shifts. Figure 5 shows reactions between TMDP and various hydroxyl function groups in bio-oils and the ^{31}P NMR assignments of the phosphitylated compounds.[58] The reactions between TMDP and hydroxyl groups require an organic base, such as pyridine. Pyridine has the ability to capture the liberated hydrogen chloride and drive the overall phosphitylation reaction to total conversion.[56] ^{31}P NMR also requires an internal standard for quantitative assessment of hydroxyl groups in bio-oils.[59] *endo-N*-Hydroxyl-5-norborene-2,3-dicarboximide (NHND) has been selected as a suitable internal standard because it has a chemical shift (152.8-151.0 ppm) that is well-separated from those of the bio-oil components.[59] Recently, Ben and Ferrell[60] examined the time-dependent changes of several commonly used internal standards for the ^{31}P NMR analysis of bio-oil. Their results showed that NHND is not stable after 12 h of storage or experiment, whereas cyclohexanol and triphenylphosphine oxide (TPPO) can be used as internal standards for long experiment or storage times. Moreover, the chemical shifts and integration regions for bio-oils after derivatization with TMDP have been studied; typical chemical shift assignments are presented in Table 10.[58]

David et al.[18] compared bio-oils from pine wood, sweetgum, softwood lignin, and cellulose isolated from pine wood using ^{31}P NMR spectroscopy. The hydroxyl contents identified by ^{31}P NMR are shown in Table 11.[18] David et al.[18] derivatized the bio-oils by TMDP and assessed the quantitative analysis against cyclohexanol as an internal standard. Their quantitative ^{31}P NMR results showed that the total hydroxyl contents in the pine wood bio-oil (2.62 mmol/g) were higher than the total hydroxyl contents in the sweetgum bio-oil (1.54 mmol/g). The bio-oil obtained from cellulose contained the highest aliphatic hydroxyl contents (2.95 mmol/g) and the lowest contents of phenolic hydroxyl groups and carboxylic acids. The bio-oil from softwood lignin contained only 0.10 mmol/g aliphatic hydroxyl groups, whereas the contents of the phenolic hydroxyls (2.53 mmol/g) and carboxylic acids (0.26 mmol/g) were the highest in the bio-oil from softwood lignin.

Naik et al.[61] upgraded the bio-oil obtained from Jatropha by catalytic cracking with vacuum gas oil. They used quantitative ^{31}P NMR spectroscopy to analyze the crude oil and the oils catalytically cracked at 250 °C and 300 °C. Figure 6 shows the quantitative ^{31}P NMR spectra of the crude and upgraded bio-oils.[61] The bio-oils were analyzed by ^{31}P NMR spectroscopy after derivatization with TMDP, and NHND was selected as an internal standard. In this study, the aliphatic OH, C5-substituted β-5 phenolic OH, guaiacyl phenolic OH, and *p*-hydroxyphenyl OH were assigned to the regions 150.02-145.07, 145.07-140.42, 140.42-138.20, and 138.20-136.96 ppm, respectively. A comparison of Figure 6a and Figure 6b indicates that the aliphatic OH (150.02-145.07 ppm) and C5-substituted β-5 phenolic OH (145.07-140.42 ppm) were almost eliminated after the deoxygenation. The deoxygenation upgrading process at 250 °C also reduced the guaiacyl phenolic OH contents in the bio-oil. Figure 6c shows that deoxygenation at 300 °C completely removed the hydroxyl contents in bio-oils obtained from the fast pyrolysis of Jatropha.

Fu et al.[62] reported a method to extract phenolic compounds as a mixture from lignin pyrolysis oil using switchable hydrophilicity solvents (SHS). Table 12 presents the results from the subfractions analyzed by ^{31}P NMR after derivatization with TMDP.[62] The ^{31}P NMR integration results showed that the guaiacyl phenolic signal (140.2-139.0 ppm) was dominant for the three subfractions. The majority of hydroxyl groups were concentrated in the phenolic compounds extract (fraction 3). For instance, the phenolic extract (fraction 3) contained 90.5% aliphatic OH (150.0-145.5) and 57.4% catechol type OH (139.0-138.2 ppm) among the three subfractions. The ^{31}P NMR analysis after derivatization with TMDP validated that fractionation using SHS is a useful method to extract phenolic compounds from bio-oils.

7. ^{19}F NMR ANALYSIS OF BIO-OILS

^{19}F comprises 100% of naturally-occurring fluorine, and this isotope is highly responsive to NMR measurement. Similar to the ^{31}P NMR analysis, ^{19}F NMR technology provides an efficient method to detect a specific type of functional group. In contrast to ^{31}P NMR, ^{19}F NMR follows treatment of bio-oils with 4-(tri-fluoromethyl)phenylhydrazine to analyze carbonyl functional groups. Carbonyl groups have been reported to play an important role in corrosion and aging problems of pyrolysis oil; however, because of the complexity of the bio-oil composition, quantitative identifying carbonyl groups is difficult. Huang et al. first studied the application of ^{19}F NMR in detecting the carbonyl groups of pyrolysis oil derivatives.[19] They treated the pyrolysis samples with 4-(tri-fluoromethyl)phenylhydrazine as described in Scheme 1.[19] For the quantitation of carbonyl contents using ^{19}F NMR method, 2-fluoroguaiacyl benzoate (δ = -57.2

ppm) is used as an internal standard, which allows the quantitative assessment of carbonyl contents. In a ^{19}F NMR spectrum, the chemical shift range of -60.60 to -62.00 ppm is assigned to the quinone 4-(trifluoromethyl)phenylhydrazine derivative, whereas the range of -58.50 to -60.60 ppm is assigned to the aldehyde and ketone 4-(trifluoromethyl)phenyl-hydrazine derivatives.

Huang et al.[19] quantitatively analyzed different pyrolysis oils by ^{19}F NMR after derivatization with 4-(tri-fluoromethyl)phenylhydrazine. The ^{19}F NMR results were then compared with the results obtained by an oximation method.[63] The comparison results are presented in Table 13.[19] The results showed that the carbonyl contents of bio-oils analyzed by ^{19}F NMR ranged from 1.38-4.54 mmol/g, which was in agreement with the values from the oximation method. The ^{19}F NMR analysis results were slightly higher than the oximation analysis results. The difference could be attributed to the incomplete reaction of the quinonic groups during the oximation process. One of the advantages of the ^{19}F NMR analysis of carbonyl groups is the ability to detect the quinoid content as well as the aldehyde/ketone content separately. Moreover, the ^{19}F NMR method is more efficient than the traditional oximation method due to its short reaction time (24 h vs. 48 h), simpler operational procedure, and smaller sample amount requirement.

8. HSQC NMR ANALYSIS OF BIO-OILS

Traditional one-dimensional (1-D) ^{1}H and ^{13}C NMR analysis can provide valuable structural information for bio-oils. The 1-D NMR characterization techniques are quantitative essentially; however, these techniques usually suffer from spectral overlapping problems or long relaxation time issues when applied in the bio-oil analysis. 2-D NMR techniques have emerged as attractive methods to compensate the limitations of 1-D NMR techniques. In a 2-D spectrum, the chances of overlapping problems are reduced because the signals are spread out into two dimensions.[64]

HSQC is a proton-detected 2-D heteronuclear correlation experiment.[65, 66] In an HSQC experiment, the detected proton is labeled with the frequency of the heteroatom attached to. ^1H-^{13}C HSQC uses successive insensitive nuclei enhanced by polarization (INEPT) transfers that exploit the strong one-bond J_{HC} on either side of the ^{13}C evolution period.[64] The HSQC is more sensitive than the traditional heteronuclear correlation (HECTOR) experiment, because the HSQC starts and ends on the sensitive ^1H nucleus whereas the HECTOR detects the insensitive nucleus.[67] Modern HSQC sequences also use z-axis gradient pulse for coherence selection, which is a benefit for sensitivity-enhancement.[68] Ben and Ragauskas[20] applied ^1H-^{13}C HSQC NMR method to investigate carbon-hydrogen bonding in bio-oils and proposed assignments for the oils from slow pyrolysis of lignin, cellulose, and pine wood. The HSQC NMR assignments of the bio-oil from pine wood are presented in Figure 7.[20]

Fortin et al.[69] used ^1H-^{13}C HSQC NMR to analyze pyrolytic lignin extracted from a switchgrass pyrolysis oil. The resulting HSQC spectra are presented in Figure 8. The HSQC NMR spectra showed that aryl methoxy groups and guaiacyl units were still present in the pyrolytic lignin after the thermal conversion. The peaks of xylose and arabinose units also existed in the HSQC spectra of pyrolytic lignin.

Recently, Yu et al.[70] characterized pyrolytic sugars in bio-oil samples. Figure 9 showed the HSQC spectra of bio-oil samples and assignments of pyrolytic sugars. The assignments of pyrolytic sugars were proposed by characterizing of sugar standards, including sugar monomers (i.e., glucose, galactose, mannose, xylose, and arabinose) and anhydrosugars (i.e., levoglucosan, cellobiosan, and cellotriosan), as shown in Figure 9a. In Figure 9b, the HSQC spectra indicated that the intensity of sugar peaks in the raw bio-oil was considerably higher, compared to those in the water-insoluble bio-oil fraction. The sugar contents in CH_2Cl_2-soluble and CH_2Cl_2-insoluble fractions did not exhibit significant difference. From the HSQC spectra, the CH_2Cl_2-soluble fraction contained the higher intensity of aliphatic, methoxy, and guaiacyl groups compared to CH_2Cl_2-insoluble fraction.

9. CONCLUSION AND OUTLOOKS

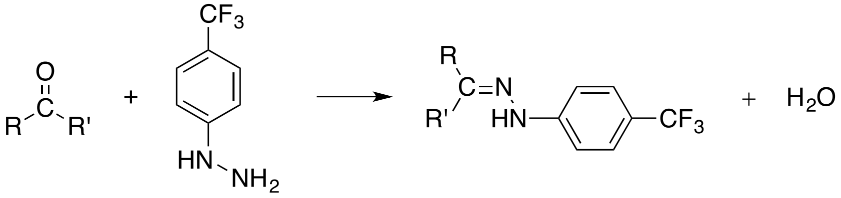
The NMR technologies presented in this review provide a facile way to analyze pyrolysis oil. Since most pyrolysis research focuses on reducing the oxygen contents in bio-oils through optimizing the pyrolysis experiment parameters (e.g., temperature, gas atmosphere), adding catalysts during pyrolysis, and post-pyrolysis treatments, ^1H, ^{13}C, ^{31}P, and ^{19}F NMR are powerful tools for obtaining structure information about the whole fraction of bio-oils. Moreover, post pyrolysis fractionation and chemical extraction have attracted increasing interest; in this area, NMR analysis also provides structural information about the bio-oil subfractions and extracted compounds. Hydroxyl and carbonyl groups, which are the primarily groups that limit the ability of bio-oils to blend with commercial fuels, can be detected by ^{31}P and ^{19}F NMR methods after derivatization. ^1H-^{13}C HSQC NMR provides carbon-hydrogen information, which is useful for elucidating possible reactive pathways during pyrolysis reactions. The 1-D NMR techniques are quantitative in nature, however, the spectral overlap problems usually occur because of the complex constitution of bio-oils. Researchers should carefully select appropriate NMR experiment parameters to let nucleus fully relaxed. Quantitative HSQC analysis of the bio-oil could be an interesting application in the future. Other 2-D NMR analysis could also bring benefit for the bio-oil studies, such as heteronuclear single quantum coherence-total correlation spectroscopy (HSQC-TOCSY).

Moreover, researchers are now focusing on several challenges of bio-oil characterization by NMR methods. For example, limited information is available about hemicellulose pyrolysis distribution because of its less well-defined structures and less mature isolation techniques. Deducing more assignments for hemicellulose pyrolysis oil in ^{13}C and 2D NMR spectra will provide further insight into hemicellulose pyrolysis behavior.[71]

^{1}H diffusion-ordered NMR spectroscopy (DOSY) is also considered for measuring the molecular weights of polymers and macromolecules and for investigating the interactions of small molecules. The application of ^{1}H DOSY to bio-oil molecular weight measurement to obtain shorter experiment times and achieve greater accuracy would be interesting.[72]

SCHEME

Scheme 1. Derivatization of Carbonyl Group [19]



FIGURES

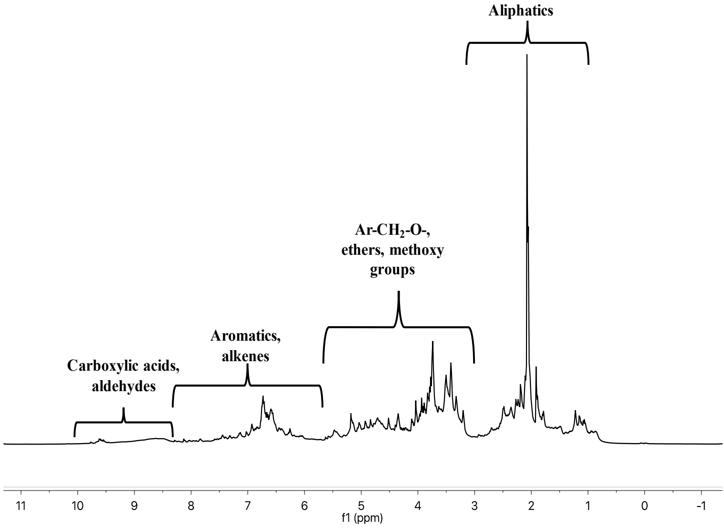


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Figure 1. ^{1}H NMR spectrum of the water-insoluble fraction of pine wood pyrolysis oil measured in DMSO-d_6.

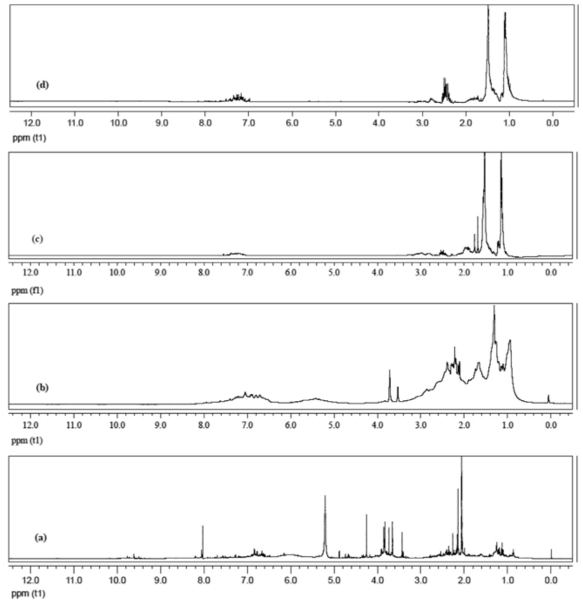

Figure 2. ^{1}H NMR spectra of a) oxidized bio-oil, b) partially deoxygenated bio-oil, c) fully deoxygenated bio-oil, and d) a commercial gasoline-jet fuel-diesel mixture.[46] (Reproduced with permission from Elsevier).

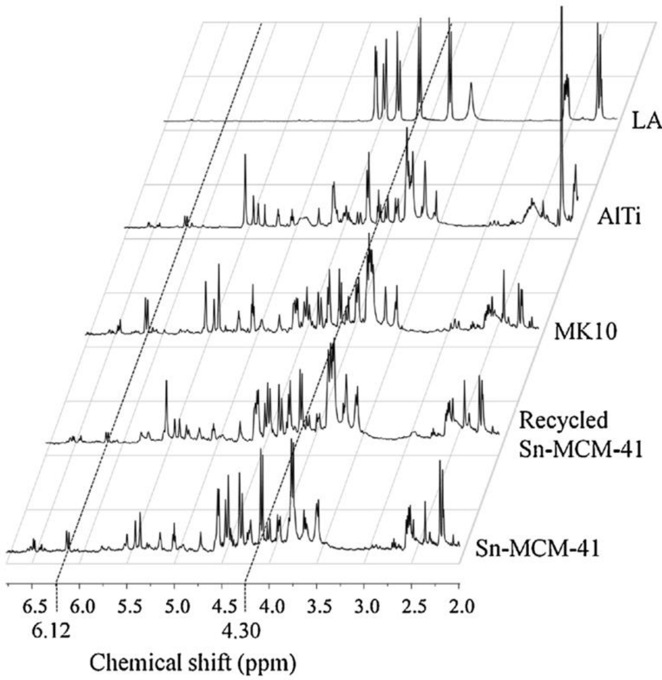

Figure 3. ^{1}H NMR spectra of pure LAC and bio-oils obtained in the presence of Sn-MCM-41, recycled Sn-MCM-41, MK10, and AlTi.[47] (Reproduced with permission from Elsevier).

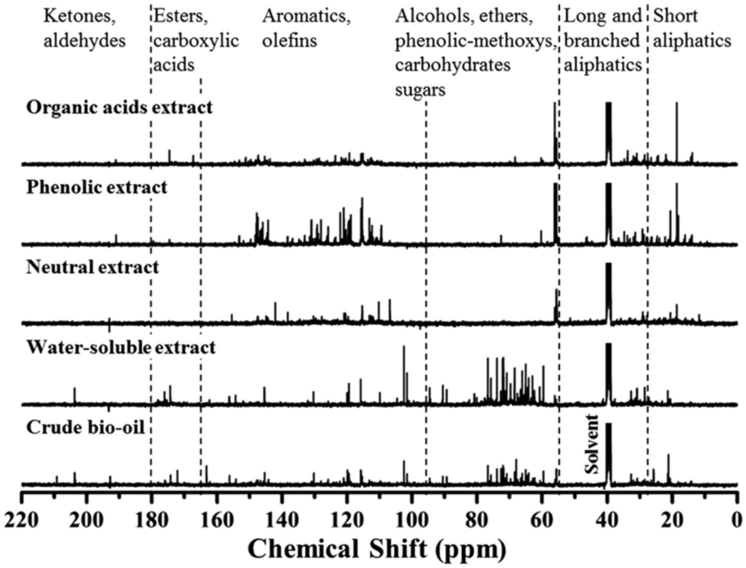

Figure 4. ^{13}C NMR spectra of the crude bio-oil, water-soluble extract, neutral extract, phenolic extract, and organic acids extract.[54] (Reproduced Ref 54 with the permission from The Royal Society of Chemistry).

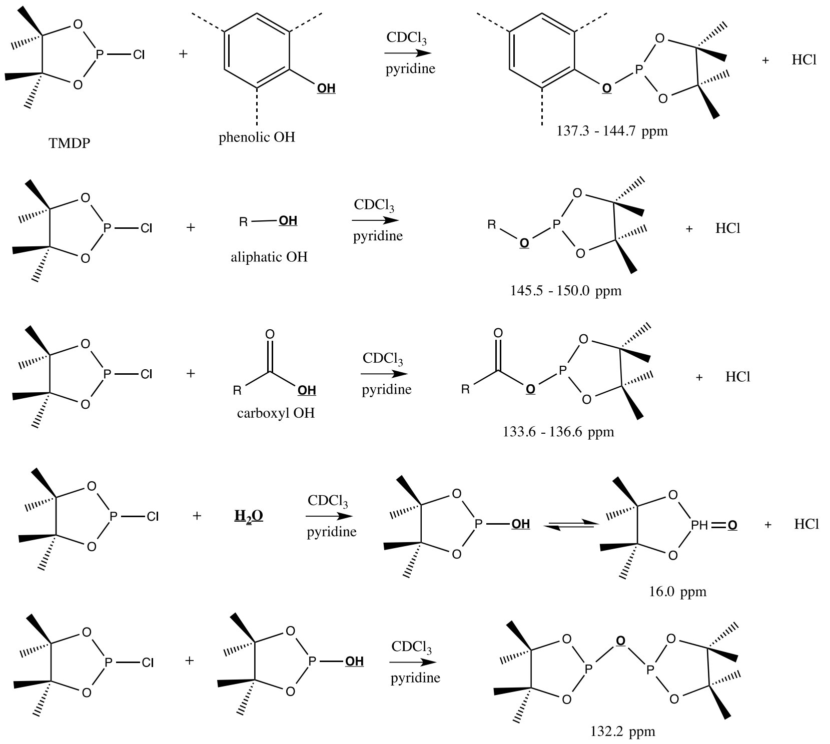

Figure 5. Reactions between TMDP and various hydroxyl functional groups and the ^{31}P NMR assignment of phosphitylated compounds.[58] (Reprinted with permission from (Ben, H.; Ragauskas, A. J., *Energy Fuels* **2011,** 25, (5), 2322-2332). Copyright (2016) American Chemical Society.

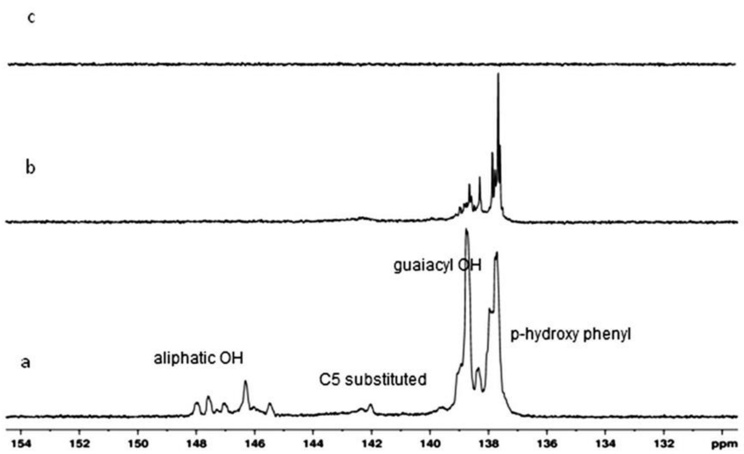

Figure 6. Quantitative ^{31}P NMR spectra of a) the crude oil, b) the bio-oil upgraded at 250 °C and c) the bio-oil upgraded at 300 °C.[61] (Reproduced Ref 61 with the permission from The Royal Society of Chemistry).

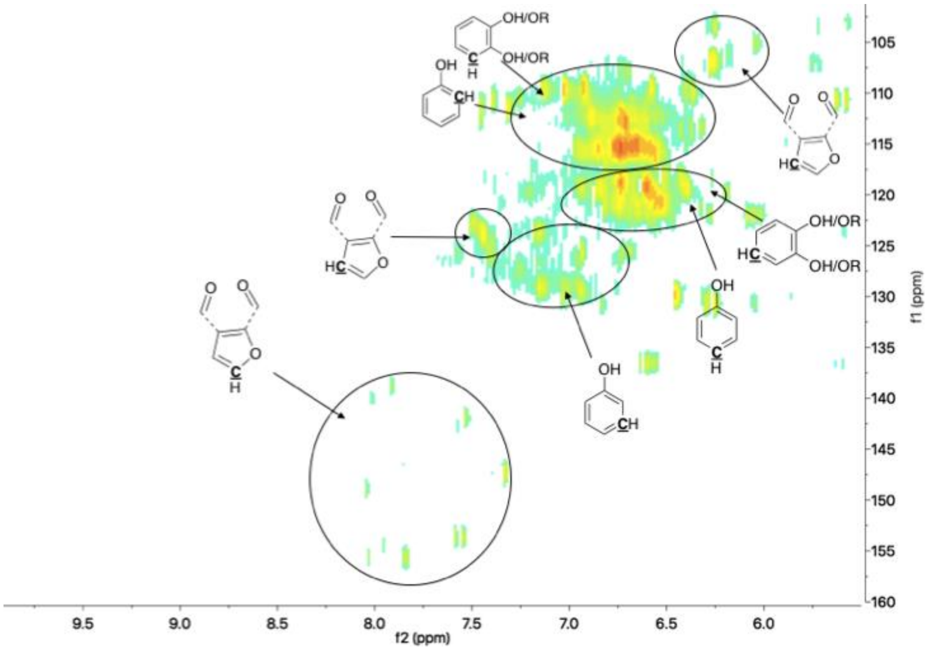

Figure 7a. Aromatic C-H bond assignments in an HSQC NMR spectrum for a bio-oil from pine wood.[20]

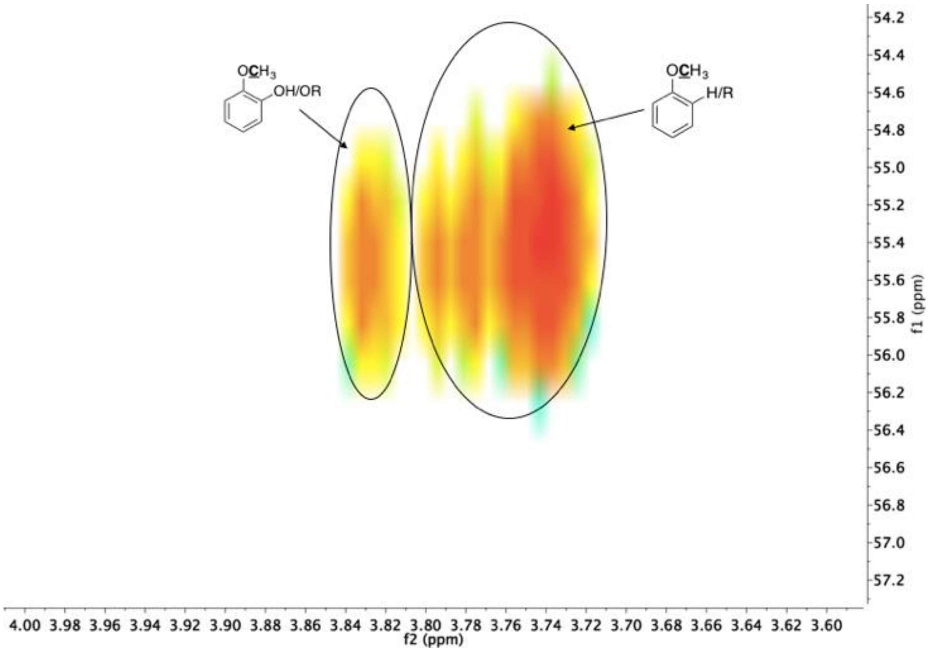

Figure 7b. Methoxy group assignments in an HSQC NMR spectrum for a bio-oil from pine wood.[20]

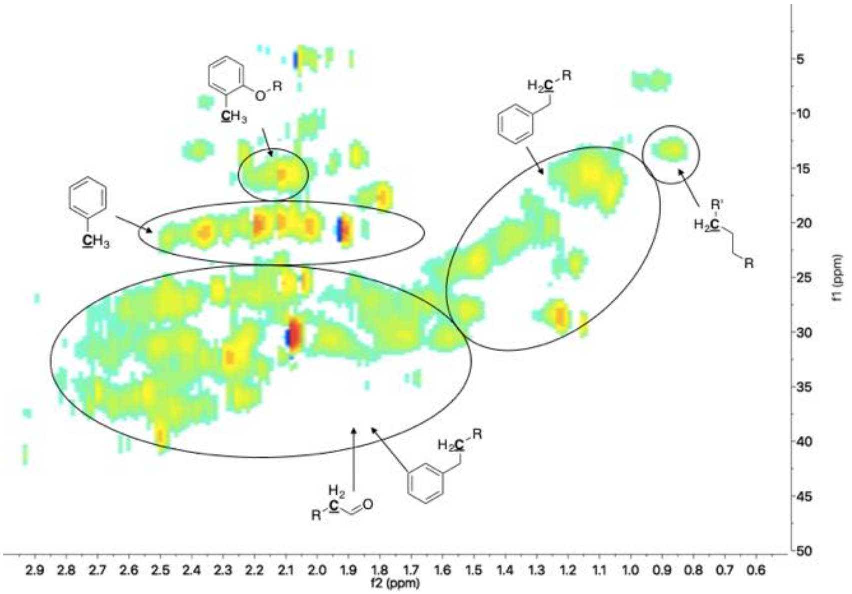

Figure 7c. Aliphatic C-H bond assignments in an HSQC NMR spectrum for a bio-oil from pine wood.[20]

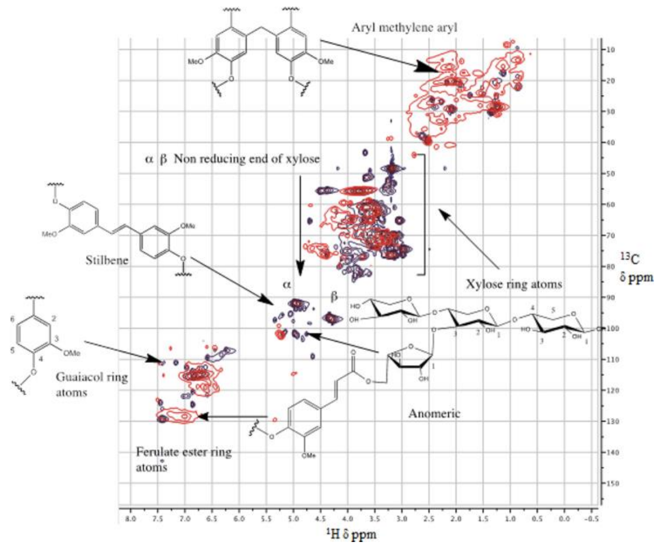

Figure 8. Comparison of the pyrolytic lignin (blue contours) and native lignin (red contours) extracted from switchgrass.[69] Reprinted with permission from (Fortin, M.; Mohadjer Beromi, M.; Lai, A.; Tarves, P. C.; Mullen, C. A.; Boateng, A. A.; West, N. M., *Energy Fuels* **2015,** 29, (12), 8017-8026). Copyright (2016) American Chemical Society.

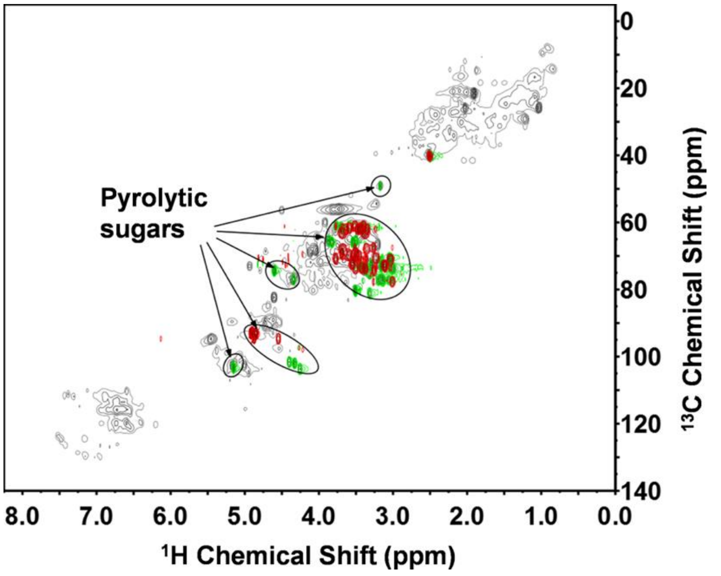

Figure 9a. HSQC spectra of bio-oil, sugar monomer standards, and anhydrosugar standards. Gray: bio-oil; Red: sugar monomer standrads (i.e., glucose, galactose, mannose, xylose, and arabinose; Green: anhydrosugars (i.e., levoglucosan, cellobiosan, and cellotriosan).[70] (Reprinted with the permission from Ref 68). Copyright (2016) American Chemical Society.

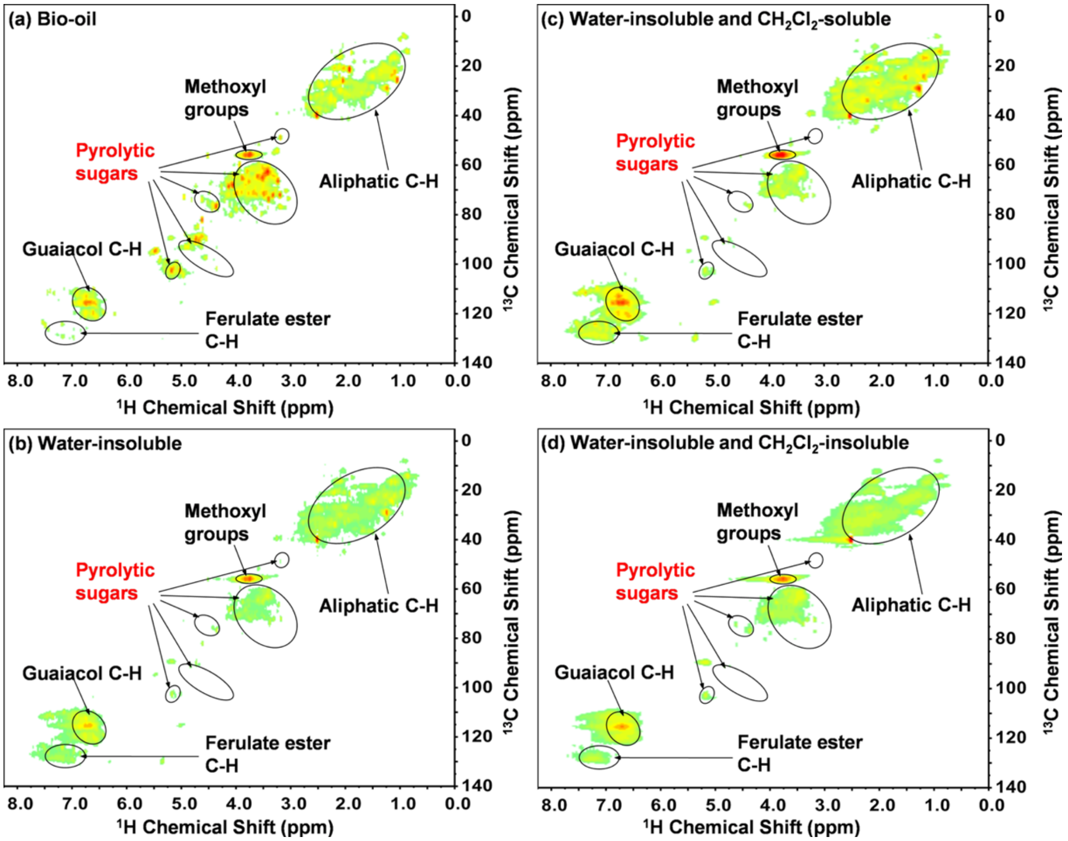

Figure 9b. HSQC spectra of bio-oil and it fractions. (a) raw bio-oil; (b) water-insoluble fraction; (c) water-insoluble and CH_2Cl_2-soluble fraction; (d) water-insoluble and CH_2Cl_2-insoluble fraction.[70] (Reprinted with the permission from Ref 68). Copyright (2016) American Chemical Society.

TABLES

Table 1. Characteristics of bio-oil and challenges for its applications.[8, 22-24]

Property	Characteristics	Challenges
Oxygen content	Usually 35-40 wt.%, depending on the original biomass source and pyrolysis parameters	High oxygen ratio results in low heating value, immiscibility with hydrocarbon fuels and instability of pyrolysis oil
Water content	Affected by feedstock and pyrolysis atmosphere	Lowers the heating value and delays ignition
Corrosiveness	A pH of 2-3	Can affect carbon steel and aluminum materials; cannot be stored in some sealing materials
Viscosity	Similar to the viscosity of crude oils in the temperature range 35-45 °C	An appropriate preheating can facilitate pumping of bio-oil
Aging	Higher-molecular-weight compounds forming over time	Makes bio-oil difficult to store and transport

Table 2. Typical Bio-oil Upgrading Methods and Characteristics.[31, 37-40]

Upgrading method	Characteristics
Catalytic cracking	Zeolites are commonly used as catalysts; cost effective; undesirable byproducts
Hydrotreating	Requires high pressures, moderate temperatures, a source of hydrogen and catalysts; high-quality products; high experimental instrument requirements
Steam reforming	Produces hydrogen-rich syngas; requires stable catalysts because of carbon deposition during the steam reforming process
Aqueous phase processing	Converts low-boiling fractions of bio-oils into hydrogen and alkanes
Esterification	Lowers concentrations of acids and carbonyl groups in the presence of an alcohol and an acid catalyst; usually accompanied by an oxidation pretreatment of bio-oils for converting aldehydes into carbonyl acids
Gasification for synfuels	Compared to the gasification of solid biomass, the process pressure requirement is much lower; reduces bio-refinery system costs by utilizing extensive commercial gasification plants

Table 3. NMR Techniques Applied in Bio-oil Analysis.

Feedstock	Pyrolysis method	Post pyrolysis upgrading method	Fraction analyzed by NMR	NMR technique
Apricot pulp[73]	Slow pyrolysis	-	Water-insoluble phase, toluene subfraction, methanol subfraction	^{1}H NMR
Cottonseed cake[74]	Zeolite-catalyzed slow pyrolysis	-	Water-insoluble phase	^{1}H NMR
Safflower seed[75]	Co-pyrolysis with lignite	-	Water-insoluble phase	^{1}H NMR
Chicken manure[76]	Fast pyrolysis	-	Light oil fraction, heavy oil fraction	^{1}H, ^{13}C NMR
Pine wood, pine bark, oak wood, oak bark[43]	Fast pyrolysis	-	Whole bio-oil, ethyl acetate subfraction	^{1}H, ^{13}C NMR
Safflower[77]	Slow pyrolysis	-	Whole bio-oil	^{1}H NMR
Rice husk[78]	Fast pyrolysis	Reactive distillation	Whole bio-oil	^{1}H NMR
Miscanthus × *giganteus*[79]	Alumina-catalyzed slow pyrolysis	-	Water-insoluble phase	^{1}H NMR
Linseed[80]	Slow pyrolysis	-	Water-insoluble phase	^{1}H NMR
Corncob[81]	Alumina-catalyzed slow pyrolysis	-	Water-insoluble phase	^{1}H NMR

Switchgrass, corn stover, alfalfa stems, guayule (whole shrub), guayule bagasse, chicken litter[17]	Fast pyrolysis	-	Electrostatic precipitator fraction	^{1}H, ^{13}C, DEPT NMR
Wheat, wood sawdust[82]	Fast pyrolysis	-	Crude bio-oil, supercritical-CO_2-extracted fractions	^{1}H NMR
Rice husk[83]	Fast pyrolysis	-	Whole bio-oil, salt induced subfractions	^{13}C NMR
Pine wood[84]	Fast pyrolysis	-	Whole bio-oil, pyrolytic lignin fraction	^{13}C NMR
Pine wood, sweetgum, loblolly pine lignin, loblolly pine lignin[18]	Fast pyrolysis	-	Whole bio-oil	^{31}P NMR
Pine wood[85]	Fast pyrolysis	-	Electrostatic precipitator fraction, water-soluble fraction, water-insoluble fraction	^{13}C NMR
Wheat-hemlock[86]	Fast pyrolysis	-	Crude bio-oil, supercritical CO_2 extracted fractions	^{1}H NMR
Cotton seed[87]	Magnesium-oxide-catalyzed pyrolysis	-	Whole bio-oil	^{1}H NMR

Hemp-seed[88]	Fast pyrolysis	Catalytic hydrotreatment	Methanol extracts, acetone extracts, acetonitrile extracts, ethyl acetate extracts, diethyl ether extracts of crude/upgraded bio-oil	^{1}H, ^{13}C NMR
Softwood kraft lignin[89]	Catalyzed slow pyrolysis	-	Heavy fraction, light fraction	^{13}C, ^{31}P NMR
Softwood kraft lignin[58]	Slow pyrolysis	-	Heavy fraction, light fraction	^{13}C, ^{31}P NMR
Pine wood, softwood lignin, cellulose[20]	Slow pyrolysis	-	Whole bio-oil	HSQC-NMR
-[90]	Fast pyrolysis	Catalytic hydrotreatment	Distillate fractions	^{13}C NMR
Grape bagasse[91]	Slow pyrolysis	-	Water insoluble fraction	^{1}H NMR
Rapeseed cake, willow, cellulose, sludge, polyethylene glycol[92]	Fast pyrolysis	-	Whole bio-oil	^{1}H NMR
Oak, rye grass, barley straw, eel grass, cow manure, pennycress presscake, camelina presscake, barley DDGS[93]	Fast pyrolysis	-	Electrostatic precipitator fraction	^{13}C, DEPT NMR
Softwood	Zeolite catalyzed	-	Heavy fraction,	^{13}C, ^{31}P,

kraft lignin[94]	slow pyrolysis		light fraction	HSQC-NMR
Corn stover, white oak, mixed hardwood, poplar, white oak[95]	Slow pyrolysis	-	Whole bio-oil	^{31}P NMR
Terebinth[96]	Slow pyrolysis	-	Water insoluble phase	^{1}H NMR
Poplar wood, softwood lignin, cellulose[44]	Slow pyrolysis	-	Fresh bio-oil, aged bio-oil	^{1}H, ^{13}C, ^{31}P NMR
Corn stover, corn cobs, bagasse, maize granulates, hay, wheat bran, wheat straw, softwood, oil palm fronds, empty fruit bunches, dynamotive[97]	Fast pyrolysis	-	Whole bio-oil	^{1}H NMR
Poplar wood[98]	Fast pyrolysis	-	Aged pyrolytic lignin	^{13}C NMR
Fir[99]	Catalytic fast pyrolysis	-	Whole bio-oil	^{1}H NMR
Poplar wood[52]	Fresh fluid catalytic cracking catalysts and zeolite-catalyzed pyrolysis	-	Whole bio-oil	^{13}C NMR
Corn	Fast pyrolysis	-	Whole bio-oil	^{1}H, ^{13}C NMR

stalks[100]				
Oil palm shell[101]	Microwave pyrolysis	-	Whole bio-oil	^{1}H NMR
Sesame, mustard, neem de-oiled cake[102]	Slow pyrolysis	-	Whole bio-oil	^{1}H NMR
Softwood kraft lignin[103]	Slow pyrolysis, fast pyrolysis	-	Heavy fraction, light fraction	^{13}C, HSQC-NMR
Softwood kraft lignin[104]	Zeolite slow pyrolysis	-	Heavy fraction, light fraction	^{13}C, ^{31}P, HSQC-NMR
Eucalyptus wood[105]	Fast pyrolysis following hydrothermal pretreatment	-	Whole bio-oil	^{13}C NMR
Forest thinnings[106]	Zeolite catalyzed fast pyrolysis	-	Whole bio-oil	^{13}C NMR
Norwegian spruce[107]	Fast pyrolysis	Hydrothermal deoxygenation	Whole bio-oil	^{31}P NMR
Pine wood[108]	Fast pyrolysis	Acid-catalyzed reaction	Whole bio-oil	^{1}H NMR
Pine wood[109]	Fast pyrolysis	-	Pyrolytic lignin	^{1}H NMR
Ash wood, birch wood[30]	Fast pyrolysis	-	Accelerated aged whole bi-oil	^{13}C NMR
Forestry residue[110]	Fast pyrolysis	Hydrodeoxygenation	Water-insoluble phase	^{1}H NMR
Jute dust[111]	Slow pyrolysis	-	Water free bi-oil	^{1}H NMR
Pongamia glabra deoiled cake[112]	Slow pyrolysis	-	Organic phase	^{1}H, ^{13}C NMR

Apricot kernel shell[113]	Slow pyrolysis	-	Water-insoluble phase	^{1}H NMR
Beech[114]	Fast pyrolysis	-	Heavy fraction, light fraction, aerosol	^{1}H NMR
Softwood kraft lignin[62]	Microwave pyrolysis	-	Phenols extracted from crude bio-oil, organic solvent subfractions	^{13}C, ^{31}P NMR
Softwood kraft lignin[115]	Zeolite-catalyzed slow pyrolysis	-	Heavy fraction	^{13}C, ^{31}P, HSQC-NMR
Pine wood[19]	Slow pyrolysis	-	Heavy fraction	^{19}F NMR
Pine wood residue, timothy grass residue, wheat straw residue[116]	Slow pyrolysis	-	Whole bio-oil	^{1}H, ^{13}C NMR
Almond shell[117]	Co-pyrolysis with high-density polyethylene	-	Organic phase	^{1}H NMR
Beech wood[118]	Fast pyrolysis	-	Pyrolytic lignin	^{1}H NMR
Spruce wood chips, waste paper, paper deinking residue[119]	Microwave pyrolysis	Curing in oven, for adhesive properties analysis	Cured bio-oil scrapings	^{13}C CP/MAS NMR
Rice husk[120]	Fast pyrolysis	Catalytic hydrotreatment and esterification	Crude whole bio-oil, upgraded whole bio-oil	^{13}C NMR

Loblolly pine wood[46]	Fast pyrolysis	Catalytic deoxygenation of oxidized bio-oil with syngas	Oxidized bio-oil, partial deoxygenated bio-oil, fully deoxygenated bio-oil	^{1}H NMR
Arundo donax L.[121]	Slow pyrolysis	-	Organic phase	^{1}H, ^{13}C NMR
Fraxinus excelsior L.[122]	Slow pyrolysis following heat pretreatment	-	Diethyl ether extracts	^{1}H NMR
Jatropha curcas cake[61]	Fast pyrolysis	Hydrodeoxygenation, catalytic cracking with vacuum gas oil	Crude heavy fraction, deoxygenated heavy fraction, fluid catalytic cracking liquid distillates	^{1}H, ^{13}C, ^{31}P NMR
Loblolly pine wood[123]	Fast pyrolysis following torrefaction	-	Accelerated aged whole bio-oil	^{13}C NMR
Saccharina japonica[124]	Fast pyrolysis	-	Whole bio-oil	^{1}H, ^{13}C NMR
Wheat straw, wheat husk[125]	Slow pyrolysis, catalyzed slow pyrolysis	-	Whole bio-oil	^{1}H NMR
Wood pallet, corn stover, miscanthus and swine manure[126]	Slow pyrolysis	-	Water-insoluble fraction	^{1}H, ^{13}C NMR
Switchgrass[69]	Fast pyrolysis	-	Pyrolytic lignin	^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBS, ^{13}C DEPT

Switchgrass, equine manure[127]	Fast pyrolysis, tail-gas reactive pyrolysis	-	Distillation residues	^{1}H, ^{13}C NMR
Wheat straw[128]	Fast pyrolysis	Catalytic hydrodeoxygenation	Light phase	^{1}H NMR
Mesua ferrea seed cover, *Pongamia glabra* seed cover[129]	Slow pyrolysis	-	Organic phase, *n*-hexane extracts, toluene extracts, ethyl acetate extracts, methanol extracts	^{1}H NMR
Rice straw[130]	Slow pyrolysis	-	Organic fraction	^{1}H NMR
Pine wood, sugarcane bagasse[45]	Fast pyrolysis, ZSM-5-catalyzed fast pyrolysis	-	Whole bio-oil	^{1}H NMR
Switchgrass[51]	Microwave pyrolysis	-	Liquid nitrogen trapped bio-oil	^{13}C NMR
Mahua seed[131]	Slow pyrolysis	-	Water immiscible phase	^{1}H NMR
Cotton residue[132]	Slow pyrolysis	-	Organic fraction	^{1}H NMR
Red pine[133]	Fast pyrolysis	-	Supercritical-CO_2-extracted fractions	^{1}H NMR
Spruce wood chips[54]	Microwave pyrolysis	-	Whole bio-oil, water-soluble extract, neutral extract, phenolic extract, organic acids extract	^{13}C NMR

Table 4. Comparison of the ^{1}H NMR Chemical Shift Integration Regions of Bio-oil[17, 41, 43, 44]

Ref 43		Ref 17		Ref 41		Ref 44	
Assignments	Chemical shift ranges (ppm) [43]	Assignments	Chemical shift ranges (ppm) [17]	Assignments	Chemical shift ranges (ppm) [41]	Assignments	Revised chemical shift ranges (ppm) [44]
$-C\underline{H}O$, $-COO\underline{H}$, downfield $Ar\underline{H}$	10.0-8.0	Aldehydes	10.1-9.5	$-COO\underline{H}$	12.5-11.0	$-COO\underline{H}$, $-C\underline{H}O$	10.0-8.3
$Ar\underline{H}$, $\underline{H}C=C-$ (conjugated)	8.0-6.8	(Hetero-) aromatics	8.5-6.0	$-C\underline{H}O$, $ArO\underline{H}$	11.0-8.25	$Ar\underline{H}$, $\underline{H}C=C-$	8.3-5.7
$\underline{H}C=C-$ (non-conjugated)	6.8-6.4	Methoxy, carbohydrates	6.0-4.4	Aromatics, conjugated – C=C-	8.25-6.0	$-C\underline{H}_n-O-$, $C\underline{H}_n-O-$	5.7-3.0
$C\underline{H}O$, $ArO\underline{H}$, $\underline{H}C=C-$ (non-conjugated)	6.4-4.2	Alcohols, methylene-dibenzene	4.4-3.0	Aliphatic $O\underline{H}$, $-C=C-$, $Ar-C\underline{H}_2-O-$	6.0-4.2	$-C\underline{H}_3$, $-C\underline{H}_n-$	3.0-0.5
$C\underline{H}_3O$, $-C\underline{H}_2O$, $C\underline{H}O$	4.2-3.0	Aliphatics α to heteroatom or unsaturation	3.0-1.5	Ether, methoxy	4.2-3.0	-	-
$C\underline{H}_3C=O$, $C\underline{H}_3-Ar$, $-C\underline{H}_2-Ar$	3.0-2.2	Alkanes	1.5-0.5	$-C\underline{H}_2C=O$, aliphatics	3.0-2.0	-	-
$C\underline{H}_2$, aliphatic OH	2.2-1.6	-	-	Aliphatics	2.0-0.0	-	-
$-C\underline{H}_3$, $C\underline{H}_2$	1.6-0.0	-	-	-	-	-	-

Table 5. Hydrogen percentage based on the ^1H NMR analysis of bio-oils from pine wood and sugarcane bagasse under different pyrolysis conditions.[45]

Assignments	Chemical shift ranges (ppm)	Hydrogen percentages[a]							
		S-550[b]	S-550-Z	P-450	P-450-Z	P-500	P-500-Z	P-550	P-550Z
$\text{-COO}\underline{\text{H}}$	12.5-11.0	4.06	0.22	1.19	0.43	0.25	0.11	1.09	0.08
$\text{-C}\underline{\text{H}}\text{O}$, $\text{ArO}\underline{\text{H}}$	11.0-8.2	8.99	3.01	8.59	5.84	5.86	3.57	5.59	4.95
Aromatics and conjugated alkene $\underline{\text{H}}$	8.2-6.0	16.28	24.53	17.74	19.90	18.18	20.05	14.26	25.33
Aliphatic $\text{O}\underline{\text{H}}$, $\text{-C}\underline{\text{H}}\text{=C}\underline{\text{H}}\text{-}$, $\text{Ar-C}\underline{\text{H}}_2\text{-O-R}$	6.0-4.2	9.13	6.55	6.50	3.62	7.86	7.56	15.05	3.44
$\text{R-C}\underline{\text{H}}_2\text{-O-R}$, $\text{C}\underline{\text{H}}_3\text{-O-R}$	4.2-3.0	14.25	9.88	15.73	15.28	13.74	14.85	24.95	12.42
$\text{-C}\underline{\text{H}}_2\text{CH=O}$, aliphatic H	3.0-2.0	16.04	28.13	24.33	32.83	28.61	32.64	18.72	31.84
Aliphatic H	2.0-0.0	31.24	27.69	25.93	22.10	25.49	21.22	20.34	21.94

a: Water region (3.7-3.3 ppm) was excluded. b: For simplicity, S denotes sugarcane bagasse, 450/500/550 denotes pyrolysis temperatures, Z denotes ZSM-5 catalyzed pyrolysis (e.g., S-550 denotes sugarcane bagasse bio-oil pyrolyzed at 550 °C without a catalyst; P-550-Z denotes pine wood bio-oil pyrolyzed at 550 °C in the presence of ZSM-5)

Table 6. Comparison of ^{13}C NMR Chemical Shift Integration Regions of Bio-oil.[41, 43]

Ref 43			Ref 41	
Assignments		Chemical shift ranges (ppm)[43]	Assignments	Chemical shift ranges (ppm)[41]
Carbonyls		215-163	Carbonyls	215-163
Aromatics		163-110	Aromatics, alkenes	163-103
Carbohydrates		110-84	Carbohydrates	103-70
Methoxy/hydroxyl		84-54	Methoxy/hydroxyl	70-54
Alkyl	General	54-0	Alkyl	54-0
	Mostly secondary and tertiary carbons	34-24		
	Mostly primary and some secondary carbons	24-6		

Table 7. ^{13}C NMR Analysis of Liquid-Nitrogen-Trapped Fractions of Bio-oils from Switchgrass Produced under Various Gas Atmospheres.[51]

Assignments	Chemical shift ranges (ppm)	Carbon percentages				
		CO	CH_4	H_2	PyGas	N_2
Ketones/aldehydes	215-180	0.8	3.3	0.3	2.1	2.6
Acids/esters	180-165	4.9	6.6	4.9	4.2	6.1
Aromatics	165-95	41.7	45.0	37.6	47.3	36.4
Alcohols/carbohydrates	95-55	8.9	9.9	10.1	9.9	18.1
Aliphatics	55-0	43.8	35.2	47.1	36.4	36.9

Table 8. The ^{13}C NMR Integration Data of Bio-oils Obtained with Catalysts.[52]

Assignments	Chemical shift ranges (ppm)	Carbon percentages								
		Sand	FCC-1[a]	FCC-2	FCC-3	ZSM5-1	ZSM5-2	PZSM5-1	PZSM5-2	PZSM5-3
Aldehydes, ketones	220-180	4.29	2.82	1.17	1.80	1.49	3.07	1.45	2.05	2.21
Carboxylic acids and derivatives	180-160	5.16	1.47	1.88	2.62	0.53	1.68	1.09	1.60	1.68
Carbons in aromatic hydrocarbons further from an oxygen atom	140-125	8.62	20.87	29.54	25.56	27.46	19.11	24.69	24.08	24.90
Total aromatics including olefins and phenolics	160-105	30.36	58.13	67.92	55.88	59.25	54.77	58.09	58.73	58.52
Levoglucosan, anhydrosugars, alcohols, ethers	105-60	24.86	5.35	1.60	9.06	10.14	11.02	10.21	8.46	8.51
Methoxy in lignin	57-55	7.66	4.68	2.91	4.95	5.10	5.63	5.24	4.72	4.50
Aliphatics	55-1	27.82	27.54	24.53	25.69	23.49	23.84	23.92	24.43	24.61

a: For simplicity, catalysts are denoted as fresh FCC catalyst (FCC-1), FCC catalyst steamed at 732 °C (FCC-2), FCC catalyst steamed at 788 °C (FCC-3), fresh ZSM-5 additive (ZSM5-1), ZSM-5 additive steamed at 732 °C (ZSM5-2), fresh phosphorous impregnated ZSM-5 additive (PZSM5-1), phosphorous-impregnated ZSM-5 additive steamed at 732 °C (PZSM5-2), phosphorous-impregnated ZSM-5 additive steamed at 788 °C (PZSM5-3)

Table 9. Comparison of the ^{13}C NMR integration data of the raw bio-oil and the bio-oil upgraded by zero-valent zinc.[53]

Assignments	Chemical shift range (ppm)	Carbon percentages	
		Raw bio-oil	Upgraded bio-oil
Carbonyls	215-170	9.8	3.1
Aromatic ethers, phenolics	150-120	12.7	12.2
Aromatics, alkenes	120-90	26.8	23.5
Alcohols, ethers	90-50	36.8	44.3
Aliphatics	50-0	13.9	16.9

Table 10. Chemical Shift Assignments for Bio-oils after Derivatization with TMDP Using NHND as an Internal Standard in a ^{31}P NMR Spectrum.[58]

Assignments		Chemical shifts (ppm)
endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (internal standard)		152.8-151.0
Aliphatic OH		150.0-145.5
C5-substituted condensed phenolic OH	β-5	144.7-142.8
	4-O-5	142.8-141.7
	5-5	141.7-140.2
Guaiacyl phenolic OH		140.2-139.0
Catechol type OH		139.0-138.2
p-Hydroxyphenyl OH		138.2-137.3
Acid-OH		136.6-133.6
Water peak		133.1-131.3
		16.9-15.1

Table 11. Quantitative ^{31}P NMR Results of the Hydroxyl Contents in Bio-oils from Pine Wood, Sweetgum, Softwood Lignin, and Cellulose.[18]

Feedstock of bio-oil	Hydroxyl contents (mmol/g)			
	Aliphatic OH	C-5 substituted phenolic OH	Guaiacyl phenolic OH/*p*-hydroxyphenyl OH	Carboxylic acids
Pine wood	0.73	0.29	1.36	0.24
Sweetgum	0.23	0.20	1.02	0.09
Softwood lignin	0.10	0.23	2.31	0.26
Cellulose isolated from pine wood	2.95	0.02	0.07	0.07

Table 12. Quantitative ^{31}P NMR Analysis of Lignin Bio-oil Subfractions after Derivatization with TMDP Using Cyclohexanol as an Internal Standard.[62]

Assignments		Chemical shifts (ppm)	Hydroxyl contents (mmol/g)		
			Fraction 1 (amine insolubles)	Fraction 2 (low-polarity portion)	Fraction 3 (phenolic compounds extract)
Aliphatic OH		150.0-145.5	0.00	0.03	0.19
Cyclohexanol (internal standard)		145.4-145.0	-	-	-
C5-substituted condensed phenolic OH	β-5	144.7-142.8	0.03	0.26	0.32
	4-O-5	142.8-141.7	0.01	0.17	0.26
	5-5	141.7-140.2	0.09	0.11	0.47
Guaiacyl phenolic OH		140.2-139.0	0.11	1.29	3.01
Catechol type OH		139.0-138.2	0.04	0.62	0.89
p-Hydroxyphenyl OH		138.2-137.3	0.01	0.32	0.31
Acid-OH		136.6-133.6	0.01	0.12	0.03

Table 13. Comparison of ^{19}F NMR and Oximation Methods in the Determination of the Carbonyl Group Contents in Different Bio-oils.[19]

Bio-oil sample	^{19}F NMR method			Oximation method
	Carbonyl contents (mmol/g)			Carbonyl contents (mmol/g)
	Aldehydes and ketones	Quinones	Total	
L	1.04	0.34	1.38	1.32
L-Z	0.90	0.37	1.27	1.20
P	4.21	0.53	4.74	4.68
P-Z	3.29	0.88	4.17	4.05
PR	3.27	0.53	3.80	3.71
PR-Z	3.31	0.58	3.89	3.77
P-1	3.27	0.47	3.74	3.70
P-2	3.53	0.62	4.15	3.99
P-3	3.96	0.68	4.54	4.50

For simplicity, the bio-oils are denoted as lignin pyrolysis oil (L), lignin pyrolysis oil obtained with ZSM-5 (L-Z), pine wood pyrolysis oil (P), pine wood pyrolysis oil obtained with ZSM-5 (P-Z), pine wood residue pyrolysis oil (PR), pine wood pyrolysis oil obtained with ZSM-5 (PR-Z); two pine wood pyrolysis oils produced from a pilot plant are denoted as P-1 and P-2, and a hardwood pyrolysis oil produced from pilot plant is denoted as P-3.

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ABBREVIATIONS

AlTi = aluminum-titanate
DDGS = dries distillers grains with solubles
DMSO-d_6 = Dimethyl sulfoxide-d_6
DOSY = ^{1}H diffusion-ordered NMR spectroscopy
FCC = fluid catalytic cracking
FT-IR = fourier transform infrared spectroscopy
GC = gas chromatography
GPC = gel permeation chromatography
HMQC = heteronuclear multiple quantum coherence
HSQC = heteronuclear single quantum correlation
HSQC-TOCSY = heteronuclear single quantum coherence-total correaltion spectroscopy
HPLC = high-performance liquid chromatography
HRMS = high-resolution mass spectrometry

INEPT = insensitive nuclei enhanced by polarization
LAC = (1*R*,5*S*)-1-hydroxy-3,6-dioxa-bicyclo[3.2.1]octan-2-one
LC = liquid chromatography
MK10 = montmorillonite K10
NHND = *endo-N*-Hydroxyl-5-norborene-2,3-dicarboximide
NMR = nuclear magnetic resonance
PLS = partial least squares
PyGas = model pyrolysis gas mixture
PZSM5 = phosphorous-impregnated zeolite socony mobil–5
SHS = switchable hydrophilicity solvents
S/N = signal-to-noise
TGA = thermo gravimetric analysis
TMDP = 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane
TPPO = triphenylphosphine oxide
ZSM-5 = zeolite socony mobil–5
2-D = two-dimensional
1-D = one-dimensional

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