

VIP Very Important Paper

Quantitative Low-Field ^{19}F Nuclear Magnetic Resonance Analysis of Carbonyl Groups in Pyrolysis OilsBridget Tang,^[a] Katie Chong,^[b] Arthur J. Ragauskas,^[c, d] and Robert Evans*^[a]

Pyrolysis bio-oils, one of the products of lignocellulosic biomass pyrolysis, have the potential to be widely used as fuels. The chemical composition of bio-oils is very complicated as they contain hundreds, if not thousands, of different, mostly oxygen-containing, compounds with a wide distribution of physical properties, chemical structures, and concentrations. Detailed knowledge of bio-oil composition is crucial for optimizing both the pyrolysis processes and for any subsequent upgrading into a more viable fuel resource. Here we report the successful use of low-field, or benchtop, nuclear magnetic resonance (NMR) spectrometers in the analysis of pyrolysis oils. Pyrolysis oils from

four different feedstocks were derivatized and analyzed using ^{19}F NMR techniques. The NMR results compare favorably with titrations for total carbonyl content. In addition, the benchtop NMR spectrometer proves able to reveal key spectral features, thus allowing the quantification of different carbonyl groups, such as aldehydes, ketones and quinones. Benchtop NMR spectrometers are typically compact, cheaper than their superconducting counterparts and do not require cryogenics. Their use will make NMR analysis of pyrolysis oils easier and more accessible to a wide range of different potential users.

Introduction

With growing concerns regarding the effect of carbon dioxide emissions and rapid depletion of fossil fuels, it is imperative to develop alternative and sustainable methods for fuel production. One approach to making sustainable fuels is by converting lignocellulosic biomass via pyrolysis processes.^[1] Lignocellulosic materials are primarily made up of cellulose, hemicellulose, and lignin, which makes up the plant cell wall.^[2,3] Lignin is a complex biopolymer containing, amongst other functional groups and repeating units, the three monolignols *p*-hydroxyphenyl (H), syringyl (S) and guaiacyl (G) (Figure 1).

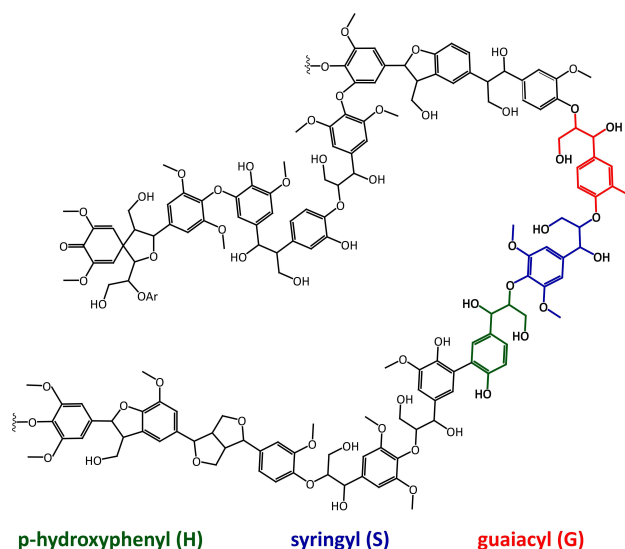


Figure 1. Schematic representation of a section of typical hardwood lignin, with monolignol units, *p*-hydroxyphenyl (H), syringyl (S) and guaiacyl (G), highlighted in green, blue, and red, respectively.

The weight distributions of cellulose, hemicellulose and lignin, as well as the different monolignols, depend on the type of biomass feedstocks present, as indicated by Scheme 1.

Pyrolysis is a process of thermal degradation of material at a high temperature, usually between 400 and 800 °C, in the absence of oxygen.^[7] The large chains in the lignocellulosic biomass break down into three products: char, pyrolysis oil and gases. The oil produced contains smaller molecules mostly made up of carbon, hydrogen and oxygen. However, these pyrolysis oils have a higher oxygen and water content compared to traditional petrol-based fuels^[8–11] and this results in pyrolysis oils having a typical pH between 2 and 3. Oxygen-containing compounds, such as aldehydes, ketones, quinones,

[a] B. Tang, Dr. R. Evans
Aston Institute of Materials Research
Aston University
Aston Triangle,
Birmingham,
B4 7ET (UK)
E-mail: r.evans2@aston.ac.uk





[b] Dr. K. Chong
Energy and Bioproducts Research Institute
Aston University
Aston Triangle,
Birmingham,
B4 7ET (UK)

[c] Prof. A. J. Ragauskas
Department of Chemical and Biomolecular Engineering
The University of Tennessee
Knoxville, Tennessee 37996 (United States)

[d] Prof. A. J. Ragauskas
Joint Institute for Biological Sciences, Biosciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37771 (United States)

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	Hardwoods	Grasses
	oak 	Virginia mallow 
	willow 	miscanthus 

Lignocellulose (weight %)	Cellulose	40-46	28-37
	Hemi-cellulose	17-23	23-29
	Lignin	18-25	17-20
Monolignols (weight %)	<i>p</i> -hydroxyphenol	0-8	5-35
	syringyl	45-75	20-55
	guaiacyl	25-50	35-80

Scheme 1. Typical lignocellulose (cellulose, hemicellulose, and lignin) and monolignol (guaiacyl, syringyl and *p*-hydroxyphenyl) compositions by weight for hardwood and grasses.^[4-6] Figure also indicates which biomass feedstocks have been used in this study.

hydroxyls, carboxylic acids and phenols, are the main contributors to the acidity of the pyrolysis oils. The acidity of the pyrolysis oil causes corrosion in storage and usage.^[12-14] These undesired properties make pyrolysis oils difficult to be used directly as fuel. To be useful, pyrolysis oils must be physically or chemically enhanced, or 'upgraded'.^[15]

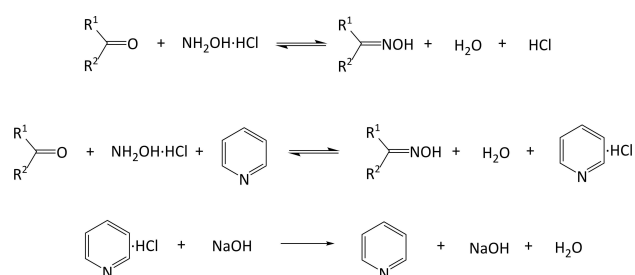
The identification and quantification of any oxygen-containing compounds is crucial for choosing the most optimum upgrading processes. Carbonyl-containing compounds, in particular, have a strongly deleterious effect on the stability of pyrolysis oils.^[16] Aldehydes, ketones and quinones are found to play a major role in the aging of pyrolysis oil, as carbonyl compounds may react with hydroxyl compounds and polymerize resulting in a change in viscosity of the pyrolysis oil.^[17] Carbonyl-containing compounds may also oxidize, producing corrosive carboxylic acids.^[18]

It is possible to quantify and analyze the total carbonyl content in pyrolysis oils by oximation followed by titration.^[19-21] The carbonyl groups are reacted with hydroxylamine hydrochloride for over a day. The reaction yields an oxime and hydrochloric acid as shown in reaction Scheme 2.

The reaction is in equilibrium, so pyridine is added to remove any excess HCl and drive the reaction to completion. The pyridine and HCl form pyridine hydrochloride salt. This salt is then titrated against NaOH with an end-point around pH 4.7.^[16,22]

The quantification of total carbonyl content is calculated using Equation (1) below:

$$\begin{aligned} & \text{moles of C = O/gram of sample} \\ &= \frac{n_{\text{NaOH}} [\text{mol}]}{\text{Dry weight of the oil [g]}} \end{aligned} \quad (1)$$

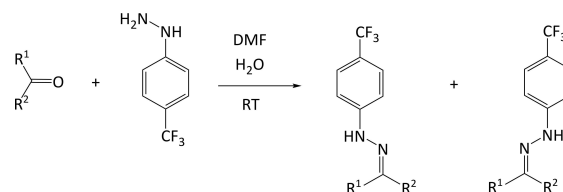


Scheme 2. Reaction scheme showing carbonyl-containing compound reacting with hydroxylamine hydrochloride producing oxime and HCl. The reaction is shifted towards the oxime in the presence of pyridine. Pyridine hydrochloride is then titrated with sodium hydroxide.

The identification and quantification of carbonyl groups in pyrolysis oil is complex as there are many different functional groups, alkyl chains of varying lengths, and rings, which can be saturated or unsaturated as well as fused together. With many different small compounds present in pyrolysis oil, simple proton NMR with its small chemical shift range is essentially impossible to analyze.

Derivatization methods react the sample with 'tagging' molecules, containing a magnetically-active nucleus such as ³¹P or ¹⁹F. This isolates compounds with particular functional groups while allowing for acquisition of the introduced nucleus.^[23,24] A general reaction scheme, where carbonyl-containing compounds react with 4-(trifluoromethyl)phenylhydrazine to form a fluorine-containing hydrazone, is shown in Scheme 3.

Several experimental methodologies have been reported. Sevillano et al. dissolved lignin samples in a mixed DMF/H₂O solution followed by the addition of 100 mg derivatization agent. This solution was left to react for 1 day in the dark.^[25] The derivatized mixture was precipitated using 100 mL of water and 3 drops of phosphoric acid. The sample was filtered using a sintered glass crucible and dried at 40 °C before analysis. Huang et al. followed a similar procedure, 60 mg pyrolysis-oil sample was dissolved in 500 μL of DMF and 1 mL of a 50:50 DMF-water (v/v) containing 110 mg of 4-(trifluoromethyl)phenylhydrazine was added.^[16] The mixture was left in the dark to react at room temperature for 24 h. The sample was then precipitated using pH 2 HCl solution, followed by freezing, thawing and drying for analysis. Constant et al. dissolved ca. 150 mg of sample and 10 mg of 1-methyl-4-(trifluoromethyl)benzene (an internal standard for the NMR experiments) in DMSO-*d*₆.^[26] 0.8 mmol of



Scheme 3. Reaction scheme for the derivatization of carbonyl-containing compounds by 4-(trifluoromethyl)phenylhydrazine.

4-(trifluoromethyl)phenylhydrazine was dissolved in 300 μL DMSO- d_6 and added dropwise to the sample. The solution was then transferred to a standard NMR tube and left to react in a pre-heated oven at 40 $^{\circ}\text{C}$ for 16 h. Integrals of the different regions are used to calculate the moles of carbonyl content per gram of pyrolysis oil using Equation (2).^[16]

$$\begin{aligned} \text{moles of C} &= \text{O/gram of sample} \\ &= \frac{\text{Integral ratio} \times n_{(\text{IS in NMR sample})} [\text{mol}]}{\text{Dry weight of the oil} [\text{g}]} \end{aligned} \quad (2)$$

To date, all reported ^{19}F NMR analysis of derivatized lignin samples has been performed on high-field NMR spectrometers. The development of NMR spectrometers has largely focused on increasing their sensitivity.^[27] This can be achieved by using higher magnetic fields^[28,29] and advances in spectrometer hardware such as cryoprobes.^[30] Superconducting magnets are used to produce the required high magnetic fields and necessitate the use of cryogens such as liquid nitrogen and liquid helium. The regular use of cryogens is expensive and cryogenic cooling requires technical maintenance. Liquid helium prices have increased significantly in the last decade due to a global helium shortage.^[31,32] Generally, NMR is not considered a low-cost analysis due to the high capital investment and maintenance costs. High-field NMR spectrometers can require a considerable investment, ranging upwards from ca. £600,000 for 500 MHz spectrometers. Larger spectrometers and attendant facilities can cost over £10 million. This limits the usage of NMR to larger research facilities.

Here the successful use of low field, or benchtop, NMR spectrometers in analyzing pyrolysis oil samples is demonstrated. Benchtop NMR spectrometers typically utilize permanent magnets that generate a static magnetic field of up to 2 T, corresponding to a proton resonance frequency of 80 MHz.^[33] Permanent magnets do not require cryogenic cooling, reducing the technical maintenance and maintenance cost.^[34] Typically, benchtop NMR spectrometer prices range from £30,000 to £150,000 providing a less expensive alternative to high-field spectrometers. Most benchtop NMR spectrometers have an external locking system and hence protiated solvents can be used. This significantly reduces the cost of operations, for example dimethyl sulfoxide (DMSO) cost ca. £35.70 (per 100 mL) and deuterated dimethyl sulfoxide DMSO- d_6 costs ca. £307.00 (per 100 g). Since the first commercial benchtop NMR spectrometer was launched in 2009,^[35] they have been used for the analysis of mixtures such as over-the-counter drugs,^[36] edible oils^[37] and crude oil-water biphasic mixtures.^[38] Recently, low-field NMR has been used for quantitative ^{31}P NMR analysis of alcohol groups in lignin.^[39–41] While low-field NMR suffers from lower sensitivity and poorer resolution than its higher-field counterpart, it is not crucial to have the multiplicity fully resolved when analyzing mixtures containing a vast number of compounds. To the best of our knowledge, this is the first time low-field ^{19}F NMR has been used to quantify the carbonyl groups in pyrolysis oils.

Experimental Section

Chemicals and materials

Sodium hydroxide reagent grade $\geq 98\%$ pellets and 4-(trifluoromethyl)phenylhydrazine were purchased from Sigma-Aldrich. N,N-dimethylformamide anhydrous 99.8%, dimethylsulfoxide (DMSO) 99+%, ethanol absolute 99.8%, 0.1 N hydrochloric acid, hydroxylamine hydrochloride 99+% and pyridine 99% extra dry over molecular sieves were purchased from Fisher Scientific. Deuterated dimethylsulfoxide (DMSO- d_6) was purchased from Cambridge Isotope Laboratories, Inc. All chemicals were used without any further purification. Model compounds containing carbonyl groups were used as simple samples for the method development of low-field ^{19}F NMR analysis. All reagents used as model compounds were obtained commercially, the origin and purity of these compounds used in this study are reported in the Supporting Information (Table S1). All pyrolysis oil samples were provided by the Energy and Bioproducts Research Institute (EBRI). The pyrolysis oil samples were produced by fast pyrolysis in a 300 g h^{-1} continuous fluidized bed reactor from oak, willow, Virginia mallow and miscanthus feedstocks. The pyrolysis oils were previously characterized using elemental analysis and pyrolysis gas-chromatography mass spectroscopy (py-GCMS). These results are outlined in Banks et al.^[40] There was at least one year between the initial analysis by Banks and the work presented here.

^{19}F NMR analysis

The derivatization of pyrolysis oil was carried out using a procedure adapted from Huang et al.^[16] 110 mg of 4-(trifluoromethyl)phenylhydrazine was dissolved in 1 mL of 50:50 DMF and water (*v/v*). This solution was added to a solution of pyrolysis oil (ca. 30 mg) dissolved in 500 μL dimethylformamide (DMF) in a 20 mL vial. The mixture was stirred in the dark for 24 h at room temperature. The derivatized pyrolysis oil was purified by the addition of 20 mL of pH 2.0 water, prepared by the dilution of 0.1 N HCl in deionized water. The mixture was precipitated by freezing. The frozen sample was melted to room temperature. The aqueous layer was carefully discarded, and the product was washed multiple times with pH 2.0 water to remove excess 4-(trifluoromethyl)phenylhydrazine. The precipitant was then air dried for 24 h. The dried sample was dissolved in protiated DMSO for NMR analysis, where 3-(trifluoromethoxy) benzoic acid was used as an internal standard (IS) and hexafluorobenzene (C_6F_6) was used for chemical shift calibration at -164.9 ppm, as depicted in Figure 2. All low-field NMR was carried out using a Magritek Spinsolve 43 MHz benchtop NMR. All high-field NMR was carried out using Bruker 500 MHz AVANCE NEO spectrometer. All data was processed using MestReNova 10 software.

Elemental analysis

Elemental analysis of all oils was carried out on a Flash 2000 elemental analyzer. Carbon, hydrogen, nitrogen and sulphur content were analyzed in triplicate, and the average values were taken. The oxygen content of the oils was found by difference.

Oximation followed by titration

The oximation of pyrolysis oil was carried out using the following procedure: Hydroxylamine hydrochloride solution was prepared by dissolving 17.50 g of hydroxylamine hydrochloride in 80.00 g of deionized water. The solution was transferred to a 500 mL volumetric flask, the volumetric flask was filled to the mark with

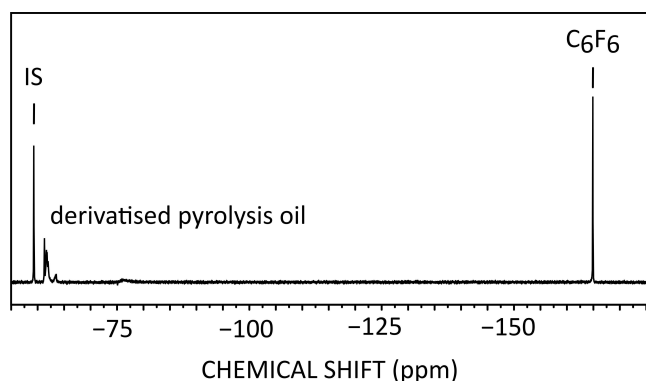


Figure 2. Low-field 1D ^{19}F NMR spectrum of derivatized pyrolysis oil sample. 3-(Trifluoromethoxy)benzoic acid used as the internal standard (IS, peak observed ca. -59.3 ppm). Hexafluorobenzene used as chemical shift reference (C_6F_6 , peak observed at -164.9 ppm).

anhydrous ethanol. The pyridine solution was prepared by adding 10 mL of pyridine into a 500 mL volumetric flask, the volumetric flask was filled with anhydrous ethanol. For the oximation reaction, ca. 0.40 g of pyrolysis oil reacted with 10.00 mL of hydroxylamine solution and 20 mL of pyridine solution in a sealed round-bottom flask. The reaction was left stirring for 48 h at room temperature. The reaction mixture was transferred to a 100 mL volumetric flask and filled with anhydrous ethanol. Aliquots of 25 mL were taken and titrated with 0.5 M sodium hydroxide solution. The titration endpoint, at $\text{pH}=4.7$, was measured using a micro pH electrode probe.

Results and Discussion

Generation of ^{19}F chemical shift map

A series of model carbonyl-containing compounds, likely to be found in pyrolysis-oil samples, were individually derivatized. Low-field 1D ^{19}F NMR spectra were acquired for all compounds and combined to produce a chemical shift map. Figure 3 shows this map, a stacked plot of all derivatized model compounds.

A summary of the chemical shift information can be found in Supporting Information (Table S2) where all chemical shifts were referenced using hexafluorobenzene -164.9 ppm. The chemical shifts of the derivatized ketones are ca. -61.0 to -61.7 ppm, those of derivatized aldehydes are ca. -1.7 to -61.9 ppm, and those of derivatized quinones are ca. -61.9 to -64.0 ppm. A summary of the chemical shift areas for ketones, aldehyde and quinones is represented in a schematic diagram (Figure 4).

Quantitative ^{19}F NMR analysis of model pyrolysis oils

To demonstrate that low-field ^{19}F NMR can be used to obtain suitably accurate integrals for quantification, four model pyrolysis-oils were studied. These model oils were derivatized using the procedure outlined in the Experimental Section. Low-field 1D ^{19}F NMR spectra were then acquired on the benchtop NMR spectrometer. Figure 5 summarizes the low-field ^{19}F NMR estimates for each class of compound, based on the integrated NMR spectra collected in Figure S5.

The compositions of the model oils and all data used to calculate the amount of carbonyl groups present in each sample are

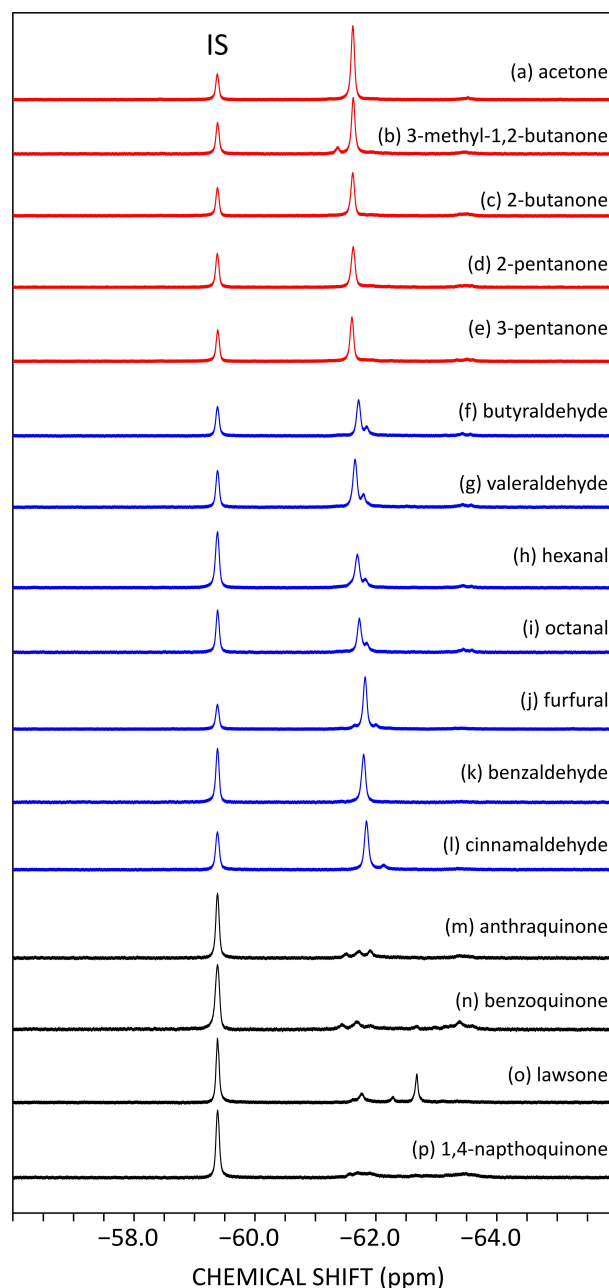


Figure 3. Stacked plot of 1D low-field ^{19}F NMR spectra of derivatized model compounds containing carbonyl groups with internal standard 3-(trifluoromethoxy) benzoic acid at -59.3 ppm. (a) Derivatized acetone, (b) derivatized 3-methyl-1,2-butanone, (c) derivatized 2-butanone, (d) derivatized, (e) derivatized 3-pentanone, (f) derivatized butyraldehyde, (g) derivatized valeraldehyde, (h) derivatized hexanal, (i) derivatized octanal, (j) derivatized furfural, (k) derivatized benzaldehyde, (l) derivatized cinnamaldehyde, (m) derivatized anthraquinone, (n) derivatized benzoquinone, (o) derivatized lawsone (2-hydroxy-1,4-naphthoquinone), and (p) derivatized 1,4-naphthoquinone.

summarized in the Supporting Information. Table S3, Table S4 and Figure S5 detail the expected amounts of ketones, aldehydes and quinones present in the model oils and compare them with the measurements obtained via NMR spectroscopy. All NMR experiments were performed in triplicate.

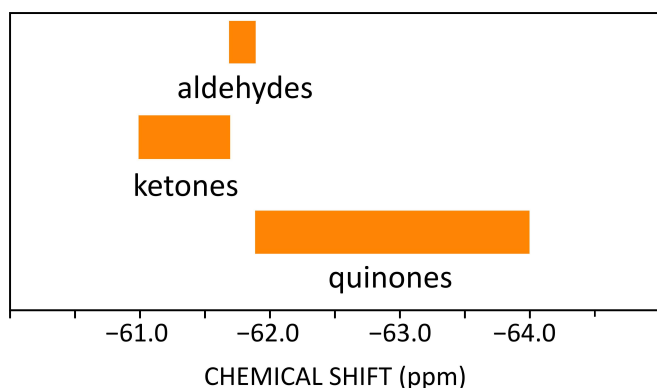


Figure 4. Schematic representation of ^{19}F NMR chemical shift regions for carbonyl-containing compounds derivatized using 4-(trifluoro)phenylhydrazine.

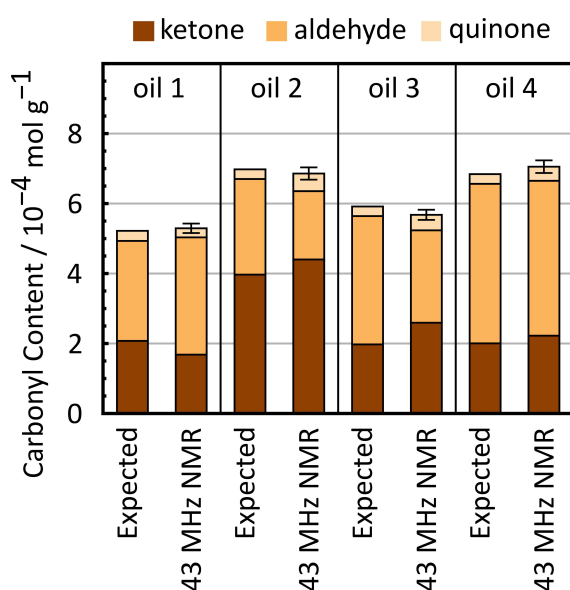


Figure 5. Bar chart comparing the estimates of ketones, aldehydes and quinones concentrations determined by low-field ^{19}F NMR spectroscopy technique with the expected amounts present in the four model oil samples.

The NMR technique may be limited due to the relatively small ^{19}F chemical shift range for the derivatized compounds and subsequent overlap of peaks from different species. While compounds chosen for the model oils were chosen to reduce the chances of two peaks completely overlapping, all recorded NMR spectra presented in this work show that there is always some overlap from the quinone region in the ketone and aldehyde regions. This will always introduce some uncertainty into the measurements and subsequent calculations. However, in practice, these prove to be minimal for the model oil compounds. Low-field ^{19}F NMR proves able to provide accurate chemical information on the different classes of compounds present.

Characterization of pyrolysis oils

Elemental analysis of the four pyrolysis oils were re-acquired to confirm the oil compositions. Table 1 summarizes the elemental composition of the four oils, where the oxygen content was

Table 1. Elemental analysis results for pyrolysis oil produced from various feedstocks (oak, willow, Virginia mallow and miscanthus). The original study, found in Reference [40], is reproduced in Table S5.

Pyrolysis Oil	C [%]	H [%]	N [%]	S [%]	O [%]
Oak	46.97	6.07	0.30	0.00	46.66
Willow	45.01	6.83	0.85	0.00	47.31
Virginia Mallow	47.17	6.73	0.42	0.00	45.68
Miscanthus	49.00	7.04	0.28	0.00	43.68

calculated from the remainder. All the data was within the instrumental error of 5% of values reported for the different feedstocks in the original paper.^[42] The results of the original study are reproduced in Table S5.

Elemental analysis provides only the full oxygen content as a weight percentage. It does not give any additional information such as structures or functional groups present, crucial for identifying the oxygen-containing compounds in pyrolysis oils. Other analytical techniques are needed to identify and quantify the oxygen-containing compounds.

The total carbonyl content of the four oils was determined using oximation reactions followed by titration, as detailed in the Experimental Section. Each reaction-titration was performed in triplicate and an average of the results, and associated errors, calculated. The total carbonyl content was calculated using Equation 1. These results are summarized in Table 2.

To complete the characterization of the pyrolysis oils, all four oils were derivatized and analyzed using ^{19}F NMR methods outlined in the Experimental Section. Figure 6 compares ^{19}F NMR spectra of the oak sample acquired on both high-field NMR and low-field NMR spectrometers. Similar figures for the other three pyrolysis oils, can be found in the Supporting Information (Figures S6, S7 and S8). All NMR experiments were performed in triplicate.

Comparison with high-field (500 MHz) ^{19}F NMR

Figure 7 summarizes the estimates of ketone, aldehyde and quinone concentrations from both low-field (43 MHz) and high-field (500 MHz) ^{19}F NMR analysis. These are both comparable to each other as well as to the total carbonyl content values determined by the oximation method (OT) (Table 2). Both NMR methods give estimates of the concentrations of ketones, aldehydes and quinones and there is little difference between experiments performed on low- and high-field spectrometers.

Overall, it was found that oils produced from hardwood-based biomass, such as oak and willow, contained more aldehydes and ketones whereas those produced from grass-based biomass, Virginia mallow and miscanthus, contained more quinones. Quinones are known to form from the oxidation of phenolic compounds in the lignin. For example 1,4-benzoquinone can be formed from the oxidation of *p*-hydroxyphenyl compounds.^[43] This is consistent with the compositions of the biomasses used. Grass-based feedstocks

Table 2. Summary of the total carbonyl groups of the different pyrolysis oils analyzed using oximation reaction followed by titration.

Pyrolysis oil	Total carbonyl content [$10^{-3} \text{ mol g}^{-1}$]
Oak	5.99
Willow	4.61
Virginia Mallow	5.58
Miscanthus	4.92

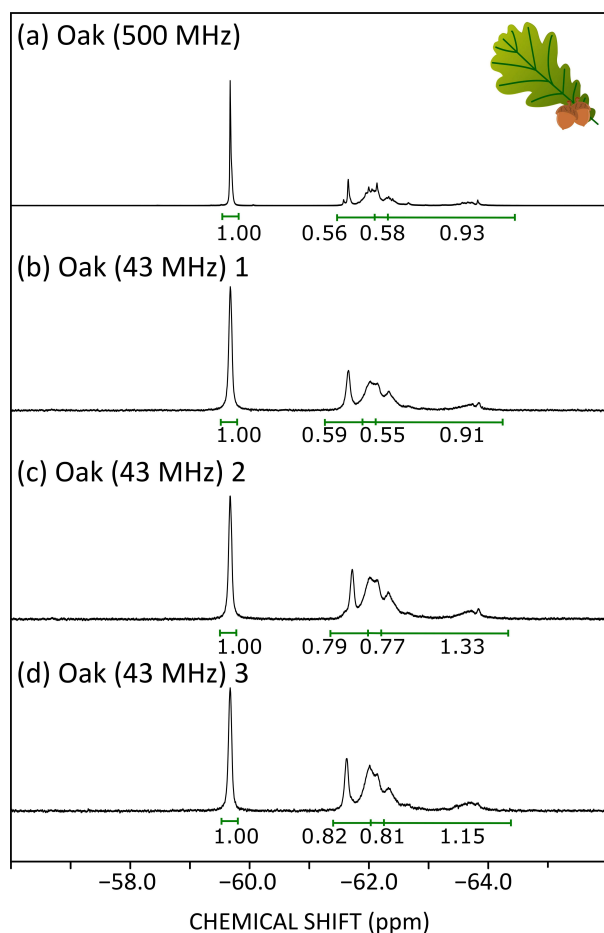


Figure 6. Stacked plot of (a) 1D ^{19}F NMR spectrum of derivatized pyrolysis oil produced from oak at 500 MHz and (b–d) 1D ^{19}F NMR spectra of derivatized pyrolysis oil produced from oak at 43 MHz in triplicate.

typically contain between 5–35% *p*-hydroxyphenyl units compared to 0–8% in hardwood-based feedstocks. This difference is reflected in the NMR analysis of the four pyrolysis oils.

Conclusions

This work details the first time low-field, or benchtop, ^{19}F nuclear magnetic resonance (NMR) analysis has been used to quantify the amounts and types of carbonyl groups in pyrolysis oil samples. Competing methods for this task are available. Elemental analysis determines the percentage of oxygen in a sample but does not provide any specific information on the types of oxygen-containing compounds present. As carbonyl-containing compounds represent only a portion of the oxygen present in pyrolysis oils, there may also be alcohols and, more importantly, carboxylic acids present which contribute to the oils' acidity. Oximation followed by titration obtains an estimate for the total carbonyl content present but is incapable of providing any further chemical or structural information, an important factor when deciding on the route of upgrading. The ^{19}F NMR estimates of the total carbonyl content are directly comparable to those obtained from this traditional alternative but also provide accurate chemical information on the quantities of different types of carbonyl-containing compounds present. This is a clear advantage of the NMR approach.

Fluorine is an excellent nucleus for NMR experiments. ^{19}F is a 100% abundant spin- $1/2$ nucleus, has a high gyromagnetic ratio, and its signals span a very broad chemical shift range. Even small changes in local chemistry can lead to big differences in the chemical shifts of ^{19}F signals. Here they are used to distinguish between different types of carbonyl compound. This also offers a clear path to an improved methodology. Derivatization reagents which leave the fluorine atoms closer to the functional groups of the analytes should result in a wider range

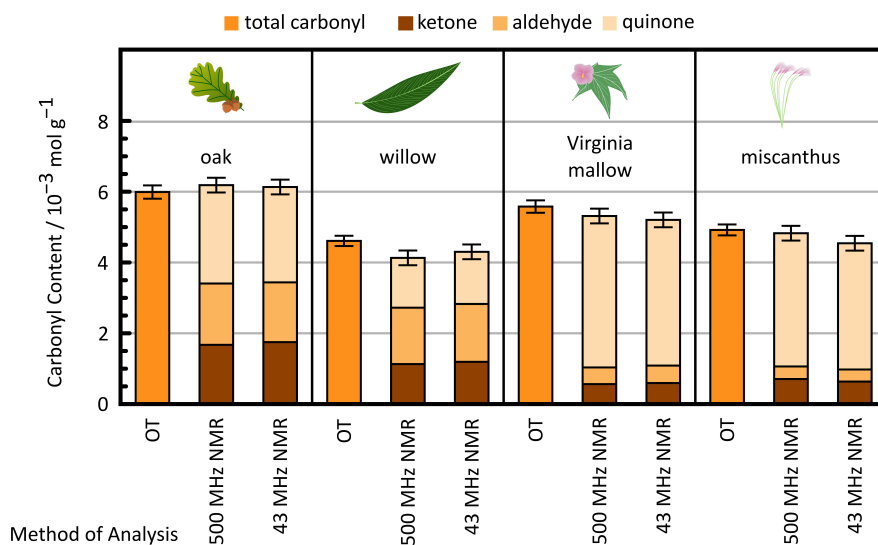


Figure 7. Bar chart comparing the concentrations of ketones, aldehydes and quinones in pyrolysis oils produced from oak, willow, Virginia mallow and miscanthus using different methodologies: oximation followed by titration (OT), high-field NMR spectroscopy (500 MHz NMR) and low-field NMR spectroscopy (43 MHz NMR).

of chemical shifts and better resolution of peaks.^[44] Better resolution of peaks will also enable the use of multidimensional NMR methods, such as diffusion-ordered spectroscopy.^[45] Other improvements could include reducing the duration of the derivatization reaction, which would facilitate increased sample throughput.

The biggest drawback for the ¹⁹F NMR methodology presented here is that each spectra contains many peaks in a small spectral width and, therefore, suffer from significant overlap of peaks. However, the resolution of individual signals is not crucial for ¹⁹F NMR analysis of pyrolysis oil. Even in high-field experiments, the spectra are severely overlapped. There is little additional ambiguity added by moving to lower field, benchtop spectrometers. The results from the low-field NMR study of pyrolysis oils provide a detailed enough description of the different carbonyl environments, comparable to quantification using high-field NMR analysis. Simple integration, using standard NMR processing packages, obtains useful, usable data for these samples. Other methods such as Global Spectral Deconvolution (GSD) could be used for the estimation of integrals.^[46] GSD deals with overlapping peaks by modelling the experimental lineshapes and often proves more accurate than sum integration.^[47]

Even though low-field NMR is less sensitive than and offers poorer resolution to high-field NMR, it is demonstrated here that a very similar quality of NMR data can be acquired for derivatized-pyrolysis oil samples, enough to accurately estimate concentrations of different classes of carbonyl-containing species. In addition, low-field spectrometers have some key advantages. They are typically compact, requiring minimal laboratory space. They are cheaper, often require less technical maintenance and do not require cryogenics, making NMR techniques more accessible to a wider range of users, particularly smaller research laboratories and institutions.

Supporting Information

Supporting information contains additional content detailing method development, ¹⁹F NMR spectra and all data used to generate the chemical shift map, and further supporting material, including ¹⁹F NMR spectra, for the characterization of both model and pyrolysis oils.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

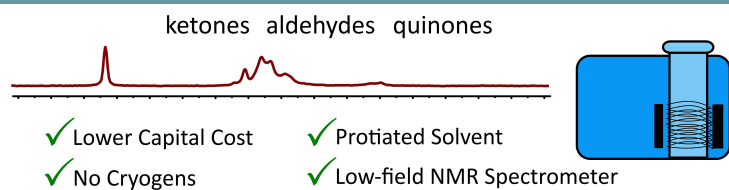
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RESEARCH ARTICLE



Simpler, cheaper, accurate: Low-field, or benchtop, nuclear magnetic resonance (NMR) spectrometers prove capable of quantitative analysis of pyrolysis oils from a range of lignocellulosic feedstocks. The NMR estimates of total carbonyl content compare favorably with titrations while the

acquired spectra allow for the quantification of carbonyl groups such as ketones, aldehydes and quinones. Benchtop NMR spectrometers are cheaper than their superconducting counterparts and require neither cryogenics nor deuteriated solvents.

*B. Tang, Dr. K. Chong, Prof. A. J. Ragauskas, Dr. R. Evans**

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Quantitative Low-Field ^{19}F Nuclear Magnetic Resonance Analysis of Carbonyl Groups in Pyrolysis Oils

