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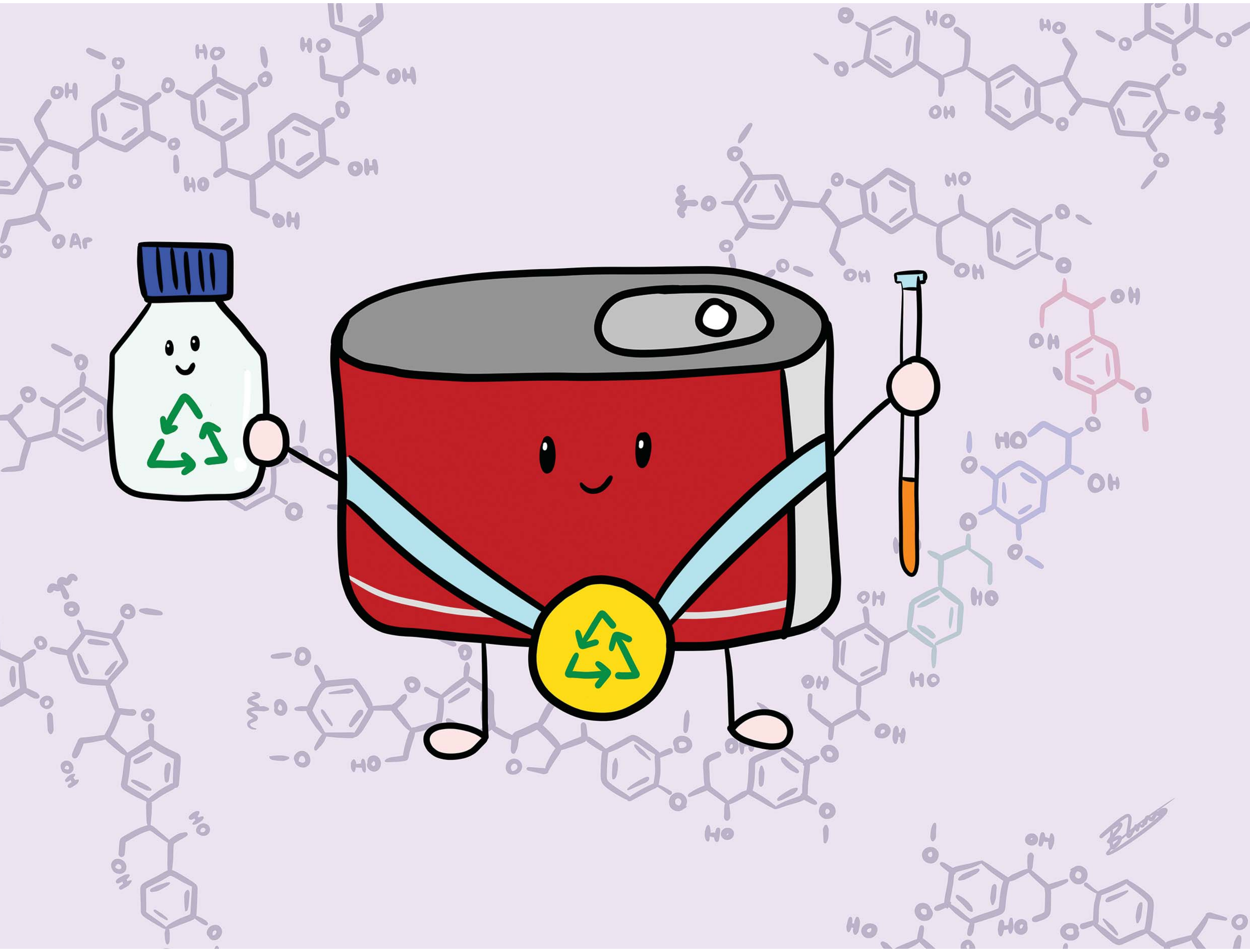

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PAPER
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Introducing bioderived solvents for safer and more sustainable ^{19}F benchtop NMR analysis of pyrolysis oils

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The development of increasingly sustainable analytical chemistry techniques is a growing area of research. Detailed knowledge of bio-oil composition is crucial for the wider use of this alternative, sustainable fuel product, whether by guiding and optimising the pyrolysis processes or for indicating appropriate upgrading methods. The oxygen-containing species in the oil are most important to analyse as they are key to the long-term stability and further processing of the oil. A common analytical method is derivatisation, inserting ^{19}F nuclei only into specific compounds in the sample, so that a sparser NMR spectrum of a subset of the compounds present can be acquired with even a benchtop NMR spectrometer. However, the derivatisation reactions themselves are not benign, with the most commonly used method relying on DMF throughout. While DMF is highly effective in facilitating the derivatisation reaction, it is not only harmful but increasingly restricted in use. By substituting DMF with ethyl lactate, the reaction is rendered safer and more sustainable. The change in solvent does not affect the NMR results, with estimates of total carbonyl content comparable with those produced by titration. The spectra acquired are detailed enough to also allow the quantification of the different carbonyl functional groups present. By switching to ethyl lactate, it is possible to increase the amount of water in the solvent mixture, further reducing the environmental impact, user risks and cost of the analytical method. By replacing harmful solvents with greener alternatives, benchtop NMR analyses of pyrolysis oils are increasingly safer to run, increasingly cheaper to run, and increasingly more accessible to a wide range of different users.

Sustainability spotlight

Nuclear Magnetic Resonance spectrometers are found in most research laboratories. However, the use of high-field, superconducting magnets, and their thirst for cryogens such as liquid nitrogen and helium, make them highly expensive to run and maintain. We believe that benchtop NMR can effectively replace their high-field counterparts, especially in the analysis of sustainable fuels and bio-oils. However, the derivatisation methodologies currently used must be made more sustainable. Harmful and unsustainable solvents are still widely used. We can replace them with bio-derived alternatives, and their aqueous mixtures, to further improve the sustainability of the bio-oil analysis. This work combines a focus on affordable and clean energy (SDG 7) and climate action (SDG 13), with responsible consumption and production (SDG 12).

Introduction

While much nuclear magnetic resonance (NMR) research and analysis takes place using superconducting magnets, there has been a recent expansion in the use of low-field, or benchtop, spectrometers.[1] Using a large permanent magnet, benchtop NMR spectrometers are smaller, typically cost a fraction of their superconducting higher field counterparts, and do not require cryogens, making them cheaper and safer to run on a day-to-day basis.[2] An additional advantage of benchtop NMR is that they often feature an external lock mechanism. Specialist deuteriated solvents are not essential. As a result of the weaker magnetic fields used, benchtop NMR suffers from lower

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sensitivity and poorer resolution than its higher-field counterpart. However, it is not always crucial to have the multiplicity fully resolved when analysing mixtures containing many similar compounds. Commercial benchtop NMR spectrometers have been used for a wide range of research and teaching analyses,[3] such as deducing the composition of edible oils,[4] the monitoring of polymerisation kinetics,[5–7] and, recently, the analysis of hydroxyl groups in both natural and modified lignins.[8–10]

The accurate analysis of complex mixtures, such as pyrolysis bio-oils, is vital to developing them as viable alternative fuel products. Pyrolysis is a thermochemical conversion process, an irreversible heat-driven decomposition of materials, such as lignocellulosic biomass, in the absence of oxygen.[11] Pyrolysis products typically contain a solid char, gases, and an oil.[12] Such bio-oils are mixtures of many dozens, if not hundreds, of different organic compounds, including a variety of oxygen-containing species such as alcohols, aldehydes, carboxylic acids, guaiacols, and water.[13] Turning bio-oils into viable fuels for wider use requires a deep understanding of their chemical compositions. In particular, carbonyl groups are typically unwanted, as they make bio-oils significantly less stable. The carbonyl groups may react with hydroxyl compounds, to form viscous polymers, or oxidise, to produce carboxylic acids.[14,15] Characterising and quantifying the carbonyl-containing species present provides a vital insight into the stability of the oil and any required processing to produce a viable fuel product.

While the use of benchtop NMR spectrometers makes this critical analysis safer, cheaper, more widely available, and more sustainable, it is not the only aspect of the analytical process that can be made greener and more sustainable. NMR analyses of bio-oils typically use derivatisation reactions. Derivatisation is required as the raw oil samples contain many compounds, and their signals overlap. Resolution can be achieved by deliberately and selectively reacting a sub-set of the compounds with molecules that contain specific functional groups containing either ^{31}P or ^{19}F nuclei. By using these nuclei, both 100% abundant and possessing reasonably high gyromagnetic ratios, a single peak for each distinct derivatised compound can be obtained. The derivatised product is then analysed using the sparser NMR spectrum of a particular subset of the sample.[16–19] An additional advantage of this method is that, unless also derivatised, the solvent signals[20] do not appear in the sparser NMR spectrum.

In the analysis of carbonyl compounds, 4-(trifluoromethyl)phenylhydrazine is widely used as a derivatising agent, and effective protocols for its use have been developed. Each derivatisation experiment uses a number of solvents, both in the reaction of oil that adds the fluorine nuclei to the oil components and then in preparation of a final NMR sample. In the analysis of carbonyl groups, the most commonly used solvent is *N*,*N*-dimethyl formamide (DMF). DMF is a dipolar aprotic solvent with varied uses across the chemical industries. It is capable of dissolving both the derivatising agent and almost all of the compounds typically found in bio-oils, as well as being mostly tolerant of the oil's relatively high water content. However, DMF is one of several solvents that have been targeted for replacement because of their harmfulness and possible environmental impact.[21] The use of DMF has been restricted in the European Union since December 2023 because of its reproductive health hazard.[22] There are numerous methods for summarising the hazards and safety information of chemicals, including safety diamonds and hazard pictograms. More recently, schemes such as the CHEM21 scoring system[23,24] allow for a quick analysis and visualisation of the hazards present. Chart 1 summarises the various hazards, hazard symbols and hazard statements for DMF. The hazard statements are colour coded according to their score indicated by the CHEM21 scheme. The H360 statement, signifying that DMF may damage fertility or the unborn child, renders the solvent unsafe for wider use.

The widespread uptake of benchtop ^{19}F NMR analysis of bio-oils will be severely hindered unless an alternative to DMF can be found. In this work, alternative, greener solvents are identified for use in benchtop NMR analyses of carbonyl content for pyrolysis oils and successfully implemented into the reaction methodology. The derivatisation reaction is analysed on the basis of potential environmental harm and the sustainability of the chemicals involved. Alternative solvents such as Cyrene™, γ-valerolactone, and ethyl lactate are suggested, based on previous successes in replacing DMF, reviewed on the basis of their physical and chemical properties, and tested for their compatibility with the derivatisation reaction. For this particular system, ethyl lactate stands out as the prime candidate, characterising both model compounds and bio-oil samples with suitable levels of accuracy and precision. The other solvents all either failed to effectively dissolve the components of the derivatisation reaction or reacted themselves. The use of ethyl lactate also allows for the system to be made increasingly aqueous, increasingly less toxic, and increasingly less environmentally damaging, yet still fully effective in the quantitative analysis of pyrolysis bio-oils.

Experimental

Chemicals and methods

N,*N*-Dimethylformamide anhydrous 99.8%, 1-butylpyrrolidin-2-one, dimethylsulfoxide (DMSO) 99+%, 0.1 M hydrochloric acid, ethyl lactate, Cyrene™, and γ-valerolactone were purchased

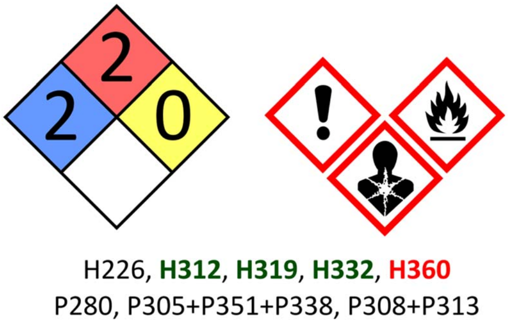

Chart 1 Summary of DMF hazards, NFPA 704 safety square, warning symbols and hazard statements. Hazard statements are colour-coded according to their CHEM21 classification.

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from Sigma Aldrich. Deuteriated dimethylsulfoxide (DMSO-d_6) was purchased from Cambridge Isotope Laboratories, Inc. All chemicals were used without further purification. While ethyl lactate does contain a stereocentre, a racemic mixture was used here.

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 SI.1, Table S1.

All pyrolysis oil samples were provided by the Energy and Bioproducts Research Institute (EBRI), Aston University. Four 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 have been previously characterized using elemental analysis, pyrolysis gas-chromatography mass spectroscopy (py-GCMS), oximation followed by titration, and ^{19}F NMR. These results are outlined in the publications of Banks *et al.*[25] and Tang *et al.*[26] Beechwood pyrolysis oil was produced by fast pyrolysis in a 1 kg h^{-1} continuous fluidized bed reactor.

^{19}F NMR analysis

The derivatization of pyrolysis oil samples was carried out using a procedure adapted from Huang *et al.*[19] and further detailed in Tang *et al.*[26] 110 mg of 4-(trifluoromethyl)-phenylhydrazine was dissolved in 1 mL of solvent. In the original procedure, this was 50 : 50 DMF and water (v/v). This solution was added to a pyrolysis oil (*ca.* 30 mg) dissolved in 500 μL solvent in a 20 mL vial. To test if the replacement solvents reacted with the derivatising agent, the oils were replaced with the same mass of each solvent at this stage. To test the viability of using different solvents, DMF was replaced by alternative solvents, as described in the later text.

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 and then 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 air dried for 24 h. The dried sample was then dissolved in the same protiated DMSO solvent as used in the reaction for NMR analysis. All experiments contained a drop of hexafluorobenzene (C_6F_6), for chemical shift calibration at −164.9 ppm, and *ca.* 15 mg of 3-(trifluoromethoxy) benzoic acid, as an internal standard (IS). All low-field NMR was carried out using a Magritek Spinsolve 43 MHz benchtop NMR. All data was processed using MestReNova 10 software. Integrals of the different regions, corresponding to different functional groups, are used to calculate the moles of carbonyl content per gram of pyrolysis oil using eqn (1):

$$\text{Moles carbonyl per gram} = \frac{\text{integral ratio} \times n_{\text{IS}}}{\text{dry weight of the oil}} \tag{1}$$

A worked example of this calculation can be found in SI.2.

Results and discussion

Solvent properties

Five possible replacement solvents for DMF have been identified. Ethyl lactate is an environmentally benign solvent with the potential to substitute toxic industrial solvents due to many attractive features: low volatility, biodegradability, noncorrosive and non-carcinogenic behaviour, broad liquid temperature range and low viscosity.[27] Due to its low toxicity, ethyl lactate is approved by the U.S. Food and Drug Administration (FDA) as a pharmaceutical and food additive.[28] Ethyl lactate has very similar solvent properties to 1-methylpyrrolidin-2-one, however, the latter solvent is known to be a reproductive toxin and has been placed on the EU "Substances of Very High Concern" list. The structurally similar 1-butylpyrrolidin-2-one has been demonstrated to be an effective replacement of its methyl analogue[29] and has been shown to successfully replace DMF in a number of synthetic procedures.[30] A number of synthetic routes for this compound are available, including *via* bio-derived compounds such as glutamic acid.[31] γ-Valerolactone is another bioderived solvent, produced from either cellulose or hemicellulose.[32] Particular advantages of γ-valerolactone include its biodegradability and non-toxicity, while its combination of low melting point, high boiling point and high thermal stability make it a robust solvent for use at larger scale and at higher temperatures. It has successfully replaced DMF in a number of synthetic reactions.[32] Cyrene™ is the market name for dihydrolevoglucosenone. This solvent can be produced in two steps from biomass, while being biodegradable, non-mutagenic and non-toxic. A "green" profile combined with its physical properties makes Cyrene™ a plausible substitute for a number of widely used toxic organic solvents, including DMF.[33] Note that all four solvents discussed above contain carbonyl function groups.

In the original experimental protocol, while the reaction was performed in DMF, the final derivatised product was dissolved in DMSO for NMR analysis. Both DMF and DMSO are dipolar aprotic solvents, and, given that it is already used in the final stage of the analysis procedure, DMSO was also tested as a possible replacement for DMF. It is worth noting two things at this stage. First, DMSO, while not hazardous, scores as 'problematic' in the CHEM21 [23,24] solvent selection guide solely on account of its boiling point. Cyrene™, 1-butylpyrrolidin-2-one, and γ-valerolactone all score worse in this category, as each has a boiling point in excess of 200 °C. A high boiling point may not be relevant for all reactions. Second, bio-derived solvents, while more sustainable in terms of their source, may be hazardous in their own right. For example, ethyl lactate carries the H318 hazard warning, indicating it may cause serious eye damage, and the H335 hazard warning, indicating it may cause respiratory irritation.

Any solvent that replaces DMF in the derivation reaction will need to be chemically similar. There are a number of schemes for characterising solvents and their chemistry. First, solvents need comparable physical parameters. Table 1 compiles two

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important physical parameters for the set of five solvents discussed above, as well as water and DMF.

The melting point indicates the temperature at which the solid solvent turns into a liquid. The separation step of the reaction involves freezing, so this requires the melting points of the replacement solvents to be lower than water and, ideally, comparable to DMF. It should be noted that organic-water solvent systems can exhibit melting point depressions. For this set of solvents, this would lower the melting points further and should not complicate the analysis. Viscosity indicates how easily the solvent flows. The green replacement solvents are all higher in viscosity, with Cyrene™ possessing a viscosity almost ten times higher than the other solvents tested, which may lead to complications in mixing and separation of solvents. We also collected flash point and boiling point data. The flash point indicates the lowest liquid temperature at which a liquid may be capable of forming an ignitable vapour/air mixture. The boiling point indicates the temperature at which the vapour pressure of the liquid equals the surrounding pressure and the liquid becomes a vapour. As the derivatisation reaction takes place at room temperature or below, these should simply be a close match to DMF and these data can be found in SI.3, Table S5. High boiling points may become an issue should further separation and recycling of the solvent be required. None of the data collected in Table 1 precludes any of the solvents from consideration.

Second, chemical similarities and differences can also be identified and discussed through the use of appropriate solvent parameters. In this work, the Hansen Solubility Parameters (HSP) have been used.[34,35] This set of parameters are a tool for identifying solvents, or combinations of solvents, that can dissolve a particular compound. They take the form of three values for each solvent, based on the energy from dispersion forces between molecules, which correlate with the van der Waals forces associated with the solvent, the energy from polar intermolecular forces between molecules, which correlate with permanent electric dipoles in the solvent molecules, and the energy from hydrogen bonds between molecules, which arise from highly electronegative atoms such as nitrogen, oxygen and fluorine. These three parameters have been collected for a broad set of solvents and illustrated in Fig. 1. Note that, for ease of display, the three-dimensional set of parameters has been reduced to two here, with the hydrogen-bonding component not shown. The possible green replacement solvents are represented by green symbols and annotated in the figure. Other classes of solvents are grouped together and coloured according to their class: purple circles represent polar aprotic solvents, orange circles represent polar protic solvents, and black circles represent nonpolar solvents. Water, DMSO and DMF are also individually labelled. Table 2 collects the Hansen solubility parameters for the seven solvents discussed in more detail throughout this work.

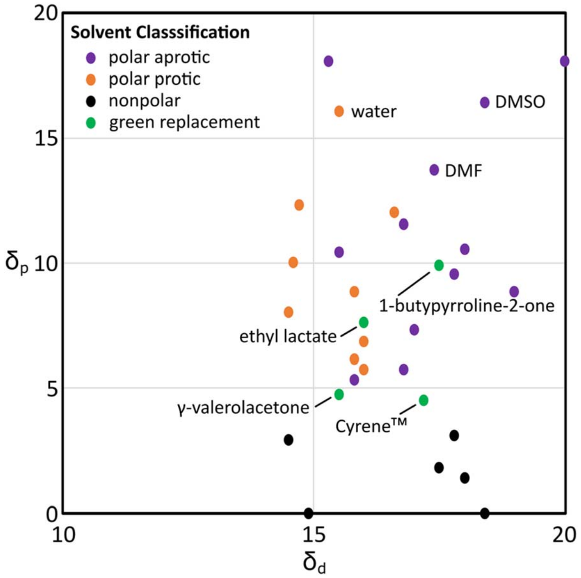

Fig. 1 2D map of pairs of Hansen solubility parameters, δ_p and δ_d, for common solvents. Purple circles indicate polar aprotic solvents. Orange circles indicate polar protic solvents. Black circles indicate nonpolar solvents. Green circles indicate green solvents selected to replace DMF.

A summary of the full set of three HSP for each solvent included in Fig. 1 is provided in SI.3, Table S6. Where possible, HSP values have been validated with an additional reference, taken from ref. 21, 27, 32, 36, 37, 38 and 39 as indicated in the table. At least three different sets of Hansen Solubility Parameters have been reported for Cyrene™,[33,38,39] with the largest differences in δ_p. Being, to the best of our knowledge, the most recent data available, the set of parameters stated in ref. 39 was used in Table 2.

Table 1 Summary of physical parameters, melting point and viscosity, for the solvents studied in this work. Asterisk indicates viscosity measured at 25 °C

Solvent	Melting point (°C)	Viscosity at 20 °C (mPa s)
DMF	−61	0.92
Water	0	1.0
DMSO	18.4	2.0
Ethyl lactate	−26	2.4*
1-Butylpyrrolidin-2-one	<−75	4.3
γ-Valerolactone	−31	2.2
Cyrene™	<−20	14.5

Table 2 Summary of Hansen solubility parameters for the seven solvents discussed in more detail throughout this work

	Hansen solubility parameters		
Solvent	δ_d	δ_p	δ_h
DMF[21,36]	17.4	13.7	11.3
Water[32,37]	15.5	16.0	42.3
DMSO[21,37]	18.4	16.4	10.2
Ethyl lactate[27,37]	16.0	7.6	12.5
1-Butylpyrrolidin-2-one[21,38]	17.5	9.9	5.8
γ-Valerolactone[32,38]	15.5	4.7	6.6
Cyrene™[39]	17.2	4.5	5.4

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Table 3 Summary of the solubility tests performed with key components of derivatization reaction

		4-Trifluorophenyl hydrazine		
Solvent	30 mg bio-oil	10 mg	110 mg	110 mg + H_2O
DMSO	✓	✓	✓	✓
Ethyl lactate	✓	✓	✓	✓
1-Butylpyrrolidin-2-one	✓	✓	✓	✓
γ-Valerolactone	✓	✓	✓	✗ phase separation
Cyrene™	✓	✓	✗ not soluble	✗ emulsion

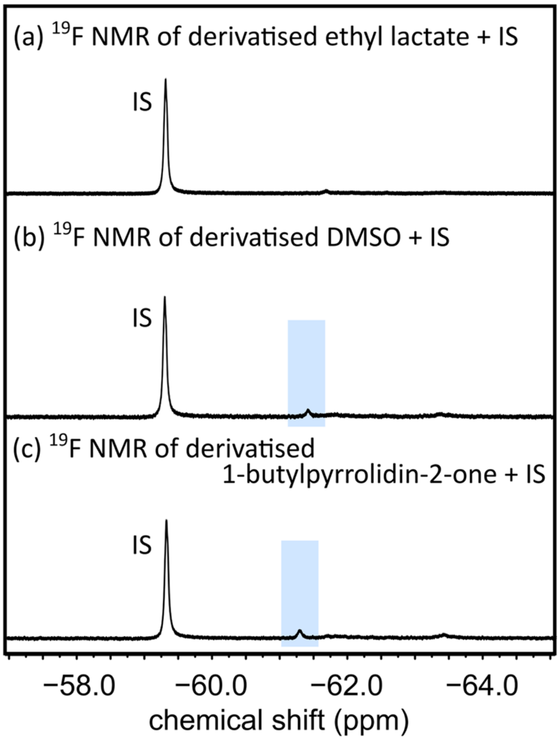

Fig. 2 Stacked plot of 1D low-field ^{19}F NMR spectra of products of derivatisation reaction using small volumes of green solvents, (a) ethyl lactate, (b) dimethyl sulfoxide and (c) 1-butylpyrrolidin-2-one. All samples contain the internal standard, 3-(trifluoromethoxy) benzoic acid, indicated by IS in the spectra.

DMSO, used as a solvent in preparing the NMR experiments, is closest to DMF in terms of the Hansen solubility parameters. The four green solvents suggested are all less polar than DMF, as would be expected from their chemical structures. The challenge here is to find a solvent that can effectively dissolve every carbonyl-containing compound present in the oil while tolerating both the relatively high water contents of many bio-oil samples and the many organic compounds present. Many of the target carbonyl-containing compounds will be more similar in chemical structure to the replacement solvents selected. While the parameters collected in Fig. 1 and Table 2 are useful, physical and chemical tests will be required to confirm which of the selected solvents are best suited to the task.

Replacing DMF

With five replacement solvents identified on the basis of both their solvent properties and green credentials, but with some doubts as to how similar they are to DMF in terms of their chemistry, physical and chemical tests are required. First, solubility tests were carried out to determine whether the replacement solvents were compatible with all the elements present in the derivatization protocol. The oak bio-oil and different masses of the derivatizing agent, 4-(trifluoromethyl)-phenylhydrazine, as well as a mixture of derivatizing agent and water, were dissolved in approximately 1 mL of each solvent. The compounds being dissolved are all coloured. Therefore, the visible change in colour of the sample was used as a positive confirmation of dissolution. Table 3 summarises the results of these solubility tests. Photos of each test are found in SI.4, Fig. S1–S3.

Solubility tests rule out two of the proposed green solvents. Cyrene™ did not fully dissolve the derivatising agent and the mixture with water produced a cloudy emulsion. While γ-valerolactone dissolved the derivatising agent, the aqueous mixture formed a biphasic system, unsuitable for the reaction methodology. The two solvents furthest from DMF in terms of their Hansen solubility parameters proved unsuited for replacing the solvent in the derivatisation reaction.

A second test, depicted in Fig. 2, was to check if the solvents themselves take part in the derivatisation reaction. Cyrene™, for example, contains an isolated carbonyl group, likely to be derivatised by the hydrazine and incompatible with this particular derivatisation reaction. Small volumes of the three solvents that passed the solubility tests were used as reagents in the derivatisation process and 1D ^{19}F spectra acquired. A revised version of Fig. 2, with inserts of the spectra magnified ten-fold can be found in SI.5 as Fig. S4. The samples prepared using DMSO and 1-butylpyrrolidin-2-one as test reagents both exhibit additional peaks in the low field 1D ^{19}F NMR spectra. In both cases, the peaks are where derivatised compounds would be expected to be found. This indicates a likely reaction between the possible replacement solvent and the derivatisation agent, ruling both compounds unsuitable for this analysis.

With ethyl lactate passing all feasibility checks and proving inert to the derivatisation reaction itself, a final test was to observe any effect of the change in solvent on the ^{19}F chemical shifts of single model compound samples. Solvents are well known to affect chemical shifts. The model carbonyl-containing

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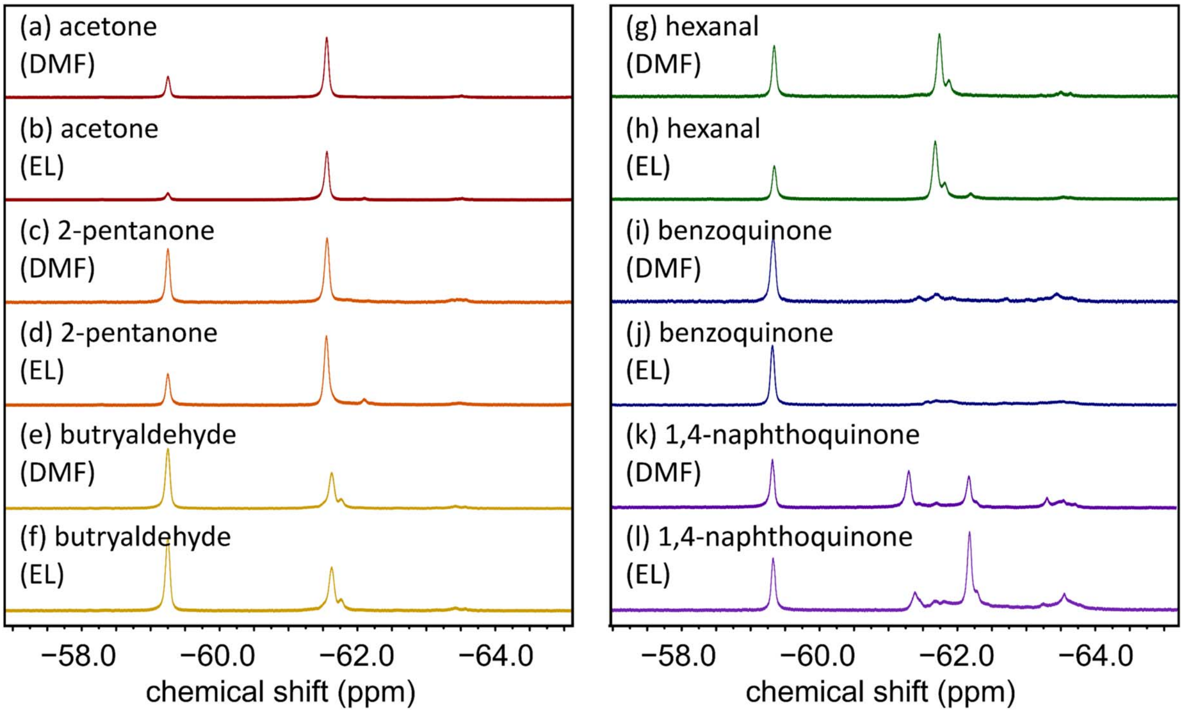

Fig. 3 Pair of stacked plots of 1D low-field ^{19}F NMR spectra of derivatized model compounds containing carbonyl groups with internal standard 3-(trifluoromethoxy) benzoic acid at −59.3 ppm. Compounds featured are derivatized acetone (a) in DMF and (b) in ethyl lactate (EL), derivatized 2-pentanone (c) in DMF and (d) in EL, derivatized butyraldehyde (e) in DMF and (f) in EL, derivatized hexanal (g) in DMF and (h) in EL, derivatized benzoquinone (i) in DMF and (j) EL, derivatized 1,4-naphthoquinone (k) in DMF, and (l) in EL. All samples contain the internal standard, 3-(trifluoromethoxy) benzoic acid.

compounds tested were selected from the chemical shift map previously developed by Tang *et al.*,[26] sampling a range of different carbonyl groups. Each compound was individually derivatised, using ethyl lactate instead of DMF, and low-field 1D ^{19}F NMR spectra acquired. These spectra were compared with those acquired using DMF as a solvent. These spectra are collected and depicted in Fig. 3. In all spectra presented, the peak at −59.3 ppm is due to the internal standard, 3-(trifluoromethoxy) benzoic acid, and the derivatised peaks are observed at lower chemical shifts.

The signals observed in ethyl lactate are at the same chemical shifts as those observed in DMF. Small differences in spectra do arise in the two quinone samples tested, particularly with 1,4-naphthoquinone where the peak at −62.2 ppm has a higher relative intensity in ethyl lactate compared with DMF. The peak itself is found at the same chemical shift. With such similarity in the chemical shifts obtained, the chemical shift map[26] developed in Tang *et al.* could be re-used for this solvent *e.g.* the chemical shifts of the derivatized ketones are *ca.* −61.0 to −61.7 ppm, those of derivatized aldehydes are *ca.* −61.7 to −61.9 ppm, and those of derivatized quinones are *ca.* −61.9 to −64.0 ppm.[22] These spectral data are collected in SI.6, Table S7.

The final test of the suitability of ethyl lactate as a replacement solvent for the analysis of pyrolysis bio-oils, the analysis of four previously studied oils was reproduced with DMF replaced with ethyl lactate. These four oils have been thoroughly characterised by elemental analysis, titration of the carbonyl groups following oximation reaction, and the original ^{19}F NMR method, using DMF, at both high and low magnetic fields. The NMR results are summarised in Fig. 4, which compares the low-field 1D ^{19}F NMR data for the two solvents for all four oils. The remaining original composition data, both elemental and carbonyl content, for the oil samples can be found in ref. 25 and is also summarised in SI.7.

The data contained within the spectra can be represented in bar chart format. Fig. 5 summarizes the estimates of ketone, aldehyde and quinone concentrations based on the results of the derivatisation reactions of four previously analysed bio-oils using both DMF and ethyl lactate (labelled as EL in the figure), as collected in Fig. 4.

Replacing DMF with ethyl lactate has very little effect on the estimates of the concentrations of ketones, aldehydes and quinones in the four oils tested. Totals of the three components are consistent with the total carbonyl content values of the oils, previously determined by the titration after oximation method, and summarised in SI.7, Table S9. The ethyl lactate method appears to slightly underestimate the concentrations of quinones present, particularly noticeable in the analysis of bio-oils produced from grass feedstocks. Phenolic motifs, such as *p*-hydroxyphenyl compounds, are more common in grasses and known to oxidise to form quinones in the resulting bio-oils.

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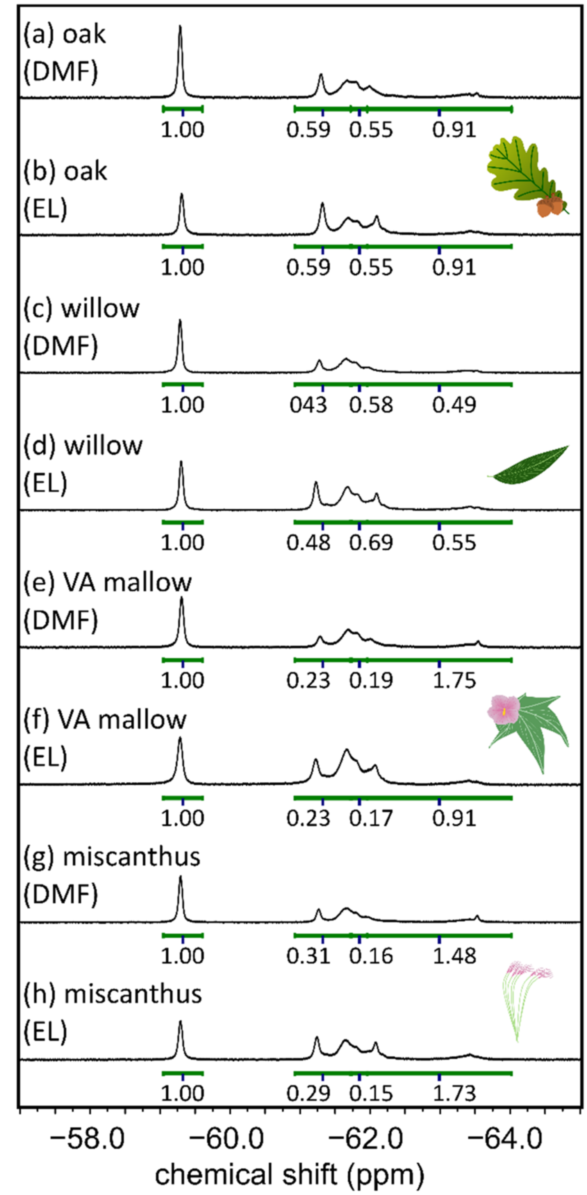

Fig. 4 Stacked plot of 1D low-field ^{19}F NMR spectra of derivatized pyrolysis oil produced from oak (a) in DMF and (b) in EL, produced from willow (c) in DMF and (d) in EL, produced from Virginia mallow (e) in DMF and (f) in EL, and produced from miscanthus (g) in DMF and (h) in EL. All samples contain the internal standard, 3-(trifluoromethoxy) benzoic acid.

Optimising solvent composition

An unforeseen advantage of switching to ethyl lactate was the improved tolerance of high bio-oil water levels, compared with DMF. While pure DMF is miscible with water, too much water content in the oil lead to biphasic or cloudy solutions forming in intermediate steps of the derivatisation process. No such issues were observed when using ethyl lactate. Water also has the advantage of being the sole solvent in the CHEM21 system that warrants green/'recommended' status for all three categories considered. In light of this, ethyl lactate was replaced with increasing amounts of water in the derivatisation reaction.

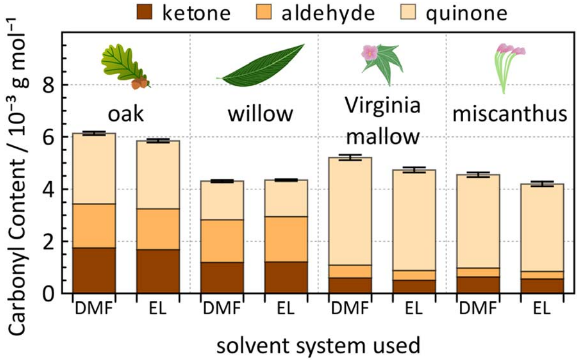

Fig. 5 Bar chart comparing the concentrations of ketones, aldehydes and quinones in pyrolysis oils produced from oak, willow, Virginia mallow and miscanthus using the two different solvents, dimethyl formamide (DMF) and ethyl lactate (EL).

Starting with a solvent composition of 500 μL water and 1000 μL ethyl lactate, the derivatisation reaction was repeated, replacing 100 μL of ethyl lactate with water, until a final solvent composition of 900 μL of water and 600 μL of ethyl lactate. The reliability of the analysis technique was tested using the oak bio-oil studied previously. Fig. 6 collects the series of analyses as a series of bar charts. The individual spectra are collected in SI.8, for the oak bio-oil, and SI.9, for the beechwood bio-oil.

The total carbonyl content of this oak bio-oil, measured by titration following an oximation reaction, was 5.99×10^{-3} g mol^{-1}, indicated in Fig. 6(b) by a dashed dark grey line. All NMR analyses in mixed water–ethyl lactate solvents reproduced this figure to within 5%. Concentrations of the different types of carbonyl-containing compounds were also reproduced across the range of water concentrations. This analysis was extended to a fifth, new bio-oil, produced from a beechwood feedstock, to further demonstrate the successful replacement of DMF with a greener solvent. Fig. 6(b) summarises the data acquired using this feedstock. First, when the derivatisation was performed in 500 μL water and 1000 μL EL, the total carbonyl content of the beech bio-oil was estimated as 5.60×10^{-3} g mol^{-1}, with an uncertainty of approximately 5%. This carbonyl content is comparable to that of oak. Repeating the experiment in a solvent mixture containing 900 μL water and 600 μL EL reproduced this estimate. Beech is a hardwood, and Fig. 6(b) confirms that the oil contains more aldehydes and ketones than quinones, consistent with the bio-oils generated from other hardwoods, depicted in Fig. 5.

Conclusions

This work builds on the use of low-field, or benchtop, ^{19}F NMR to effectively quantify the amounts and types of carbonyl groups present in pyrolysis oil samples. By considering the solvents used, the most common species present in the analysis in terms of the volume used, the environmental footprint of the derivatization reactions can be further reduced.

Selecting ethyl lactate as a greener replacement solvent was achieved by identifying likely solvent candidates based on

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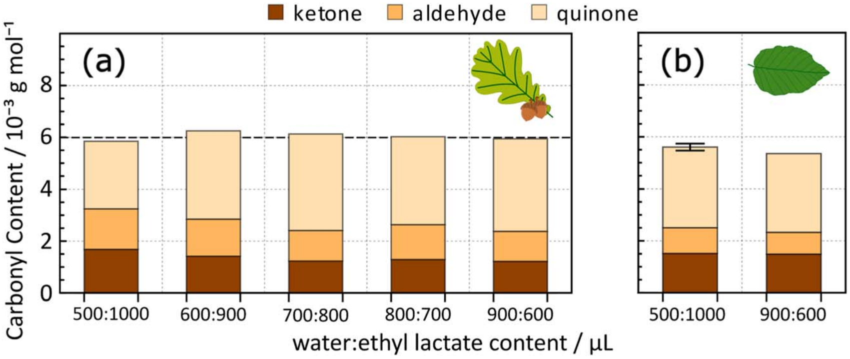

Fig. 6 (a) Bar charts summarising the results of 1D low-field ^{19}F NMR spectra of derivatized pyrolysis oil produced from oak in mixed solvents comprising of 500 µL water and 1000 µL EL, 600 µL water and 900 µL EL, 700 µL water and 800 µL EL, 800 µL water and 700 µL EL, and 900 µL water and 600 µL EL. Grey dashed line indicates previously determined carbonyl content of oak bio-oil of 5.99×10^{-3} g mol^{-1}. (b) Bar charts summarising the results of 1D low-field ^{19}F NMR spectra of derivatized pyrolysis oil produced from oak in mixed solvents comprising of 500 µL water and 1000 µL EL, and 900 µL water and 600 µL EL.

previous reports of replacing DMF in organic syntheses, by considering the physical, chemical and environmental characteristics of a shortlist of five solvents, and then testing the solvents against key steps of the derivatisation reaction. Solubility tests indicated that not all solvents would be completely suitable, with emulsions and biphasic mixtures observed, and the shortlist was further refined by reacting the solvents against the derivatizing agent. Note that the combined use of 1D ^{19}F benchtop NMR and derivatisation reaction has a synergy that allows for a wider range of solvents to be considered. The external lock means that deuteriated solvents are not required. Using ^{19}F NMR means that the more complex spectra[20] of the solvents used in this study do not appear in the final spectrum.

Other challenges remain. In our analysis, we used a simplified set of Hansen solubility parameters. More advanced approaches are available, such as the AI4Green Solvent Surfer,[40] which may provide more accurate insight into greener alternative solvents. The final NMR spectra are always very poorly resolved. The integral method used here works well enough for these samples and has the advantage of being present on all NMR processing software packages. This is also the case for high-field experiments and the analytical method remains widely used. More advanced methods for deconvoluting the peaks and identifying particular species within the sample would be a welcome boost for the method. Other alternatives could be to identify a derivatising agent that produces a wider range of ^{19}F chemical shifts or to pre-treat the oil sample, reducing the carbonyls selectively so that only one subset of the carbonyl-containing compounds is then derivatized. It could be possible to find a solvent nearer in character to DMF. This was effectively achieved here by mixing ethyl lactate with water. Measuring and confirming the solvent parameters of the mixed solvent systems will help guide future efforts in this area.

The strategy described here to replace DMF for this specific reaction can be adapted, not only to the other derivatization reactions commonly used in bio-oil research but to any synthetic methodology. Improved, sustainable practices are achieved by identifying key steps in a procedure, followed by analysis of the steps with appropriate chemical tools supported by experimental tests of the feasibility of any possible changes. In this case, replacing the harmful DMF with a greener, safer alternative will make benchtop NMR analysis of pyrolysis oils an increasingly safer, cheaper and more sustainable technique, and lead to wider use of benchtop NMR spectrometers in the analysis of complex mixtures and sustainable fuels.

Author contributions

BT: investigation, visualisation, writing original draft, review and editing. JR: investigation, writing original draft, review and editing. HP: investigation, visualisation. KC: supervision, review and editing. AJR: review and editing. MJD: supervision, review and editing. RE: conceptualisation, funding acquisition, supervision, visualisation, resources, funding acquisition, writing, review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI.

Additional content detailing compounds used, an example calculation, summary of solvent parameters, solubility tests, generation of chemical shift map, bio-oil compositions, and original ^{19}F spectra for results presented in manuscript. See DOI: **https://doi.org/10.1039/d5su00388a**.

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