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Quantitative ^{13}C NMR Characterization of Fast Pyrolysis Oils

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Quantitative ^{13}C NMR analysis of model catalytic fast pyrolysis (CFP) oils following literature procedures showed poor agreement for aromatic hydrocarbons between NMR measured concentrations and actual composition. Modifying integration regions based on DEPT analysis for aromatic carbons resulted in better agreement. Solvent effects were also investigated for hydrotreated CFP oil.

Introduction

As the global population expands and corresponding energy demands increase, the need for sustainable fuel sources becomes imperative. One of the largest fuel consumers is heavy-duty transportation. Currently, there are no sustainable options for heavy-duty transportation in the way that hybrid and electric vehicles can replace light-duty travel.[1] Fortunately, biomass derived hydrocarbon fuels are well suited to replace their fossil-fuel counterparts and both research and commercialization in this area is ongoing.

Biomass consists of two major biopolymers, cellulose and lignin, providing an abundant resource for fuel production. In order to convert biomass to fuel, the lignocellulosic material must be depolymerized. Thermochemical conversion of biomass via pyrolysis provides a promising pathway to fuel.[2] Fast pyrolysis of biomass produces high yields of energy-dense oil that has the potential to replace crude oil in both fuel and chemical precursor production. This fast pyrolysis (FP) oil, however, possesses many characteristics that make it unattractive when compared to fossil fuels. FP oil's high oxygen content is responsible for most of its less desirable properties, and deoxygenation is required to produce a more stable liquid.[3] Catalytic fast pyrolysis (CFP) involves upgrading pyrolysis oil vapors over a catalyst, inducing various reactions that reduce oxygen content, such as hydrogenation, cyclization, cracking, isomerization, and aromatization.[4-6] Both in situ and ex situ catalytic fast pyrolysis have been assessed, as have several different catalysts.[7-9] Another method for deoxygenating FP oil, hydroprocessing, involves the use of catalysts and high hydrogen pressures, similar to methods currently employed in petroleum refining. While hydroprocessing produces a stable product ready for co-streaming with fossil fuel derived products, it may not be cost efficient.[10] Much on-going research focuses on reducing hydroprocessing costs[11], whether through partial hydroprocessing of the pyrolysis oil, or different processes such as hydroprocessing catalytic pyrolysis oils.[12]

Fast pyrolysis oil is a complex mixture of hundreds of individual chemicals which presents a significant analytical challenge.[13] Many analytical methods are currently used to evaluate both physical and chemical characteristics of pyrolysis oil.[14] Some basic properties of pyrolysis oil can be reliably evaluated based on several accepted techniques including elemental composition by ultimate analysis, water content by Karl-Fischer titration, pH, viscosity, density, and solids content. Recently, FP oil has begun to see applications as a burner fuel, and an ASTM specification has been adopted based on physical characterizations.[15] However, information on chemical functional groups and individual species present in pyrolysis oils is needed to inform upgrading and refinery integration. Therefore accurate and reliable chemical characterization techniques must be developed to enable

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the production of renewable fuels and chemicals from pyrolysis oils. Recently, several chemical characterization methods have been standardized for raw pyrolysis oil, including titrations for both carboxylic acid and carbonyl content.[14] Despite recent progress, further analytical method development and standardization is needed. Likely candidates include gas chromatography (GC), liquid chromatography (LC) and nuclear magnetic resonance spectroscopy (NMR). Though GC is commonly used and provides very useful information, it only sees a small portion[16] of the oil as significant portions (up to 50 wt%) of raw pyrolysis oil are not volatile enough for GC analysis. LC methods have a lot of potential for more complete chemical characterization of pyrolysis oils, as they are able to quantify heat-sensitive and non-volatile species. However, no standard LC methods currently exist for pyrolysis oils, and more work is needed in this area. For both GC and LC, characterization of all species present is highly unlikely.

NMR methods have a unique opportunity for chemical characterization, as 100% of chemical functional groups present in pyrolysis oils can be quantified. Both ^{13}C NMR and ^{31}P NMR provide valuable information about the chemical composition of pyrolysis oil. Recently, a detailed method for quantifying hydroxyl content in pyrolysis oil via the application of ^{31}P NMR was established.[17,18]
Additionally, previous work has been published describing ^{13}C NMR as a quantitative method for analyzing the carbon functional groups present in fast pyrolysis oil; however, many methods only looked at raw FP oil and did not investigate other types of upgraded pyrolysis oils.[19-22] The work presented here modifies the method put forth by Ben and Ragauskas[22] to better characterize different types of pyrolysis oils by ^{13}C NMR. This study evaluates three major types of pyrolysis oil: raw FP oil, CFP oil, and hydrotreated CFP oil, and reports the considerations necessary to ensure quantitative analysis of the functional groups present in each of these fast pyrolysis oils by ^{13}C NMR.

Materials and Methods

Production of pyrolysis oils. The raw pyrolysis oil tested was produced from oak using the National Renewable Energy Laboratory's (NREL) Thermochemical Process Development Unit (TCPDU) operated in entrained flow mode at 500 °C without hot gas filtration, as described previously.[23] The catalytic pyrolysis oils were produced by ex situ catalytic fast pyrolysis of pine using a ZSM-5 catalyst either in the NREL 2-inch fluidized bed reactor system[24] or a Davison circulating riser reactor connected to a biomass pyrolysis unit.[25] Hydrotreated oils were produced from the CFP oils by hydrotreating them in a Parr reactor over sulfided CoMo catalyst.[26]

Model catalytic pyrolysis oils (Model Oils A, B, C) corresponding to three different oxygen contents (3, 8, 15 wt% oxygen on dry basis) were prepared with compositions based on micro-scale experiments of catalytic pyrolysis of pine over ZSM-5. The model oils consist of varying amounts of aromatic hydrocarbons and a variety of oxygenated molecules.[27] Table 1 lists the percent composition of each model oil used in this study.

Characterization of Pyrolysis Oils by ^{13}C NMR. Quantitative ^{13}C NMR spectra were acquired with ~200 mg bio-oil solubilized in 300 µL of either deuterated dimethyl sulfoxide (DMSO-d_6) or deuterated dichloromethane (DCM-d_2). Later experiments included a relaxation reagent, chromium acetylacetonate ($Cr(acac)_3$) at a final concentration of 5 mg/mL, to reduce T_1 relaxation times without affecting spectrum quality.[19] Experiments were run using either a Bruker AVANCE III 600 MHz spectrometer (14.7 T) or a Bruker AVANCE Nanobay 400 MHz spectrometer (9.4 T). Both are equipped with a room temperature BBO (broad band optimized) 5 mm probe head. All spectra were measured at 25 °C using a 90° pulse

Table 1: Percent Composition of Model Oils

	Model Oil A	**Model Oil B**	**Model Oil C**
toluene	28.0%	19.5%	13.0%
p-xylene	22.4%	17.6%	13.0%
benzene	5.6%	2.0%	0.0%
methylnaphthalene	16.0%	12.0%	8.0%
indene	4.0%	4.5%	3.0%
indane	4.0%	4.5%	3.0%
acetone	0.0%	3.5%	4.8%
4-hydroxy-2-methoxycinnamaldehyde	0.0%	0.0%	2.4%
cyclopentenone	0.0%	6.5%	4.8%
methylfuran	5.0%	7.0%	4.5%
benzofuran	5.0%	3.0%	0.0%
furfural	0.0%	0.0%	2.3%
2-furancarboxaldehyde, 5-methyl-	0.0%	0.0%	2.3%
methylphenol	10.0%	10.0%	12.0%
acetic acid	0.0%	0.0%	6.0%
2-methoxy-4-vinylphenol	0.0%	4.0%	9.0%
phenol, 2-methoxy-	0.0%	4.0%	9.0%
2-naphthalenol	0.0%	2.0%	3.0%

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angle, inverse-gated decoupling, at least 2048 scans, and a delay of 10 s for samples run without relaxation reagent, 3 s for samples with relaxation reagent. Distortionless Enhancement by Polarization Transfer (DEPT) experiments were run with selection angle parameter of 90° for CH groups only and the coupling constant, J_{CH}, was set to 145 Hz.

Results and Discussion

Analysis of Model Catalytic Fast Pyrolysis Oils using ^{13}C NMR. Results from quantitative ^{13}C NMR analysis of model catalytic fast pyrolysis (CFP) oils following the procedure given in Ben and Ragauskas[22] is shown in Figure 1. The values are compared to those calculated from the model oil compositions (actual). For the calculated values, carbons with double C=C bonds were included with aromatic C-H bonds and those connected to oxygen in furan rings were included with aromatic C-O carbons. The NMR analysis showed poor agreement between the values quantified by NMR and the calculated values for aromatic hydrocarbons (aromatic C-C vs. aromatics C-H carbons) with other functional groups showing reasonable agreement between actual and measured content. The model CFP oils are composed of ~15% aromatic C-C and between 50 and 62% aromatic C-H components. The NMR measurements have almost the exact opposite numbers: between 46 and 67% aromatic C-C and between 12 and 20% aromatic C-H. In fact, Figures 5 and 6 in Ben and Ragauskas show significant overlap in aromatic C-H and aromatic C-C ^{13}C chemical shifts for compounds present in pyrolysis oil.[22] Given this significant overlap, one can reasonably assume that the model oils contain a large percentage of components with aromatic C-H chemical shifts that overlap in the aromatic C-C chemical shift region. Analysis of oils with similar composition using integration regions given in Ben and Ragauskas would result in largely incorrect results regarding aromatic content.

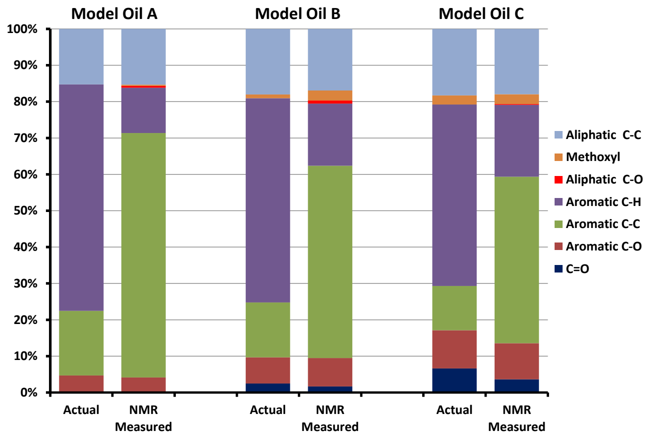

Figure 1 Three model catalytic fast pyrolysis oils were quantified using ^{13}C NMR measurements made using the integration regions found in Ben and Ragauskas. The discrepancies between the actual and NMR measured composition were particularly large for the aromatic content of the oils. The remaining components show good agreement.

Separating aromatic C-C from aromatic C-H using NMR spectroscopy. In order to investigate the overlap between different types of aromatic carbon signals, we employed the use of Distortionless Enhancement by Polarization Transfer (DEPT) experiments to determine the number of hydrogen atoms attached to a carbon atom. DEPT experiments transfer magnetization between proton and carbon atoms and use variation of the tip angle of the final ^{1}H pulse to select carbon atoms: 90° angle gives only C-H groups (C-H_2, C-H_3 eliminated); 135° angle gives all CH and CH_3 in a phase opposite to CH_2; and 45° angle gives all carbons with protons attached in-phase, and C-C are eliminated in all DEPT experiments due to no attached hydrogen to allow for magnetization transfer.[28] For this analysis, the simplified spectrum of a DEPT90 should allow for clear distinction between aromatic C-C and aromatic C-H as aromatic C-C signals will be absent in the DEPT90 experiment and thus, any overlap of aromatic C-H signals into the aromatic C-C region set by Ben and Ragauskas should be made clear.

DEPT Analysis of Model Catalytic Fast Pyrolysis (CFP) Oils. DEPT90 experiments were run on model CFP oils to distinguish between aromatic C-C and aromatic C-H content. The results can be seen in Figure 2A. Analysis of DEPT spectra for model CFP oils shows heavy overlap of aromatic C-H groups into the aromatic C-C region, most profoundly from the C-C/C-H border at 125 ppm up to 132 ppm. Based on this analysis of DEPT spectra, we re-quantified the ^{13}C spectra for model catalytic fast pyrolysis oils using the following integration regions: Carbonyl (215-166.5 ppm), Aromatic C-O (166.5-142 ppm), Aromatic C-C (142-132 ppm), Aromatic C-H (132-95.8 ppm), Aliphatic C-O (95.8-60.8 ppm), Methoxyl (60.8-55.2 ppm), and Aliphatic C-H (55.2-0 ppm, with exclusion of solvent). Importantly, the agreement between the NMR results and the actual composition data is much better, as shown in Figure 2B.

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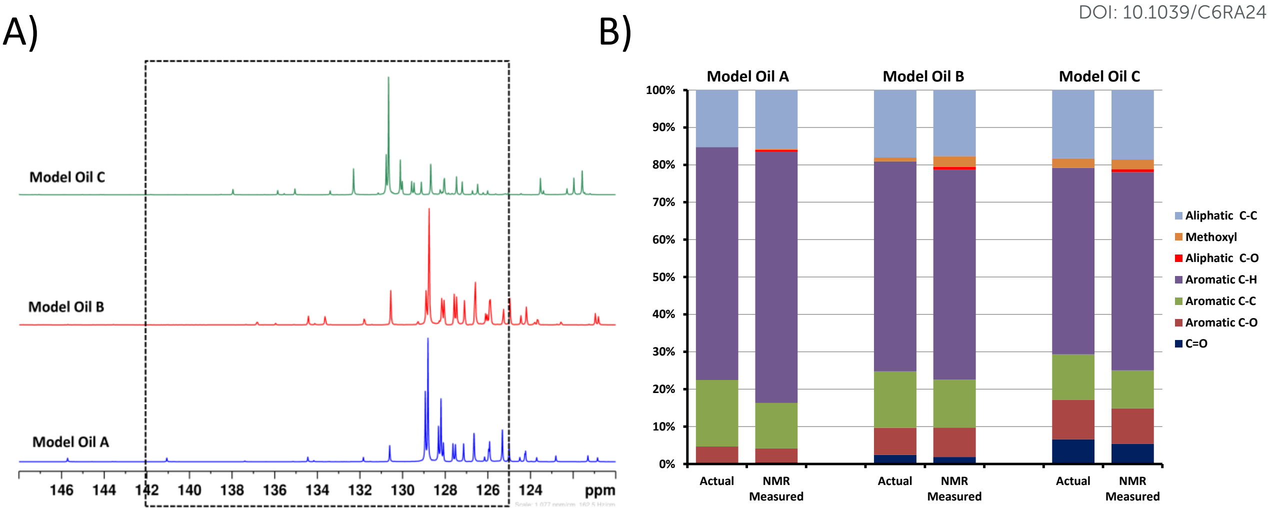

Figure 2 A) DEPT 90 experiments on three model oils: A (bottom, blue); B (middle, red); and C (top, green). The dashed box represents the Aromatic C-C region defined in Ben and Ragauskas as 142 ppm to 125 ppm. The model catalytic fast pyrolysis oils have many strong C-H signals in the aromatic C-C region, particularly between 125 and 132 ppm. B) The ^{13}C NMR results when using the new integration regions for aromatic C-C (142 to 132 ppm) and aromatic C-H (132 to 95.8 ppm).

Experimental Results from DEPT NMR of Raw, Catalytic, and Hydrotreated Catalytic Fast Pyrolysis Oils. In continuing our investigation of the overlap of aromatic ^{13}C chemical shifts for fast pyrolysis oils, DEPT90 experiments were run on traditional raw fast pyrolysis oils, catalytic fast pyrolysis oils, and hydrotreated catalytic fast pyrolysis oils. Figure 3 illustrates the results of these experiments. The analysis of DEPT spectra for CFP and hydrotreated CFP oils show the same trend: there is heavy overlap of aromatic C-H groups into the aromatic C-C region, most heavily from the C-C/C-H border at 125 ppm up to 132 ppm. In contrast, pyrolysis oils that have not been produced under catalytic conditions have little to no bleed-through of aromatic C-H signal into the aromatic C-C region, and thus the integration regions presented by Ben and Ragauskas are accurate for raw FP oils. Figures 5 and 6 in Ben and Ragauskas illustrate the chemical shift overlap for compounds reported present in pyrolysis oil and this overlap is particularly heavy for the three major groups of aromatic compounds.[22] Upgraded oils have higher aromatic content than raw FP oils and thus contain more of the compounds with overlapping chemical shifts. Based on this finding, and consistent with the results from the model oils, we re-quantified the spectra for CFP and hydrotreated CFP oils using the integration regions from the model oils: Carbonyl (215-166.5 ppm), Aromatic C-O (166.5-142ppm), Aromatic C-C (142-132ppm), Aromatic C-H (132-95.8 ppm), Aliphatic C-O (95.8-60.8), Methoxyl (60.8-55.2), and Aliphatic C-H (55.2-0 ppm, with exclusion of solvent). From the DEPT analysis results, we can reasonably conclude that the border between Aromatic C-C and Aromatic C-H needs to move downfield from 125 ppm to 132 ppm for CFP and hydrotreated CFP oils, but not for raw FP oils.

Solvent Considerations for Hydrotreated CFP Oils. During the course of these experiments, we found that hydrotreated CFP oils would also require a different solvent than most FP and CFP oils given their low oxygen

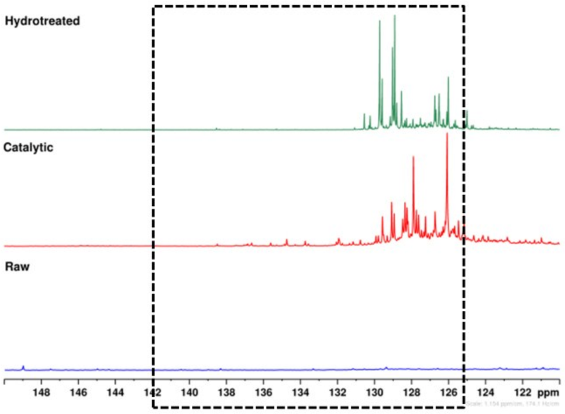

Figure 3 DEPT 90 experiments on three types of FP oils: Raw FP oil (bottom, blue); CFP oil (middle, red); and hydrotreated CFP oil (top, green). The dashed box represents the aromatic C-C region defined in Ben and Ragauskas as 142 ppm to 125 ppm. The CFP and hydrotreated CFP oils have many strong C-H signals in the aromatic C-C region, particularly between 125 and 132 ppm. The FP oil sample has virtually no C-H signals overlapping into the aromatic C-C region, and thus the integration regions do not need to be changed for these types of oils.

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content (less than 1% for hydrotreated CFP oils, 15-20% for CFP oils, 40% for raw FP oils, wt% dry basis; oxygen content data not shown). When hydrotreated CFP oils were solubilized in DMSO-d_6, it was quickly observed that a portion of the samples was separating out from the solvent and remaining at the top of the NMR tube, creating a heterogeneous mixture. Given that hydrotreated CFP oils contain significantly less oxygen and likely have a larger portion of aliphatic and/or non-polar aromatic carbon, the separation out of a highly polar solvent, such as DMSO, is not surprising. A less polar solvent, dichloromethane (DCM-d_2), was used instead for solubilization of hydrotreated CFP oils to create homogeneous mixtures for NMR analysis. DCM has much lower polarity index than DMSO (3.1 vs 7.2)[29], and the aliphatic carbon is thus miscible in DCM. Figure 4 illustrates the differences in solvent choices.

Effect of Solvent Choice on ^{13}C Quantification. In addition to the modified integration regions from the DEPT analysis discussed previously, the effect of solvent on the ^{13}C quantitation of hydrotreated CFP oils is striking. Quantitative ^{13}C NMR spectra were acquired on several samples that were solubilized in both DMSO-d_6 and DCM-d_2, with varying amounts of separation from solvent. The results in Figure 5 clearly illustrate the relative changes in carbon functional group content both when CFP oils are hydrotreated and when those upgraded oils are solubilized in DCM versus DMSO. The oil content that separates out in a layer on top of DMSO-d_6 is NMR "invisible" (above the coil for detection in the NMR probe) and therefore not quantified. This becomes clear when one compares results for hydrotreated CFP oils in different solvents. Note that samples 1A and 3A show a dramatic increase in aliphatic content (~7 %) when solubilized in DCM, and these samples showed the most separation when solubilized in DMSO. The changes in relative carbon content in Figure 5 clearly indicate that non-polar aliphatic carbon was separating out of DMSO. While the CFP oils studied here have ~15% oxygen content, making them ideal for solubilization in DMSO, the hydrotreated CFP oils have less than 1% oxygen, and thus need to be solubilized in DCM. Additionally, hydrotreated CFP oils generally contain anywhere between 10 and 20 % more aliphatic carbon than their corresponding CFP oils.

Furthermore, DCM-d_2 is also an ideal solvent choice for hydrotreated CFP oils due to the downfield shift of the residual solvent peak. DCM-d_2 is further out in the aliphatic C-H region (55.2-0 ppm) than DMSO-d_6 (53.84 and 39.52 ppm, respectively)[30], so there is less skewing of values from solvent peak elimination during integration. This is not as important in raw and CFP oils given the higher oxygen content, but for hydrotreated CFP oils, DCM-d_2 is right at the edge of the aliphatic C-H integration region, with most peaks falling at lower chemical shifts

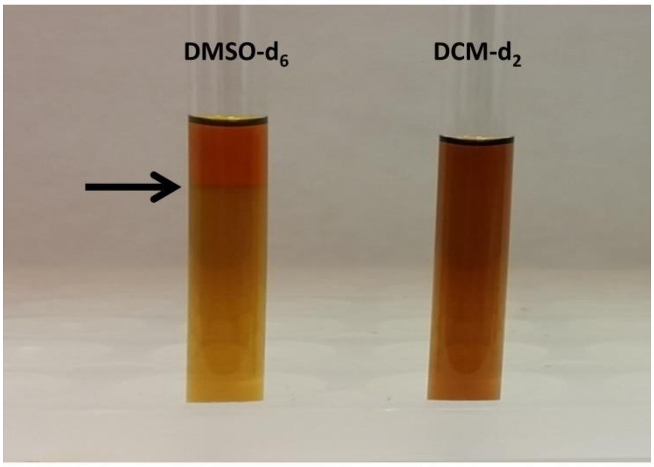

Figure 4 A hydrotreated CFP oil sample was solubilized in both DMSO-d_6 and DCM-d_2. The aliphatic content of the hydrotreated CFP oil separates out immediately and forms a distinct layer on top of DMSO-d_6 (see arrow) and continues to separate out after mixing. When an additional aliquot of oil is solubilized in DCM-d_2, the mixture remains homogenous and does not show any separation, even after 24 hours. The samples contain 200 µL hydrotreated CFP oil solubilized in 325 µL solvent.

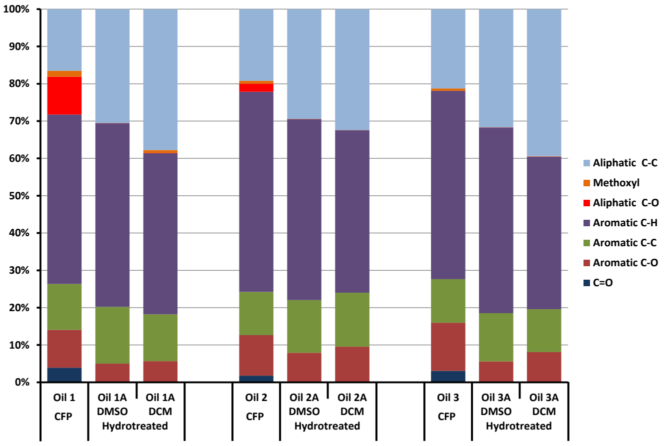

Figure 5 Three CFP oils (1, 2, 3) and their corresponding hydrotreated oils (1A, 2A, 3A) are shown with quantitative ^{13}C NMR functional group analysis. The CFP oils were solubilized in DMSO-d_6 only. The hydrotreated oil samples were solubilized in both DMSO-d_6 and DCM-d_2 for comparison. Samples were run under identical NMR acquisition and processing parameters. Integration regions are the same for all samples, with the solvent peak properly excluded.

than the residual solvent peak. While it was not studied here, chloroform ($CDCl_3$), which has a polarity index of 4.1[29], slightly higher than DCM, may be desirable as a solvent for oils with no aliphatic C-O as the chemical peak of the residual $CHCl_3$ is 77.16 ppm[30] which would allow for more accurate integration of the aliphatic C-H region. As oils become more upgraded towards a true hydrocarbon fuel and the oxygen content subsequently decreases, the solvent needs to decrease in polarity. Table 2 summarizes both the ^{13}C integration regions and the solvent required for accurate quantitation of carbon content.

Conclusions

This study makes clear that CFP and hydrotreated CFP oils need revised integration regions for the quantitative ^{13}C NMR analysis to provide an accurate representation of carbon functional groups present in oils, particularly when determination of differing aromatic content is desired. DEPT experiments provide a straightforward way to ensure integration regions are correct by allowing for clear distinction between carbon atoms with different numbers of hydrogen atoms attached. Both CFP and hydrotreated CFP oils require the use of modified integration regions in order to accurately quantify and distinguish carbon functional groups. Additionally, sample preparation and solvent choice are important to ensure all functional groups are properly quantified. Hydrotreating significantly increases the aliphatic content, while simultaneously decreasing oxygen content, requiring the use of a lower polarity solvent for complete miscibility of all components present in the oil. Improper solvent choice can lead to inaccurate quantification if components are not miscible with the chosen solvent. An important advantage of ^{13}C NMR analysis lies in its ability to characterize all the carbon in a sample simultaneously, regardless of vaporization properties of the compounds, and with minimal sample preparation. Thus, quantitative ^{13}C NMR provides powerful analytical information for distinguishing between carbon functional groups in pyrolysis oil, allowing for further refinement of pyrolysis oil production and upgrading as growth in the biofuel industry continues. In summary, this advances the reliable chemical characterization of upgraded pyrolysis oils.

Acknowledgements

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Table 2: Solvent and ^{13}C Integration Regions for Three Major Types of Bio-Oil

	^{13}C Chemical Shift Region (ppm)	
Carbon Type	**Raw Oil**	**CFP, Hydrotreated CFP Oil**
C=O, Carbonyl	215.0 - 166.5	215.0 - 166.5
Aromatic C-O	166.5 - 142.0	166.5 - 142.0
Aromatic C-C	142.0 - 125.0	142.0 - 132.0
Aromatic C-H	125.0 - 95.8	132.0 - 95.8
Aliphatic C-O	95.8 - 60.8	95.8 - 60.8
Methoxyl	60.8 - 55.2	60.8 - 55.2
Aliphatic C-C	55.2 - 0	55.2 - 0
Solvent	Dimethyl Sulfoxide-d_6 (DMSO)	Dichloromethane-d_2 (DCM)

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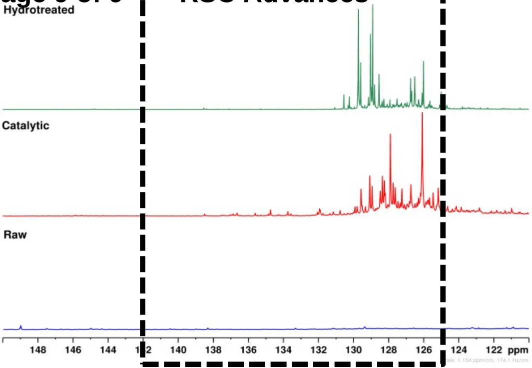
DEPT spectra illustrate the overlap of aromatic C-H signals into the aromatic C-C region for catalytic and hydrotreated pyrolysis oils.


Hydrotreated
Catalytic
Raw
148
146
144
140
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132
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ppm
ale: 1.154 ppm/cm, 174.1 Hz/cm