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# Development of quantitative $^{13}\text{C}$ NMR characterization and simulation of C, H, and O content for pyrolysis oils based on $^{13}\text{C}$ NMR analysis†

 Rui Wang,<sup>ab</sup> Ying Luo,<sup>ab</sup> Hang Jia,<sup>ab</sup> Jack R. Ferrell, III<sup>c</sup> and Haoxi Ben<sup>\*ab</sup>

Bio-oil is a valuable liquid product obtained from pyrolysis of biomass and it contains tens of hundreds of compounds, which brings about difficulties for characterization with various analytical methods.  $^{13}\text{C}$  NMR has advantages over other detection methods as it can characterize the entire composition of bio-oil and distinguish different types of carbon. But various shortcomings limit the application of  $^{13}\text{C}$  NMR. This study was carried out to develop a quantitative  $^{13}\text{C}$  NMR method to determine different functional groups in pyrolysis bio-oils with short NMR time and good accuracy, and propose a simulation of C, H, and O content for pyrolysis oils based on  $^{13}\text{C}$  NMR analysis. In order to solve long-term NMR problems, relax reagent has been added and the results show that it is an effective way to shorten the NMR time. Moreover, the aging problem is not obvious in the short-term NMR test, so the effect of aging on the test results can be neglected. Three types of substances with different oxygen content have been employed to verify the feasibility of the C, H, and O calculation methods and the result errors of all elements are small, which shows it is reliable for the simulation data of C, H and O content.

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## 1. Introduction

Pyrolysis is a process in which a substance isolated from air is heated to a certain temperature to form solid, liquid and gaseous products<sup>1</sup> and a series of physical changes and chemical reactions take place. Among the various conversion technologies for the utilization of biomass resources<sup>2,3</sup> that are under study, pyrolysis as a thermochemical conversion process has been reported<sup>4,5</sup> as one of the feasible approaches of producing precursors of biofuels, known as pyrolysis bio-oil.<sup>6–8</sup> Pyrolysis technology of biomass can transform biomass, which is low in energy density and tough to process by general means, into a high calorific value substance at a low cost. During the pyrolysis process, the volume of biomass is greatly reduced, and biomass is converted into bio-oil that is easy to transport and store. Bio-oil, which can be used for the precursors of biofuels, is a kind of dark-brown, polar and viscous liquid with a high moisture content and a very low nitrogen and sulfur contents. The composition of bio-oil is extremely complex since it consists of various kinds of organic substances derived from the

thermal decomposition of cellulose, hemicellulose and lignin. Bio-oil is mainly used in the production of combustion heating, electric power, fuels<sup>9</sup> and chemicals. Moreover, high value-added chemicals can also be extracted<sup>10</sup> from bio-oils, and the potential value of certain compounds<sup>11</sup> in bio-oil is much higher than that of the recovered oil even if the recovery amount is very small. However, on account of the complex ingredient of pyrolysis oil, subsequent upgrading is indispensable for the research of development in the future.<sup>12</sup> Simultaneously, the in-depth and quantitative characterization of pyrolysis oil is in urgent need.<sup>13</sup>

But traditional analysis strategies have difficulties in characterization of bio-oil, since the various undesirable properties and extreme complexity nature of bio-oil bring a great barrier to usual analysis methods, such as GPC, GC-MS and FT-IR. Individual components are usually detected by GC-MS, however, due to the poor volatility of some components in bio-oil, only a small part of bio-oil can be analysed by GC. Moreover, the ability to provide detailed information and insight into the whole portion of bio-oil for spectroscopic technique, *e.g.*, FT-IR, is limited because of the complexity for bio-oil. Owing to the complicated components, characterization of the whole portion of bio-oil will provide insight into the following chemical upgrading process, which is a challenging but crucial undertaking.

Nuclear magnetic resonance (NMR) has the ability to analyse the whole portion of bio-oil and has some advantages over

<sup>a</sup>Southeast University, Nanjing 210096, China. E-mail: benhaoxi@gmail.com

<sup>b</sup>Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Nanjing 210096, China

<sup>c</sup>Catalytic Carbon Transformation & Scaleup Center, National Renewable Energy Laboratory, Golden, CO, USA

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traditional methods as it can characterize different functional groups in the bio-oil and provide quantitative results.<sup>14–16</sup> Sundry NMR researches<sup>17–19</sup> have been used to better comprehend the structures and compositions of thermally converted bio-oils. In organic synthesis, NMR technology with wide applications can not only analyse the structure and determine the configuration of reactants or products, but also study the charge distribution, positioning effect in synthesis reactions and discuss the reaction mechanism.<sup>20–22</sup>

<sup>13</sup>C NMR is one of the most commonly used NMR methods to characterize different functional groups in the organic compounds or mixtures. Compared with <sup>1</sup>H NMR, although <sup>13</sup>C NMR takes a relatively long testing time, it can get more information about functional groups of bio-oil owing to less spectral overlap and broader chemical shift range of <sup>13</sup>C NMR, which means <sup>13</sup>C NMR has more advantages over <sup>1</sup>H NMR.<sup>23</sup> It also has been developed to identify more than 15 different functional groups in the pyrolysis oils.<sup>10,24,25</sup> Besides, the Distortionless Enhancement by Polarization Transfer (DEPT) spectra of <sup>13</sup>C NMR could be able to tell the differences from various carbons including primary, secondary, tertiary and quaternary carbons.<sup>13</sup> Shahrzad Hosseinnzhad *et al.*<sup>10,26</sup> detailed the bio-oil obtained from the slow pyrolysis of wood pallet, corn stover, miscanthus and swine manure through <sup>13</sup>C NMR to provide more information about various functional groups and successfully confirmed the conversion of carbohydrates during thermal conversion process. Xiaoxiang Jiang *et al.*<sup>10,27</sup> observed the changes for different peaks in specific regions with <sup>13</sup>C NMR experiments to investigate the thermal stability of bio-oil and bio-diesel blends. Comparison of <sup>13</sup>C NMR spectra has been made between extracted fractions of bio-oil and the unfractionated crude bio-oil, which indicated the extraction process divided the crude bio-oil into two parts.<sup>28</sup> Great efforts have been made to characterize bio-oil using <sup>13</sup>C NMR method in order to fully understand the composition of this complex mixture. But one of the drawbacks of <sup>13</sup>C NMR is long NMR test time, which will take >20 h for a quantitative <sup>13</sup>C NMR test. Relax reagent will be needed for saving the NMR time. Moreover, the produced pyrolysis oils always have limitations in applications due to several undesirable properties including poor volatility, corrosiveness, cold flow problems and relatively high molecular weight, oxygen content, acidity, and viscosity.<sup>29–31</sup> But the most challenging one is the aging process, during which molecular weight, oxygen content, acidity and viscosity will increase.<sup>32,33</sup> Aging problems in the NMR process can cause inaccurate measurement results, which should be avoided. Therefore, it is essential to test the aging process for the bio-oil in <sup>13</sup>C NMR solvent to measure the effects of aging problem.

Elemental analysis is also a chemical analysis method for studying the composition of elements in organic compounds. By using the traditional elemental analyser, the carbon, hydrogen and nitrogen contents in the sample can be quickly and quantitatively obtained. However, since there is no simple qualitative method for the determination of oxygen, the oxygen content of the sample is used to obtain by mass difference. Rohan Stanger *et al.* introduced a new thermal characterization

method—Dynamic Elemental Thermal Analysis (DETA) and demonstrated it as a means of calculating the intrinsic pyrolysis yields (*i.e.* char, tar, gas), analysing elemental compositions and estimating thermal properties.<sup>34</sup> Accordingly, based on the employment of quantitative <sup>13</sup>C NMR, DEPT 90 and DEPT 135 means for determining different functional groups in pyrolysis oils, a novel method of simulation of C, H and O contents by <sup>13</sup>C NMR is very valuable, during which the oxygen content can be directly calculated.

This report details the results of experiments with model compounds mixtures and duplicated tests that demonstrate the accuracy and precision of the quantitative <sup>13</sup>C NMR method measuring different functional groups in bio-oil and the C, H, O contents calculation method for bio-oil. Chromium acetylacetonate (Cr(acac)<sub>3</sub>) was chosen as the relax reagent and the influences of different concentrations of relax reagent on NMR time have been examined to find the most suitable concentration. Moreover, the comparison of the quantitative NMR results between long NMR time without relax reagent and short NMR time with relax reagent for various bio-oil samples has been provided to inspect the accuracy of the quantitative <sup>13</sup>C NMR method with relax reagent. In order to examine the effect of aging on quantitative <sup>13</sup>C NMR test results, the aging experiments for 3 different types of bio-oil with the use of 5 mg ml<sup>-1</sup> Cr(acac)<sub>3</sub> were conducted. The accuracy of C, H, O calculation method was tested with three different types of substances with different oxygen contents. This study will built up a new standard quantitative <sup>13</sup>C NMR method with good precision and short NMR time, and develop a novel approach of simulation of C, H and O contents based on quantitative <sup>13</sup>C NMR results, which few studies discussed before.

## 2. Experimental section

The experiment first developed a quantitative <sup>13</sup>C NMR methodology by testing bio-oil samples under various NMR conditions, and checked the aging process for three different kinds of bio-oil under the optimized NMR condition. The bio-oil samples used in this investigation were produced from four different kinds of raw materials, which can be classified into two groups: single biomass (oak wood and cottonwood) and the mixture of biomass and coal (the mixture of saw powder and GBW11110 and the mixture of cottonwood and GBW11110). Oak wood was obtained in Georgia, USA. Cottonwood and saw powder were collected in Sipailou Campus, Southeast University, Nanjing, China. GBW11100, a type of standard coal, was produced in Shandong Metallurgical Research Institute, Jinan, China.

Later, the experiment, examining the accuracy for the simulation of C, H and O contents for pyrolysis oils based on <sup>13</sup>C NMR analysis, was divided into three parts according to different oxygen contents of different samples including oxygen-free mixtures, oxygen-deficient compounds and oxygen-rich raw tars (all experiments for the calculation of C, H, O contents of bio-oil were performed on dry basis of bio-oil). Two standard mixtures obtained from AccuStandard Inc. (USA) containing Stock Sim Dis Paraffin Solution/#1 ASTM-P-0050



(standard #1) and Hydrocarbon Test Mixture/#2 D-5443-93-HTM (standard #2) were chosen as oxygen-free mixtures. The contents for various components in these two standards have been summarized in Tables S1 and S2.† Oxygen-deficient compounds were obtained from 8 products from industrial fluid catalytic cracking units and the vapours were produced by the pyrolysis of two types of oak wood. Detailed descriptions of each feed mixture are shown in Table S3.† Six kinds of oxygen-rich pyrolysis oils were prepared for test, including the bio-oils obtained from the pyrolysis of bituminous coal under N<sub>2</sub> (NSC(N<sub>2</sub>)) or CO<sub>2</sub> (NSC(CO<sub>2</sub>)) atmosphere at 773 K, platanus sawdust under N<sub>2</sub> (PS(N<sub>2</sub>)) or CO<sub>2</sub> (PS(CO<sub>2</sub>)) atmosphere at 773 K and two types of oak wood (OW1, OW2) under N<sub>2</sub> atmosphere at 773 K. All liquid products in this section were examined by using developed standard method before.

### 2.1 Preparation of pyrolysis oils

All pyrolysis experiments were processed in the tube furnace under N<sub>2</sub> or CO<sub>2</sub> atmosphere, which is discussed previously.<sup>35,36</sup> The flow rate of carrier gas was 500 ml min<sup>-1</sup> and ventilation was required for 10 minutes before pyrolysis to ensure the pyrolysis gas environment. Around 10 g feedstock was placed in two quartz sample boats, positioned in the middle of pyrolysis equipment, at 773 K with heating rate of 100 K min<sup>-1</sup>, 20 min char residence time and 3 min gas residence. Condensing tube was connected to the quartz tube and the condensed pyrolysis oil was collected at the outlet of the condensing tube.

### 2.2 NMR methods

Bio-oils (~250 μl) were dissolved in dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>, Adamas, 99.8 atom% D) (250 μl) with different concentrations (0, 1 or 5 mg ml<sup>-1</sup>) of Cr(acac)<sub>3</sub> (Aldrich, 99.99% trace metals basis), which was chosen as relax reagent. A AVANCE III HD 600 MHz NMR spectrometer (Bruker Inc., Zurich, Switzerland) was used to record NMR spectral data reported in this study at room temperature. An inverse gated decoupling pulse sequence (zgig) and 90° pulse angle were chosen as the NMR parameters used in quantitative <sup>13</sup>C NMR. Different pulse delays have been examined for different samples. During DEPT experiments, selection angle parameter of 90° was set for DEPT 90 and selection angle parameter of 135° was applied for DEPT 135. DEPT 90 spectrum only shows the upward peaks for tertiary carbons. Downward peaks for secondary carbons and upward peaks for primary and tertiary carbons are presented on DEPT 135 spectrum. Therefore, according to DEPT 90 and DEPT 135, different kinds of carbons can be distinguished on the <sup>13</sup>C NMR spectrum.

Inversion-recovery method was employed to measure the *T*<sub>1</sub>, which was calculated with Bruker's TopSpin software.

The integrations for different functional groups of pyrolysis oil have been conducted by using assignment ranges listed in Table S4.† The results for different functional groups in the whole portion of bio-oils can be reported as carbon % (mol or wt).

### 2.3 Elemental analysis of pyrolysis oils

EURO EA3000 elemental analyser (Euro Vector Inc., Pavia, Italy) was used to explore the constituents of tar which utilized combustion to obtain hydrogen, carbon, sulfur, nitrogen contents and confirm the oxygen content by mass difference. The water content of bio-oil was obtained by Moisture Analyser (HE53/02, METTLER TOLEDO). According to the measured moisture content of bio-oil and the C, H, O content of bio-oil measured by traditional methods, the C, H, O content based on dry basis can be obtained, which can later compare with the C, H, O content obtained by NMR methods.

## 3. Results and discussion





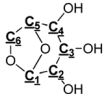





### 3.1 Quantitative characterization of pyrolysis oils by NMR

**Measurement for relaxation delay time (*T*<sub>1</sub>).** *T*<sub>1</sub> is a very important parameter for quantitative <sup>13</sup>C NMR. The pulse delays (*d*<sub>1</sub>) should be set as five times of *T*<sub>1</sub> to provide quantitative result. For a normal bio-oil, the *T*<sub>1</sub> could be as long as 10 s, which will require a >50 s pulse delay and a lot of NMR time (>20 h). Relax reagent will be needed for saving the NMR time. The influences for concentrations of relax reagent on the *T*<sub>1</sub> of bio-oil calculated by Bruker's TopSpin software have been examined and the results have been shown in Table S5.†<sup>37</sup> After adding 1 mg ml<sup>-1</sup> Cr(acac)<sub>3</sub>, the longest *T*<sub>1</sub> decreased to 2.2 s, which will require at least 2.2 s × 5 = 11 s pulse delay. After adding 5 mg ml<sup>-1</sup> Cr(acac)<sub>3</sub>, the longest *T*<sub>1</sub> decreased to 0.46 s, which will only require a 0.46 s × 5 = 2.3 s pulse delay. Although high concentration relax reagent can decrease *T*<sub>1</sub>, it will also reduce the resolution of the spectrum, which indicates concentrations greater than 5 mg ml<sup>-1</sup> will affect the accuracy of the results. Therefore, adding 5 mg ml<sup>-1</sup> Cr(acac)<sub>3</sub> was proved to be an appropriate way to shorten NMR time.

**Optimization of NMR test conditions.** To find the optimal NMR conditions, 7 pyrolysis bio-oil samples produced from oak wood were tested under different NMR conditions, in which various concentrations of Cr(acac)<sub>3</sub> and numbers of scans were set. The quantitative <sup>13</sup>C NMR result for pyrolysis oil sample without relax reagent, for which pulse delay was set as 60 s (Fig. S1† and Table 1), was chosen as the control sample. After adding 1 mg ml<sup>-1</sup> Cr(acac)<sub>3</sub>, quantitative <sup>13</sup>C NMR result for pyrolysis oil sample with pulse delay set as 15 s was examined (Fig. S2† and Table 1). The pulse delay (*d*<sub>1</sub>) decreased rapidly from 60 s to 15 s with 1 mg ml<sup>-1</sup> Cr(acac)<sub>3</sub> as it calculated by software, which indicated NMR time was greatly reduced compared with the NMR time for pyrolysis oil without relax reagent, and the differences between these two NMR results were <5.5%, showing small errors between these two samples. Moreover, this result proved the correctness of the calculation that relax reagent could greatly reduce NMR time. The pyrolysis oil sample with 5 mg ml<sup>-1</sup> relax reagent and 15 s pulse delay was also tested (Fig. S3† and Table 1) and the results were very close to those of the control group as the biggest difference is 2.2%. The results of samples with different concentrations of Cr(acac)<sub>3</sub> proved that the use of relax reagent would not only reduce test time but also provide precise results. Moreover,



**Table 1** Quantitative  $^{13}\text{C}$  NMR for bio-oil samples produced from oak wood with 0, 1, 5  $\text{mg ml}^{-1}$  relax reagent and different pulse delay ( $d_1$ ), the results shown as carbon mol%

Functional groups	Integration						
	0 $\text{mg ml}^{-1}$ , $d_1 = 60$ s	1 $\text{mg ml}^{-1}$ , $d_1 = 15$ s	5 $\text{mg ml}^{-1}$ , $d_1 = 15$ s	5 $\text{mg ml}^{-1}$ , $d_1 = 3$ s	5 $\text{mg ml}^{-1}$ , $d_1 = 3$ s	5 $\text{mg ml}^{-1}$ , $d_1 = 3$ s	5 $\text{mg ml}^{-1}$ , $d_1^a = 3$ s
	16.2	14.7	14.0	14.8	15.6	15.3	13.8
	7.7	7.0	9.3	9.2	8.6	9.5	10.2
	3.0	3.0	3.4	2.0	2.4	1.8	3.9
	12.6	12.8	13.1	13.4	13.1	10.9	13.3
	30.4	28.8	28.8	30.9	27.0	31.0	28.8
	40.0	45.5	40.7	44.6	44.6	45.9	43.8
	3.3	3.4	2.8	3.3	3.1	3.6	4.0
	17.2	13.7	16.7	12.8	12.6	12.9	11.0
	7.3	6.3	6.6	6.9	5.1	6.5	5.1
	1.0	0.8	0.8	0.6	0.6	0.8	0.5

<sup>a</sup> This experiment used 8k scans and other experiments used 1k scan.

examinations have been taken for three quantitative  $^{13}\text{C}$  NMR tests for pyrolysis oil sample with 5  $\text{mg ml}^{-1}$  relax reagent and shorter pulse delay (3 s) and the results are provided in Fig. S4† and Table 1. Averages and standard deviations for the condition performed in triplicate were calculated to compare with other values at other conditions. The averages show that the bio-oil was composed of 15.2% carbonyl, 9.1% aromatic C–O, 2.1% aromatic C–C, 12.5% aromatic C–H, 29.6% levoglucosan, 45.0% aliphatic C–O, 3.3% methoxyl, 12.8% aliphatic C–C, 6.2% methyl-aromatic and 0.7% methyl-aromatic'. The maximum standard deviation was 1.9 for levoglucosan, which indicated that the three measurements were very stable and accurate. The errors between average calculation results and the results under base condition (0  $\text{mg ml}^{-1}$ ) were <5.0%. Although these three NMR tests only took 1.5 h NMR time, the accuracy of the results was comparable to that of the result taken more than 20 h NMR time. All results of quantitative  $^{13}\text{C}$  NMR for bio-oil samples with 0, 1, and 5  $\text{mg ml}^{-1}$   $\text{Cr}(\text{acac})_3$  have been examined and summarized in Table 1. Although there are some differences between different bio-oil samples, which may be from the sampling of bio-oil, all of the carbon mol% for different functional groups in different pyrolysis oil samples are close to each

other. The influence from numbers of scans also has been examined and the results have been shown in Fig. S5† and Table 1. When compared different spectrums in Fig. S5,† it seems that 1k scans are enough for most of the peaks since the largest difference is 1.8%, and the integration results are also comparable with long time scan (>8 h NMR time). All NMR results indicate the optimized experimental condition will be the use of 5  $\text{mg ml}^{-1}$   $\text{Cr}(\text{acac})_3$ , 3 s pulse delay and 1k scans, which only requires 1.5 h NMR time.

**Aging process for bio-oil under optimal condition.** Bio-oil is an unstable organic mixture owing to aging problems, which brings about changes in physicochemical properties. It is necessary to examine the aging process during the  $^{13}\text{C}$  NMR test since long NMR time will cause aging problems.

To test the aging process for the bio-oil in quantitative  $^{13}\text{C}$  NMR solvent, 48 hour *in situ* aging tests for three bio-oil samples with 5  $\text{mg ml}^{-1}$  relax reagent have been examined. To make sure the bio-oil is “fresh”, these bio-oil samples were prepared just before the aging test, therefore, due to the sampling, there are some differences between these samples, which has been discussed previously. For the pyrolysis oil produced from oak wood, samples were tested every 8 h





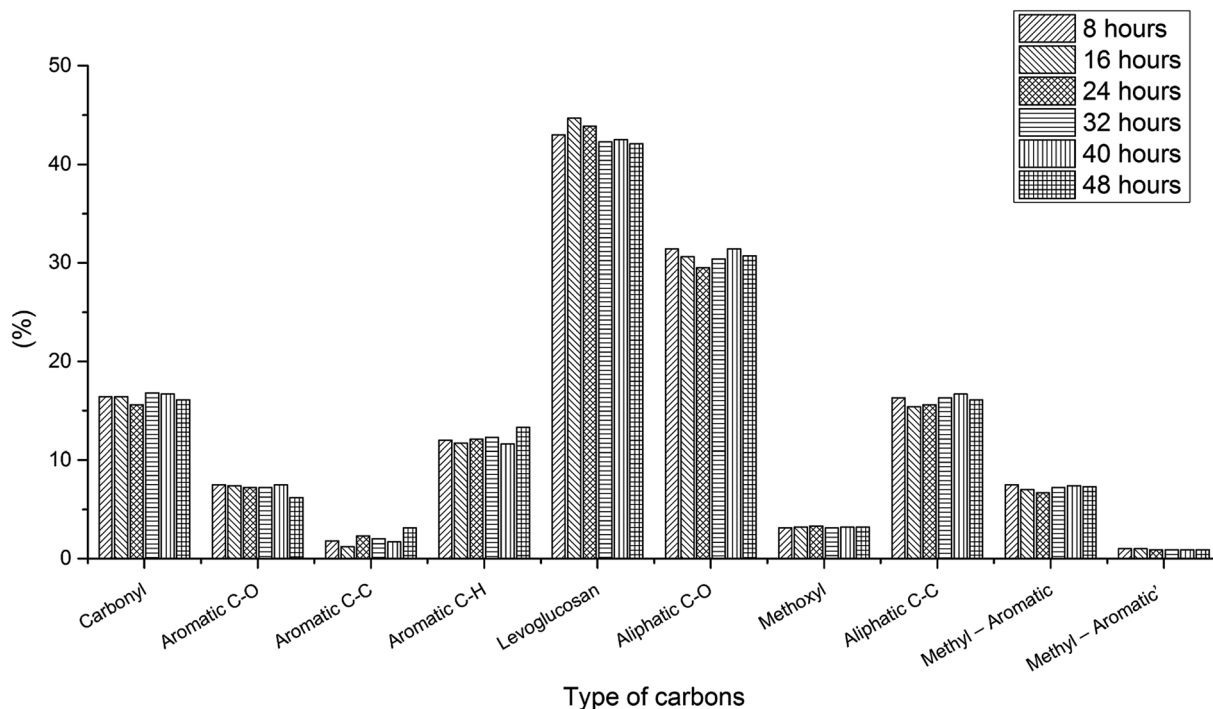


Fig. 1 Comparison of changes in contents of different functional groups during 48 hour aging process for bio-oil sample produced from oak wood with  $5 \text{ mg ml}^{-1}$  relax reagent.

(Fig. S6,† 1 and Table S6†). The results of 8 hour aging test showed that levoglucosan (43%) and aliphatic C–O (31.4%) still took the most part of the whole portion after 8 h aging process,

and other components of the sample stayed constant compared with the “fresh” bio-oil (Table 1). And the results for the bio-oil produced from oak wood after 16, 24, 32, 40 and 48 h aging

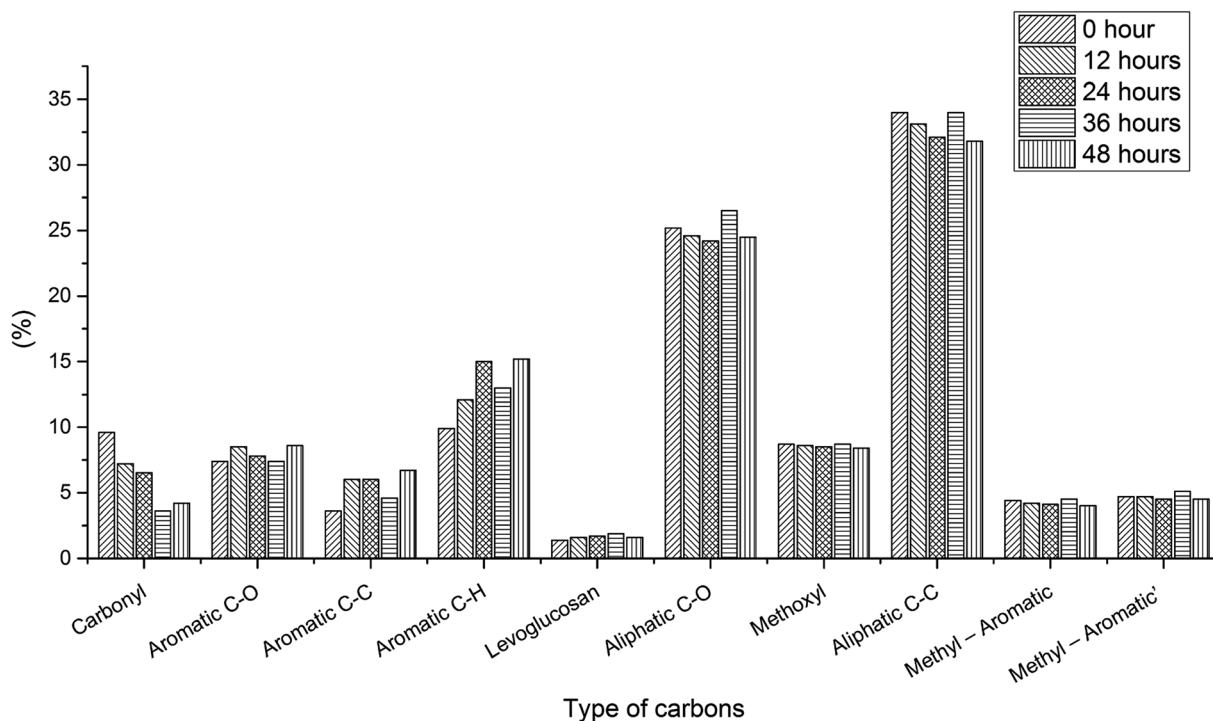


Fig. 2 Comparison of changes in contents of different functional groups during 48 hour aging process for bio-oil sample produced from cottonwood with  $5 \text{ mg ml}^{-1}$  relax reagent.



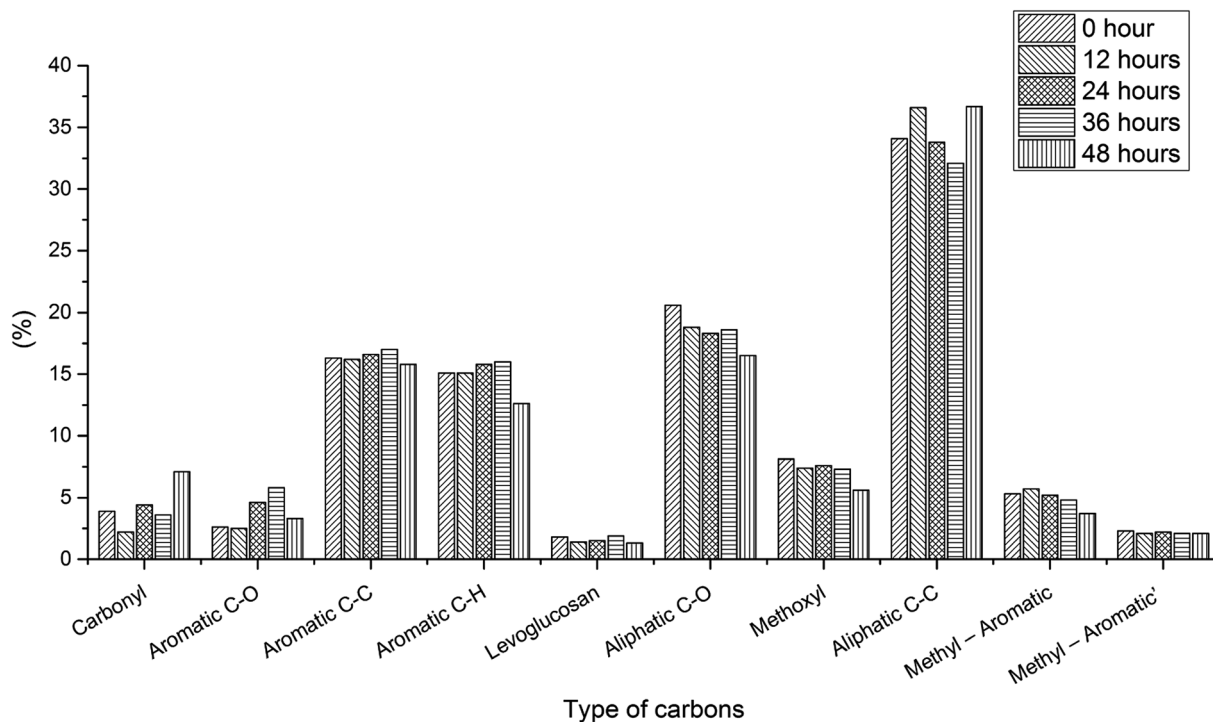


Fig. 3 Comparison of changes in contents of different functional groups during 48 hour aging process for bio-oil sample produced from the mixture of cottonwood and coal with 5 mg ml<sup>-1</sup> relax reagent.

process also showed that there were very limited differences (<3%) for different functional groups before and after aging process, which indicated that the aging process for this bio-oil in <sup>13</sup>C NMR solvent was very slow and aging would not affect test result. The limited differences may be due to the processing of different spectrums. To verify if the aging process is also slow in other types of bio-oil with relax reagent, two additional aging tests for bio-oil produced from cottonwood and bio-oil produced from the mixture of cottonwood and coal were examined (every 12 h). Fig. S7,† 2 and Table S7† showed the quantitative <sup>13</sup>C NMR results for the bio-oil produced from cottonwood. Different from the oak wood bio-oil, the composition of cottonwood bio-oil changed a lot *versus* time, especially for carbonyl, aromatic C-C and aromatic C-H, which suggested aging problem occurred in this bio-oil. With the aid of acids, aldehydes were active compounds in bio-oil, and aldehydes could react with other compounds in bio-oil *via* condensation reaction such as aldol condensation reaction, during which the number of C=O bonds would decrease.<sup>38,39</sup> Instable organic peroxides, present in pyrolysis bio-oil, could produce radicals, which would later cause the condensation reaction to form new aromatic C-C bonds.<sup>40</sup> But in the first few hours, the change of bio-oil was small. Therefore, short-term testing helps to get accurate results. And the quantitative <sup>13</sup>C results for the bio-oil produced from the mixture of cottonwood and coal are presented in Fig. S8,† 3 and Table S8,† which show complex composition different from the other two types of bio-oil. After 48 hour aging process, the change of the composition was obvious as well. These aging tests for different kinds of bio-oil

indicated that aging process during the quantitative <sup>13</sup>C NMR process with 5 mg ml<sup>-1</sup> relax reagent also existed. But after adding 5 mg ml<sup>-1</sup> relax reagent, it will only take 1.5 h for a quantitative <sup>13</sup>C NMR test. Short testing time can reduce the error for quantitative <sup>13</sup>C NMR results and the results are relatively accurate. Therefore, the quantitative <sup>13</sup>C NMR test for bio-oil developed in this study is valuable and necessary.

### 3.2 C, H, O contents simulation based on <sup>13</sup>C NMR

**Oxygen-free mixtures.** The evaluations for quantitative <sup>13</sup>C NMR of standard #1 and standard #2 are listed in Tables 2 and 3. Two oxygen-free mixtures were employed to verify the feasibility of determining the C, H and O contents based on NMR data, which can be calculated as follows:

$$m_{\text{total}} = M_{\text{C}}m_{\text{C}} + M_{\text{CH}}m_{\text{CH}} + M_{\text{CH}_2}m_{\text{CH}_2} + M_{\text{CH}_3}m_{\text{CH}_3} \quad (1)$$

$$w_{\text{C}} = \frac{M_{\text{C}}(m_{\text{C}} + m_{\text{CH}} + m_{\text{CH}_2} + m_{\text{CH}_3})}{m_{\text{total}}} \times 100\% \quad (2)$$

$$w_{\text{H}} = \frac{M_{\text{H}}(m_{\text{CH}} + 2m_{\text{CH}_2} + 3m_{\text{CH}_3})}{m_{\text{total}}} \times 100\% \quad (3)$$

$$w_{\text{O}} = 100\% - w_{\text{C}} - w_{\text{H}} \quad (4)$$

(*M*: the molar mass; *m*: the contents of different types of carbons in Tables 2 and 3).

The standard substance of ASTM-P-0050 consists of saturated alkanes from pentane to eicosane. The comparison of results based on concentrations and NMR data was employed to



Table 2 Evaluations for quantitative  $^{13}\text{C}$  NMR of standard #1

Calculation methods	Different types of carbons (carbon mol%)			
	C	CH	CH <sub>2</sub>	CH <sub>3</sub>
Based on the concentrations listed in Table S1	0	0	82.35	17.65
Based on NMR data	0	0	82.79	17.21

Calculation methods	C, H, O contents (wt%)		
	C	H	O
Based on the concentrations listed in Table S1	84.7	15.3	0.0
Based on NMR data	84.6	15.4	0.0

verify the feasibility of NMR method. It could be seen that the difference of carbon or hydrogen content is only 0.1%, which shows precision of the developed  $^{13}\text{C}$  NMR method and correctness of this C, H, O simulation method.

The standard substance of D-5443-93-HTM is composed of saturated alkanes and unsaturated hydrocarbons such as alkenes and aromatics. The final results showed that the error of elemental content measured based on concentrations and NMR data was only 0.2%. These two standard mixtures were also examined by Ben<sup>37</sup> using quantitative  $^{13}\text{C}$  NMR method, and the precision of the quantitative  $^{13}\text{C}$  NMR method has been proved. Therefore, both of these two evaluations for the  $^{13}\text{C}$  NMR of complex mixtures approve that the NMR method used in this report could provide quantitative results. The simulated C, H and O contents are also reliable based on the evaluations for oxygen-free mixtures.

**Oxygen-deficient compounds.** Quantitative  $^{13}\text{C}$  NMR results for 8 products obtained from industrial fluid catalytic cracking units have been summarized in Table 4 to verify the feasibility of determining the C, H, O contents based on NMR data for oxygen-deficient compounds. The results indicated that the feed of pyrolysis vapours with kerosene would produce more aliphatic carbons, and the feed of pyrolysis vapours with vacuum gas oil would produce more condensed aromatic carbons. The contents for the C=O bonds were very low, which indicated that the catalysts used in industrial fluid catalytic cracking units were good for the decarboxylation. Based on the  $^{13}\text{C}$  NMR results, some simulations have been done for the C, H and O contents for the oxygen-deficient samples, which can be calculated as follows:

$$m_{\text{total}} = M_{\text{C}}m_{\text{C}} + M_{\text{CH}}m_{\text{CH}} + M_{\text{CH}_2}m_{\text{CH}_2} + M_{\text{CH}_3}m_{\text{CH}_3} + M_{\text{CO}}m_{\text{CO}} \quad (5)$$

$$w_{\text{C}} = \frac{M_{\text{C}}(m_{\text{C}} + m_{\text{CH}} + m_{\text{CH}_2} + m_{\text{CH}_3} + m_{\text{CO}})}{m_{\text{total}}} \times 100\% \quad (6)$$

$$w_{\text{H}} = \frac{M_{\text{H}}(m_{\text{CH}} + 2m_{\text{CH}_2} + 3m_{\text{CH}_3})}{m_{\text{total}}} \times 100\% \quad (3)$$

Table 3 Evaluations for quantitative  $^{13}\text{C}$  NMR of standard #2

Calculation methods	Functional groups (carbon mol%)		
	Aliphatic carbons	Aromatic carbons	Double bonds
Based on the concentrations listed in Table S2	73.0	26.3	0.7
Based on NMR data	71.2	28.0	0.8

Calculation methods	Different types of carbons (carbon mol%)			
	C	CH	CH <sub>2</sub>	CH <sub>3</sub>
Based on the concentrations listed in Table S2	9.7	20.0	41.3	29.0
Based on NMR data	9.2	18.7	41.8	30.3

Calculation methods	C, H, O contents (wt%)		
	C	H	O
Based on the concentrations listed in Table S2	86.9	13.1	0.0
Based on NMR data	86.7	13.3	0.0

$$w_{\text{O}} = \frac{M_{\text{O}}m_{\text{CO}}}{m_{\text{total}}} \times 100\% \quad (7)$$

( $M$ : the molar mass;  $m$ : the contents of different types of carbons in Table 4).

The simulated results were also compared with the normal C, H, N analysis results, which were exhibited in Table 5. Obviously, the contents of carbon and hydrogen were around 86% and 13%, as well as the amount of oxygen was extremely small, less than 1%. As shown in Fig. S9,† the maximum absolute error and relative error of carbon content were 1.1% and 1.3%, which fully reflected the accuracy of using NMR method to determine carbon content. Similarly, the maximum absolute error of hydrogen was 0.9% while the maximum relative error was 7.4% due to the small percentage of hydrogen. The gap of oxygen content between the results based on NMR data and figures obtained by elemental analysis was also narrow. It is not hard to find that though there is a small amount of oxygen in the sample oil, the determination of C, H and O contents by quantitative  $^{13}\text{C}$  NMR analysis is still very accurate. As a result, for all the simulated results based on  $^{13}\text{C}$  NMR are comparable with the C, H, N analysis results, which indicated that such simulation is a very reliable method to provide C, H and O contents for oxygen-deficient compounds.

**Oxygen-rich pyrolysis oils.** Six pyrolysis oil samples have been tested to verify the feasibility of determining the C, H and O contents of oxygen-rich pyrolysis oils based on NMR data in this report. The quantitative  $^{13}\text{C}$  NMR results for these six samples have been examined and shown in Table 6. It could be seen that the compositions of biomass and coal pyrolysis oils under different atmospheres were significantly different. For



Table 4 Quantitative  $^{13}\text{C}$  NMR results for oxygen-deficient products

Sample	Different types of carbons (carbon mol%)							
	Aliphatic carbons				Aromatic carbons (overlap with some double bond carbons)		Terminal double bond carbons	
	C	CH	CH <sub>2</sub>	CH <sub>3</sub>	C	CH	=CH <sub>2</sub>	C=O
KO105	0.0	7.3	52.8	26.0	5.2	8.7	0.0	0.0
VO105	0.0	1.9	29.6	30.8	13.4	24.1	0.1	0.1
KO110	0.0	7.0	50.9	26.5	5.3	10.2	0.0	0.1
VO110	0.0	3.9	34.3	28.4	10.2	22.5	0.1	0.6
KO205	0.0	6.7	49.5	25.2	6.6	11.9	0.0	0.1
VO205	0.0	1.9	26.6	32.0	13.3	25.9	0.3	0.0
KO210	0.0	7.8	44.3	28.8	6.9	12.1	0.0	0.1
VO210	0.0	3.0	29.9	29.7	11.4	25.9	0.1	0.0

the pyrolysis oil of bituminous coal, CO<sub>2</sub> increased the number of aromatic compounds and decreased aliphatic compounds in the liquid product. In contrast to the pyrolysis of NSC, the amount of aromatic substances in the tar of PS pyrolysis became smaller while aliphatic structure contents increased. The sample OW1 had more levoglucosan, aliphatic C–O bonds and methyl-aromatic bonds than the sample OW2. However, there were more aromatic bonds in the sample OW2, which indicated that sample OW2 contained more “lignin” part of pyrolysis components than the sample OW1, while sample OW1 contained more “carbohydrates” part of pyrolysis components.

To further investigate the pyrolysis oils by the  $^{13}\text{C}$  NMR, two additional tests have been done for each liquid sample – DEPT 90 and DEPT 135 (as shown in Fig. S10†), which could be able to tell the differences from different carbons (primary, secondary, tertiary and quaternary carbons). The results have been shown in Table 7, seven more different types of functional groups could be detected by this method. The results showed that there were much more ketones than the aldehydes in the bio-oils. Some possible overlaps between aromatic C–H and C–C bonds have also been observed. There were less primary alcohol/ethers than the secondary alcohol/ethers. For all the samples, there were much less secondary and tertiary aliphatic carbons than primary carbons.

To explore the application of  $^{13}\text{C}$  NMR analysis, some simulations of C, H and O contents have been done for each sample. Table 8 listed all the proposed tentative C, H and O contents for each functional groups based on the results in Table 7. Although, there may have some overlaps for the C–O bonds, the proposed C, H and O contents could represent the elemental ratios for each functional group very well. Based on the proposed elemental ratios for each functional group and the content for these functional groups listed in Table 7, the simulated C, H and O contents for each sample have been shown in Table 9, which can be calculated as follows:

$$m_{\text{total}} = \sum M_{\text{FG}} m_{\text{FG}} \quad (8)$$

$$w_{\text{C}} = \frac{M_{\text{C}} \sum N_{\text{C}} m_{\text{FC}}}{m_{\text{total}}} \times 100\% \quad (9)$$

$$w_{\text{H}} = \frac{M_{\text{H}} \sum N_{\text{H}} m_{\text{FC}}}{m_{\text{total}}} \times 100\% \quad (10)$$

$$w_{\text{O}} = \frac{M_{\text{O}} \sum N_{\text{O}} m_{\text{FC}}}{m_{\text{total}}} \times 100\% \quad (11)$$

(FG: functional groups;  $M_{\text{FG}}$ : the molar mass calculated by the results in Table 8;  $m_{\text{FG}}$ : the carbon contents of functional groups in Table 7;  $M_{\text{C}}$ ,  $M_{\text{H}}$ ,  $M_{\text{O}}$ : the molar mass of C, H, O;  $N_{\text{C}}$ ,  $N_{\text{H}}$ ,  $N_{\text{O}}$ : the number of C, H, O in Table 8).

The results of calculation based on NMR data were also compared with the normal C, H, O analysis results, which were exhibited in Table 9. Different from the first two kinds of experimental samples, this type of pyrolysis oils contained a large amount of oxygen and even a small amount of nitrogen, which would affect the determination of C, H and O contents by NMR simulation. As shown in Fig. S11,† the maximum absolute error and relative error of carbon were 3.6% and 5%, which indicated that NMR simulation was quite accurate for the determination of carbon elements in oxygen-rich pyrolysis oils. It was equally precise for hydrogen content whose maximum






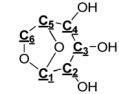
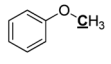



Table 5 Comparison of simulated C, H, O contents based on NMR and based on C, H, N test

Sample	C (wt%)		H (wt%)		O (wt%)	
	By NMR	By CHN	By NMR	By CHN	By NMR	By CHN
KO105	85.7	85.4	14.3	14.5	0.0	0.1
VO105	87.0	86.6	12.9	13.2	0.1	0.2
KO110	85.7	86.5	14.2	13.4	0.1	0.1
VO110	86.3	87.4	13.0	12.1	0.7	0.5
KO205	86.0	86.6	13.9	13.3	0.1	0.1
VO205	87.1	87.7	12.9	12.2	0.0	0.1
KO210	85.9	86.4	14.0	13.5	0.1	0.1
VO210	87.1	87.4	12.9	12.5	0.0	0.1





Table 6 Quantitative  $^{13}\text{C}$  NMR for the samples of pyrolysis oil, the results shown as carbon mol%<sup>a</sup>






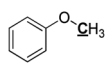

Functional groups	NSC(N <sub>2</sub> )	NSC(CO <sub>2</sub> )	PS(N <sub>2</sub> )	PS(CO <sub>2</sub> )	OW1	OW2
	3.5	8.7	2.4	6.3	9.2	6.9
	0.9	1.3	1.7	5.0	16.2	20.7
	6.0	14.2	27.9	17.9	10.7	11.8
	17.6	12.4	17.3	9.8	24.1	28.2
	4.0	3.2	0.2	0.2	7.0	6.7
	28.5	28.8	3.3	4.0	8.7	7.5
General (including levoglucosan)	28.5	28.8	3.3	4.0	8.7	7.5
	11.6	12.5	14.7	16.5	2.0	2.8
General (including two methyl-Ar)	32.0	22.1	32.7	40.6	29.2	22.0
	3.1	3.0	4.3	2.3	7.9	6.6
	0.9	1.1	1.2	1.0	4.4	3.9
						

<sup>a</sup> The first four columns of data are from the article.<sup>41</sup>

absolute error and relative error were 0.5% and 6.8%. Due to the low oxygen content of the samples in the two experiments above, it was not clear whether the determination of oxygen in elemental analysis by NMR method was up to standard. However, the research about oxygen-rich pyrolysis oils solved the puzzle. The maximum absolute error and relative error of

carbon were 3.6% and 9.4%, which proved that the calculation based on NMR data could meet the requirement of determining oxygen content. On the whole, the preliminary comparison indicated that this developed simulation of C, H and O contents based on the  $^{13}\text{C}$  NMR analysis for oxygen-rich pyrolysis oils is very reliable.

Table 7 Detailed analysis for the pyrolysis oil samples, the results shown as carbon mol%<sup>a</sup>

Functional groups	NSC(N <sub>2</sub> )	NSC(CO <sub>2</sub> )	PS(N <sub>2</sub> )	PS(CO <sub>2</sub> )	OW1	OW2	
	R or R'=C	3.1	7.7	2.3	5.2	9.0	6.9
	R or R'=H	0.4	1.0	0.1	1.1	0.2	0.2
	Ar-O-R	0.9	1.2	1.7	4.1	16.2	20.7
	Possible overlap with aromatic C-H	0.1	0.1	0.0	0.9	0.0	0.0
	Ar-C-R	5.3	12.2	20.2	13.2	6.9	7.5
	Possible overlap with aromatic C-H	0.6	2.1	7.8	4.8	3.8	4.3
		17.6	12.4	17.3	9.8	24.1	28.2
	H = 1	20.7	23.9	2.3	3.4	5.1	5.4
	H = 2	7.8	4.8	1.0	0.7	3.6	2.1
		11.6	12.5	14.7	16.5	2.0	2.8
	H = 1	1.1	0.9	5.7	6.7	0.0	0.0
	H = 2	2.8	1.9	7.8	10.5	9.8	6.3
	H = 3	28.1	19.4	19.2	23.3	19.4	15.7

<sup>a</sup> The first four columns of data are from the ref. 41.



**Table 8** Proposed tentative C, H and O contents for each functional group in the pyrolysis oils

Functional groups		C	H	O
	R or R' = C	1	0	1
	R or R' = H	1	1	1
	Ar-O-R	1	0	0
	Possible overlap with aromatic C-H	1	1	0
	Ar-C-R	1	0	0
	Possible overlap with aromatic C-H	1	1	0
		1	1	0
	H = 1	1	1	1
	H = 2	1	2	1
		1	3	1
	H = 1	1	1	0
	H = 2	1	2	0
	H = 3	1	3	0

**Table 9** Comparison of simulated C, H, O contents based on NMR and based on C, H, N test<sup>a</sup>

Sample	C (wt%)		H (wt%)		O (wt%)	
	By NMR	By CHN	By NMR	By CHN	By NMR	By CHN
NSC(N <sub>2</sub> )	57.8	55.8	8.7	8.5	33.5	35.4
NSC(CO <sub>2</sub> )	55.9	58.4	7.0	7.2	37.2	34.0
PS(N <sub>2</sub> )	71.5	71.1	9.1	9.3	19.4	18.0
PS(CO <sub>2</sub> )	66.8	67.0	9.4	9.0	23.9	22.6
OW1	73.1	69.8	7.6	7.3	19.4	21.1
OW2	75.5	71.9	6.9	7.4	17.5	19.2

<sup>a</sup> The first four columns of data are from the ref. 41.

**Accuracy and limitations.** From the above, it can be confirmed that a developed simulation of C, H, O contents based on the <sup>13</sup>C NMR analysis for pyrolysis oils is reliable. It can predict the C content with an absolute accuracy of 4%, the H content with an absolute accuracy of 1.5% and the O content with an absolute accuracy of 2%. Since this method still has some errors, this method is suitable for magnitude analysis but cannot be used to determine differences between oils from similar conditions. For example, for NSC(N<sub>2</sub>) and NSC(CO<sub>2</sub>) oils, the traditional C, H and O analysis suggests that the N<sub>2</sub> sample has a higher O content, but the NMR method predicts the opposite. A similar difference in the relative magnitudes for the O contents of OW1 and OW2 samples is evident.

Because the method still has some limitations, the error analysis seems to be an indispensable choice. Firstly, the instrument performance and the mode of operation have an impact on the experimental results. Therefore, accurate instrumentation and professional operation can effectively reduce the error impact on the experimental data and improve the correctness of the data. Secondly, the pyrolysis oil can not

contain water as an inorganic substance because the <sup>13</sup>C NMR spectrum is unable to detect the functional group therein. The more water content, the less accurate the simulation results. If there will be some water in the pyrolysis oil samples, the C, H and O contents based on the C, H, N tests need to be further adjusted by the water contents. Finally, “impurity” elements (such as nitrogen and sulfur) other than carbon, hydrogen and oxygen can also affect the experimental results. If the proportion of these elements in the pyrolysis oils is too large, the error of C, H and O contents measured based on NMR data will be equally large. Therefore, it is more accurate to simulate the C, H and O contents of pyrolysis oils by selecting pyrolysis oils with few “impurity” elements.

## 4. Conclusion

We demonstrated accuracy and precision of using quantitative <sup>13</sup>C NMR to characterize bio-oil. The developed method was found to be accurate and can provide very valuable information for different functional groups in the bio-oil. The influences for concentrations of relax reagent on the *T*<sub>1</sub> of bio-oil have been examined and discussed. The use of 5 mg ml<sup>-1</sup> Cr(acac)<sub>3</sub> can decrease the *T*<sub>1</sub> by 95%. It can be found that, by using this developed quantitative <sup>13</sup>C NMR method, the testing time of <sup>13</sup>C NMR can be greatly reduced and the aging process of bio-oil during <sup>13</sup>C NMR experiment is negligible due to the short NMR process, suggesting that this method can significantly improve the efficiency of the experiment while ensuring the accuracy. <sup>13</sup>C NMR and DEPT 90 and 135 could further investigate the bio-oil, 15 + 7 different functional groups could be analysed by this method. A simulation of C, H and O contents for the bio-oil based on the <sup>13</sup>C NMR has been proposed, and it can directly calculate the O content of bio-oil, which few studies focus on. Compared with traditional C, H, O contents calculation method, the absolute error in calculating C content using this method is 4%, the absolute error in calculating H content is 1.5%, and the absolute error in calculating O content is 2%, indicating that this new developed method is reliable to calculate C, H, O contents of bio-oil. Considering that there are more than three elements in bio-oil, more researches on elemental analysis, for example, simulation of N and S contents for pyrolysis oil, need to be carried out in the future study.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## Notes and references

- 1 N. H. Leibbrandt, J. H. Knoetze and J. F. Görgens, *Biomass Bioenergy*, 2011, **35**, 2117–2126.
- 2 D. Chen, K. Cen, X. Jing, J. Gao, C. Li and Z. Ma, *Bioresour. Technol.*, 2017, **233**, 150–158.
- 3 A. Jain, R. Balasubramanian and M. P. Srinivasan, *Chem. Eng. J.*, 2016, **283**, 789–805.
- 4 R. P. Anex, A. Aden, F. K. Kazi, J. Fortman, R. M. Swanson, M. M. Wright, J. A. Satrio, R. C. Brown, D. E. Daugaard, A. Platon, G. Kothandaraman, D. D. Hsu and A. Dutta, *Fuel*, 2010, **89**, S29–S35.
- 5 A. V. Bridgwater, *Biomass Bioenergy*, 2012, **38**, 68–94.
- 6 H. Ben and J. R. Ferrell III, *RSC Adv.*, 2016, **6**, 17567–17573.
- 7 A. V. Bridgwater, D. Meier and D. Radlein, *Org. Geochem.*, 1999, **30**, 1479–1493.
- 8 S. Yaman, *Energy Convers. Manage.*, 2004, **45**, 651–671.
- 9 E. Su, P. You and D. Wei, *Bioresour. Technol.*, 2009, **100**, 5813–5817.
- 10 X. Zhang, H. Lei, S. Chen and J. Wu, *Green Chem.*, 2016, **18**, 4145–4169.
- 11 A. Aho, A. Tokarev, P. Backman, N. Kumar, K. Eränen, M. Hupa, B. Holmbom, T. Salmi and D. Y. Murzin, *Top. Catal.*, 2011, **54**, 941–948.
- 12 D. A. Ruddy, J. A. Schaidle, J. R. I. Ferrell, J. Wang, L. Moens and J. E. Hensley, *Green Chem.*, 2014, **16**, 454–490.
- 13 G. D. Strahan, C. A. Mullen and A. A. Boateng, *Energy Fuels*, 2011, **25**, 5452–5461.
- 14 N. Hao, H. Ben, C. G. Yoo, S. Adhikari and A. J. Ragauskas, *Energy Fuels*, 2016, **30**, 6863–6880.
- 15 Q. Wang, D. Cui, P. Wang, J. Bai, Z. Wang and B. Liu, *Fuel*, 2018, **211**, 341–352.
- 16 W. Qing, J. Chunxia, G. Jianxin and G. Wenxue, *Energy Fuels*, 2015, **30**, 2478–2491.
- 17 P. C. Tarves, C. A. Mullen and A. A. Boateng, *ACS Sustainable Chem. Eng.*, 2015, **4**, 930–936.
- 18 H. Ben and A. J. Ragauskas, *Energy Fuels*, 2011, **25**, 5791–5801.
- 19 F. Huang, S. Pan, Y. Pu, H. Ben and A. J. Ragauskas, *RSC Adv.*, 2014, **4**, 17743.
- 20 D. P. Gallegos, K. Munn, D. M. Smith and D. L. Stermer, *J. Colloid Interface Sci.*, 1987, **119**, 127–140.
- 21 I. Ohtani, T. Kusumi, Y. Kashman and H. Kakisawa, *J. Am. Chem. Soc.*, 1991, **113**, 4092–4096.
- 22 D. J. Crockford, E. Holmes, J. C. Lindon, R. S. Plumb, S. Zirah, S. J. Bruce, P. Rainville, C. L. Stumpf and J. K. Nicholson, *Anal. Chem.*, 2006, **78**, 363–371.
- 23 E. D. Christensen, G. M. Chupka, J. Luecke, T. Smurthwaite, T. L. Alleman, K. Iisa, J. A. Franz, D. C. Elliott and R. L. McCormick, *Energy Fuels*, 2011, **25**, 5462–5471.
- 24 H. Ben and A. J. Ragauskas, *ChemSusChem*, 2012, **5**, 1687–1693.
- 25 H. Ben and A. J. Ragauskas, *Energy Fuels*, 2011, **25**, 5791–5801.
- 26 S. Hosseinezhad, E. H. Fini, B. K. Sharma, M. Basti and B. Kunwar, *RSC Adv.*, 2015, **5**, 75519–75527.
- 27 X. Jiang, Z. Zhong, N. Ellis and Q. Wang, *Chem. Eng. Technol.*, 2011, **34**, 727–736.
- 28 A. S. Alwehaibi, D. J. Macquarrie and M. S. Stark, *Green Chem.*, 2016, **18**, 2762–2774.
- 29 Y. Wang, S. Wang, F. Leng, J. Chen, L. Zhu and Z. Luo, *Sep. Purif. Technol.*, 2015, **152**, 123–132.
- 30 H. Ben, F. Huang, L. Li and A. J. Ragauskas, *RSC Adv.*, 2015, **5**, 74821–74827.
- 31 S. No, *Renewable Sustainable Energy Rev.*, 2014, **40**, 1108–1125.
- 32 J. Joseph, M. J. Rasmussen, J. P. Fecteau, S. Kim, H. Lee, K. A. Tracy, B. L. Jensen, B. G. Frederick and E. A. Stemmler, *Energy Fuels*, 2016, **30**, 4825–4840.
- 33 H. Jo, D. Verma and J. Kim, *Fuel*, 2018, **232**, 610–619.
- 34 R. Stanger, T. Wall, J. Lucas and M. Mahoney, *Fuel*, 2013, **108**, 656–667.
- 35 Y. Luo, H. Ben, Z. Wu, K. Nie, G. Han and W. Jiang, *Polymers*, 2019, **11**, 1370.
- 36 H. Ben, F. Wu, Z. Wu, G. Han, W. Jiang and A. J. Ragauskas, *Polymers*, 2019, **11**, 1387.
- 37 H. Ben, Z. Wu, G. Han, W. Jiang and A. Ragauskas, *Polymers*, 2019, **11**, 324.
- 38 S. K. R. Patil, J. Heltzel and C. R. F. Lund, *Energy Fuels*, 2012, **26**, 5281–5293.
- 39 E. Alsbou and B. Helleur, *Energy Fuels*, 2014, **28**, 3224–3235.
- 40 H. Ben and A. J. Ragauskas, *ChemSusChem*, 2012, **5**, 1687–1693.
- 41 Y. Luo, H. Ben, Z. Wu, K. Nie, G. Han and W. Jiang, *Polymers*, 2019, **11**, 1370.

