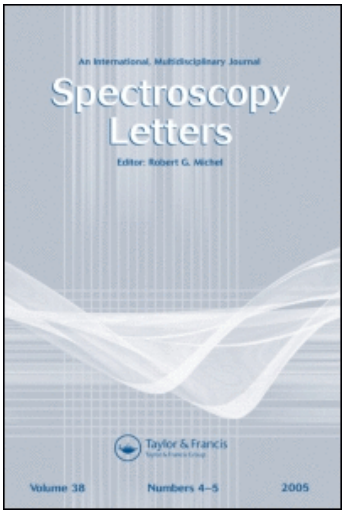


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# Quantification of Hydroxyacetaldehyde in a Biomass Pyrolysis Liquid Using $^{13}C$ NMR Spectroscopy

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**Abstract:** We report on a method that allows direct identification and quantitative determination of hydroxyacetaldehyde using $^{13}C$ NMR spectroscopy. The quantitative procedure was checked and validated with commercially available hydroxyacetaldehyde and then applied to the carbohydrate fraction of a biomass pyrolysis liquid (bio-oil).

**Keywords:** Biomass pyrolysis liquids, bio-oil, carbon-13 NMR, hydroxyacetaldehyde, quantitative analysis

## INTRODUCTION

Although biomass pyrolysis liquids (bio-oils) are viscous, corrosive, and relatively unstable, they are used as fuel (directly or after upgrading by catalytic hydrogenation) and as a source of natural products (gasoline additives, food

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antioxidants and food flavoring, precursors for the manufacturing of resins and pesticides, etc.).[1] They are quite complex mixtures by the number and the nature of their components. Because of their complexity, pyrolytic oils require separation into chemical families before analysis, generally carried out by liquid-liquid partition[2,3] or silica gel chromatography.[4] Thus, the fractions are analyzed by high-performance liquid chromatography,[5] gas chromatography,[4] or gas chromatography–mass spectrometry (GC-MS).[1,4] Bio-oils contain mainly polysubstituted phenols, sugars, anhydrosugars, and mono- and polycyclic aromatic hydrocarbons. Other compounds are present at noticeable content: acetic acid, hydroxypropanol (acetol), as well as hydroxyacetaldehyde (HAA).[6] Finaly, it was demonstrated that bio-oils contain also an appreciable content (20–40%) of oligomers of lignin.[2,7]

Hydroxyacetaldehyde is one of the more abundant products of the thermal degradation of cellulose.[8–11] This compound, which may be regarded as the "simplest sugar", is of considerable biochemical interest. In food chemistry, it participates in the production of brown pigments and flavor change.[12–14]

HAA has been identified and quantified, among low-molecular-weight volatiles, in the pyrolyzate from pyrolysis of cycloheptaamylose, using $^{1}H$ NMR.[15] Only a few papers reported on qualitative and quantitative determination of HAA in biomass pyrolysis liquids. The quantification of this compound has been carried out after fractionation of the bio-oil, by HPLC,[6] or by GC using a Porapak Q column.[10] It is claimed that quantification was also carried out by GC-MS (capillary column DB-1701), directly from the crude oil, after a simple step of filtration, without derivatization.[16] However, in that procedure, the capillary column is undoubtedly polluted by the heavy components such as oligomers of phenols, which are not eluted.

During the course of our studies on the chemical characterization of the biomass pyrolysis liquids by $^{13}C$ NMR spectroscopy, we identified and quantified the major polysubstituted phenols[17] and anhydrosugars.[18] The aim of the current work was to identify and quantify HAA in the carbohydrate fraction of a biomass pyrolysis liquid, directly from the $^{13}C$ NMR spectrum of the mixture.

## MATERIALS AND METHODS

### Fractionation of the Biomass Pyrolysis Liquid

Biomass pyrolysis liquid (ENSYN, Greely, Ontario, Canada) was added dropwise, with vigorous stirring into distilled water. The water-insoluble fraction (pyrolytic lignin, 40.0% of the crude oil) was removed by filtration. The water-soluble fraction was further extracted with diethyl ether. The organic fraction contained mainly polysubstituted phenols (11.7% of the crude oil). The diethyl ether–insoluble fraction (carbohydrate fraction) was vacuum-dried, and the residues represented 43.3% of the bio-oil.

### Hydroxyacetaldehyde and Reagents

Hydroxyacetaldehyde was purchased from Aldrich (Saint-Quentin, France), diglyme was obtained from Janssen (Beerse, Belgium), and dimethylsulfoxide-d6 from Euriso-top (Gif-sur-Yvette, France).

### $^{13}C$ NMR Spectra

All NMR spectra were recorded on a Bruker AVANCE 400 Fourier transform spectrometer operating at 100.13 MHz for $^{13}C$ NMR, equipped with a 5-mm probe, in dimethylsulfoxide-d6. $^{13}C$ NMR spectra were recorded with the following parameters: pulse width, 2.7 μs (flip angle 30°); acquisition time, 2.6 s, relaxation delay, 0.1 s for 128K data table with a spectral width of 25,000 Hz (250 ppm); CPD mode decoupling; digital resolution, 0.183 Hz/pt. The number of accumulated scans was 3000 for the carbohydrate fraction (around 2 hr of analysis) and 1000 for pure hydroxyacetaldehyde.



### $T_1$ Measurements

The longitudinal relaxation delays of the $^{13}C$ nuclei ($T_1$ values) were determined by the inversion-recovery method, using the standard sequence: $180°-\tau-90°-D1$, with a relaxation delay D1 of 20 s. Each delay of inversion ($\tau$) was thus taken into account for the computation of the corresponding $T_1$ using the function $I_p = I_0 + p \cdot e^{-\tau/T_1}$.

### Calibration Line

A weighted amount of 5.2 to 29.2 mg of commercial hydroxyacetaldehyde was diluted in 0.5 mL of dimethylsulfoxide-d6 containing 7.8 mg of diglyme. $^{13}C$ NMR spectra were recorded 72 hr after dissolution.

### Carbohydrate Fraction

The spectrum of the carbohydrate fraction was recorded with 76.2 mg of mixture diluted in 0.5 mL of DMSO-$d_6$ containing 7.8 mg of diglyme.

## RESULTS

In order to carry out the identification and quantitative determination of hydroxyacetaldehyde in the carbohydrate fraction of a bio-oil, using $^{13}C$ NMR, we first characterized the different forms of that compound (commercially

available sample) in solution, then we checked and validated the quantitative procedure, and finally, we applied it to the analysis of a sample of bio-oil. $^{13}C$ NMR was preferred to $^{1}H$ NMR for two principal reasons: recording spectra with a larger sweep width (250 ppm vs. 14 ppm) and by decoupling of the proton band (each signal appears as a singlet).

## Characterization of Hydroxyacetaldehyde

The commercially available crystalline compound is a dimer of hydroxyacetaldehyde, namely *trans*-2,5-dihydroxy-1,4-dioxane. In aqueous solution, that dimer dissociates into a monomeric form and rearranges into several dimeric forms. The equilibrium between these molecular forms has been investigated using $^{1}H$ NMR.[19] The authors pointed out six principal forms, four dimeric monocyclic isomers (forms A–D), the basic monomeric form E, and a monomeric hydrated form F (Fig. 1). Three dimeric acyclic forms were present at very low contents. In DMSO, proton NMR allowed the observation of the monomeric form and three[20] or four[21] cyclic dimeric forms. The mechanism of dissociation during heating of hydroxyacetaldehyde dimer (form A) in $D_2O$ or dioxane was studied by FTIR spectroscopy: the cyclic dimer A undergoes a ring opening to form an acyclic dimer that can recyclize into the dimeric form D or dissociate into the monomeric form E.[22]

The carbohydrate fraction of the bio-oil being not totally soluble in water (at concentration required for NMR analysis) but perfectly soluble in DMSO, we investigated the equilibrium between the different forms of hydroxyacetaldehyde in that solvent (DMSO-d6). The $^{1}H$ NMR spectrum of the commercial crystalline compound was recorded immediately after dissolution and corresponded with the pure form A. The equilibrium between the different forms was reached after 72 hr. The $^{1}H$ NMR spectrum exhibited the signals

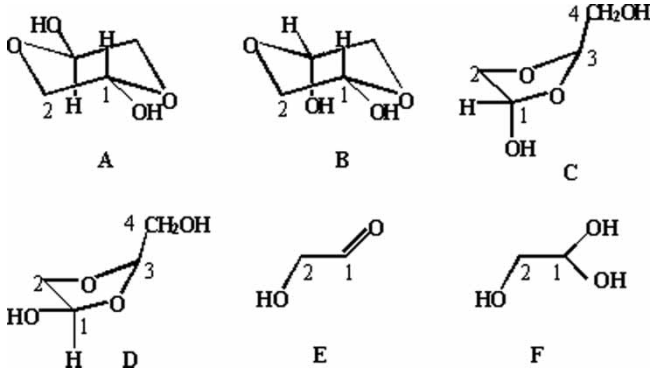


***Figure 1.*** Structure of the six principal forms of hydroxyacetaldehyde (A–F) in water.

belonging to the five nonhydrated main forms (A–E) reported in the literature.[19] The three minor acyclic forms as well as the monomeric hydrated form were not observed. The assignment of the chemical shifts of the carbons of these five forms was carried out by comparison with literature data for A, C, and E[23,24] and by taking into account the classical electronic and steric effects for B and D (Table 1; Fig. 2).

## Quantification of Hydroxyacetaldehyde

Whatever the technique used, quantitative determination of a component in a mixture needs the comparison of the signals of that compound with those of an internal standard or the utilization of calibration curves (external standardization). Several methods have been developed for the quantification of individual components of a mixture using $^{13}C$ NMR spectroscopy with an internal standard:

- Waiting a period of $5T_1$ of the longest $T_1$ value (component or internal standard) before applying another pulse, combined with a 90 degree pulse angle, in association with the gated decoupling technique, is well-known as the standard sequence for quantitative NMR measurements.[25–27] However, this procedure is time consuming;
- Conversely, quantitative determination can be led using a rapid train of short pulses, because a small flip angle provides less difference in the steady-state magnetization than a larger one in presence of nuclei having different $T_1$ values.[28]
- Finally, it has been suggested that a good approach for the quantitative analysis of complex mixtures containing nuclei with a wide range of $T_1$ is a compromise between the two aforementioned procedures.[29] For instance, quantification of carbohydrates in honeys,[30] anhydrosugars in bio-oils,[18] and diterpenes in oleoresin of pine[31] has been performed in our laboratories, using this approach. In these conditions, it is obvious that quantitative estimations will be led from not fully relaxed spectra.

In order to quantify hydroxyacetaldehyde in biomass pyrolysis liquids, we chose the same approach using diglyme as internal standard. First, we

***Table 1.*** Chemical shift (ppm) of the carbons of the five forms A–E of hydroxyacetaldehyde in DMSO-$d_6$

| Carbons | A | B | C | D | E |
|---|---|---|---|---|---|
| 1 | 90.31 | 89.14 | 94.20 | 94.41 | 203.55 |
| 2 | 66.44 | 64.30 | 71.15 | 71.23 | 68.29 |
| 3 | — | — | 104.42 | 102.30 | — |
| 4 | — | — | 63.20 | 62.18 | — |

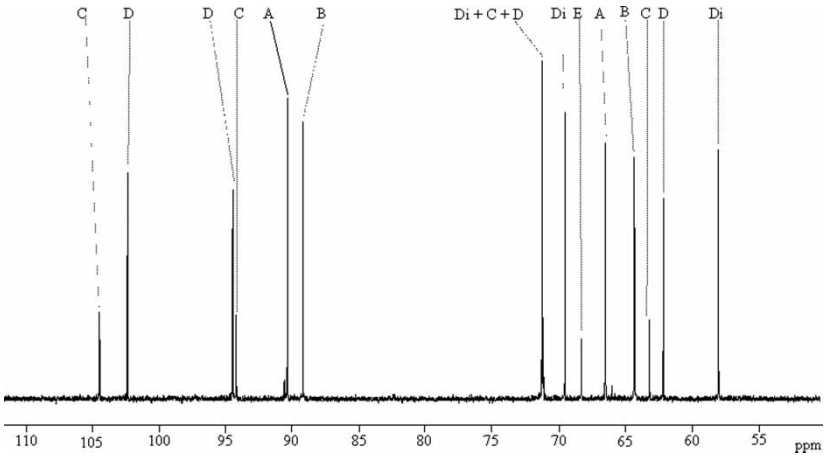


***Figure 2.*** Part of the $^{13}C$ NMR spectrum of hydroxyacetaldehyde. A–E, forms A–E of hydroxyacetaldehyde; Di, diglyme.



measured by the inversion recovery method, the $T_1$ values of the carbons of A–E and diglyme (Table 2). Then, according to Becker et al.[32], we determined and plotted the percentage of recovered signal, expressed as S/N (%), as a function of the pulse angle $\alpha$, for the carbons whose $T_1$ values are

- 0.8 s and 2.5 s [range comprising the $T_1$ of the carbons of the four dimeric cyclic forms (A–D) of HAA];
- 5.5 and 8.7 s corresponding with the two carbons of the monomeric form E; and
- 3.8 s ($T_1$ of the two methylenes of diglyme) (Table 2; Fig. 3).

The curves were drawn taking into account the lowest recycling time of 2.7 s (acquisition time 2.6 s and relaxation delay 0.1 s, cf. "Materials and Methods" section) required by 128K data table. In comparison with the standard pulse sequence (90° pulse angle, gated decoupling technique), applying a 30° pulse angle must provide appreciable recovery of signal and

***Table 2.*** Longitudinal relaxation times ($T_1$) of the carbons of the five forms A–E of hydroxyacetaldehyde

| Carbons | A | B | C | D | E |
|---|---|---|---|---|---|
| 1 | 1.7 | 1.5 | 1.8 | 2.1 | 8.7 |
| 2 | 0.9 | 0.8 | 1.3 | 1.3 | 5.5 |
| 3 | — | — | 2.5 | 2.3 | — |
| 4 | — | — | 1.5 | 1.5 | — |

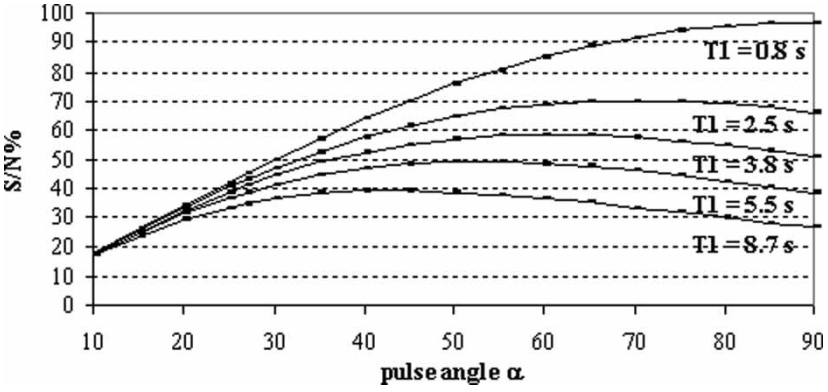


***Figure 3.*** Plot of S/N (%) *versus* flip angle for selected values of $T_1$ and total recycling time of 2.7 s. (*plotted from $S/N = M_0\,(1 - e^{-\tau/T1})\sin\alpha/\sqrt{\tau}(1 - e^{-\tau/T1})\cos\alpha$ [Ref. 32]. $\tau$: minimum of total recycling time (2.7 s using a 128 K data table).



reduce significantly the difference of steady-state magnetization between carbons of hydroxyacetaldehyde and those of diglyme (Fig. 3).

Such a procedure ($\alpha = 30$degrees and total recycling time 2.7 s) was validated (accuracy and response linearity) by experiments carried out on commercially available hydroxyacetaldehyde, 72 hr after dissolution in DMSO-d6:

- We checked the linearity by plotting the ratio $A_{HAA}/A_D$ against the weighted amount ($m_{HAA}$) of hydroxyacetaldehyde in a range of 5.2 to 29.2 mg (Fig. 4). The response linearity was ensured by linear determination factors $R^2$, which ranged from 0.990 and 0.999.
- The accuracy was validated by comparison of the weighted amount of hydroxyacetaldehyde with the sum of the masses of the five forms (A–E) measured by NMR (Table 3). The mass $m_c$ of each form was calculated using the formula:

$$m_c = \frac{2A_{HAA} \times M_{HAA} \times m_D}{A_D \times M_D} \quad (1)$$

- where, $A_{HAA}$ is mean area of the signals of the carbons of each form of hydroxyacetaldehyde, $A_D$ is area of the signal of the methylene of diglyme at $\delta = 69.5$ ppm, $m_D$ is weighted amount (mg) of diglyme, $M_D$ is molecular weight of diglyme, and $M_{HAA}$ is molecular weight of hydroxyacetaldehyde (forms A–E). The factor 2 is due to the symmetry of diglyme, and it was not taken into account for the forms A and B, which are also symmetrical.

The relative errors, measured against the weighted amount of hydroxyacetaldehyde, ranged from 1.9% to 8.9%, which indicated a reasonable accuracy of the measurements. The results obtained on commercial hydroxyacetaldehyde demonstrated that its quantification can be carried out using $^{13}C$ NMR

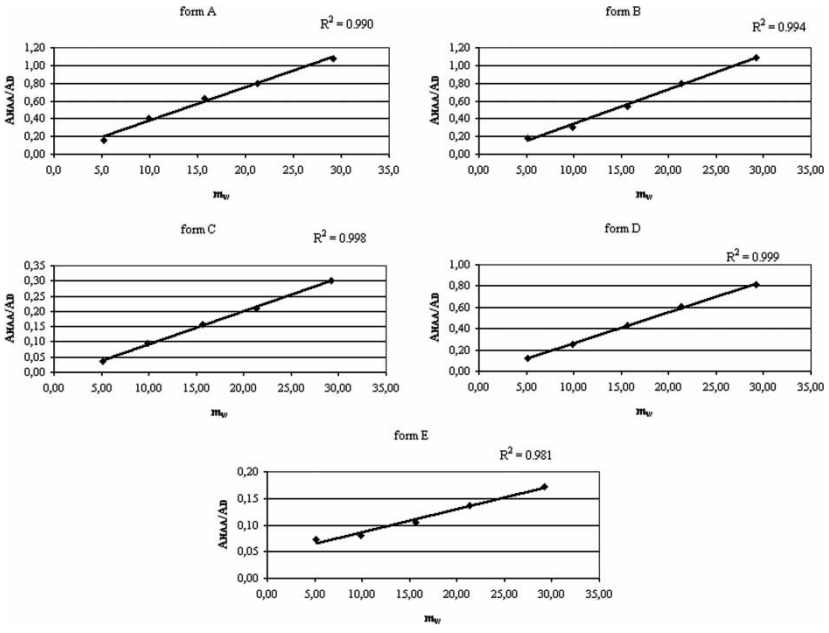


***Figure 4.*** Calibration curves of the forms A–E of hydroxyacetaldehyde. $A_{HAA}$, mean peak area of the signals of the carbons of HAA; $A_D$, peak area of the methylene of diglyme at $\delta = 69.5$ ppm; $m_w$, weighed amount (mg) of HAA.

spectra acquired with the selected parameters. Therefore, the same method was applied for the quantification of HAA in a biomass pyrolysis liquid.

## Application to the Quantitative Determination of Hydroxyacetaldehyde in a Biomass Pyrolysis Liquid

We used a partition scheme based on the water solubility of the constituents of the bio-oil, developed by Sipilä et al.[3] Such a procedure allowed the isolation of the carbohydrate fraction (see "Materials and Methods" section), the most abundant of the bio-oil (43.3% w/w). From the $^{13}C$ NMR spectrum of this fraction (recorded in DMSO-d6) (Fig. 5), we identified an anhydrosugar, levoglucosan, which was already reported in a previous study carried out in our laboratories.[18] We also observed the signals belonging to hydroxyacetaldehyde, which allowed the identification of the five aforementioned dimeric and monomeric main forms A–E of this compound. Indeed, the chemical shifts of the five forms of HAA in the spectrum of the carbohydrate fraction were compared with those of the pure compound (Fig. 5). As seen in this spectrum, there were no overlapped signals between levoglucosan and HAA. A few signals, with very low

***Table 3.*** $^{13}C$ NMR quantification of commercial HAA using diglyme as internal standard[a]

| Form | A | B | C | D | E |
|---|---|---|---|---|---|
| Experiment 1 | | | | | |
| $A_{HAA}$ | 2.461 | 2.945 | 0.583 | 1.898 | 1.165 |
| $m_C$ | 1.1 | 1.3 | 0.5 | 1.7 | 0.5 |
| total $m_C$ | | | 5.1 | | |
| $m_W$ | | | 5.2 | | |
| RE% | | | 1.9 | | |
| Experiment 2 | | | | | |
| $A_{HAA}$ | 5.472 | 4.012 | 1.266 | 3.404 | 1.066 |
| $m_C$ | 2.9 | 2.1 | 1.3 | 3.5 | 0.6 |
| total $m_C$ | | | 10.4 | | |
| $m_W$ | | | 9.9 | | |
| RE% | | | 5.1 | | |
| Experiment 3 | | | | | |
| $A_{HAA}$ | 6.638 | 5.709 | 1.671 | 4.520 | 1.113 |
| $m_C$ | 4.3 | 3.7 | 2.2 | 6.0 | 0.7 |
| total $m_C$ | | | 16.9 | | |
| $m_W$ | | | 15.7 | | |
| RE% | | | 7.6 | | |
| Experiment 4 | | | | | |
| $A_{HAA}$ | 6.363 | 6.423 | 1.679 | 4.856 | 1.100 |
| $m_C$ | 5.5 | 5.5 | 2.9 | 8.4 | 0.9 |
| total $m_C$ | | | 23.2 | | |
| $m_W$ | | | 21.3 | | |
| RE% | | | 8.9 | | |
| Experiment 5 | | | | | |
| $A_{HAA}$ | 6.774 | 6.852 | 1.903 | 5.132 | 1.089 |
| $m_C$ | 7.5 | 7.5 | 4.2 | 11.4 | 1.2 |
| total $m_C$ | | | 31.8 | | |
| $m_W$ | | | 29.2 | | |
| RE% | | | 8.9 | | |

[a]For the experiments 1 to 5, the mass of diglyme $m_D$ was 7.8 mg and the peak area of its methylene at $\delta = 69.5$ ppm was 16.033, 13.405, 10.540, 8.027, and 6.300, respectively. A–E: hydroxyacetaldehyde forms A, B, C, D, and E. Molecular weight: forms A–D = 120.10 g mol$^{-1}$, form E = 60.05 g mol$^{-1}$, and diglyme = 134.17 g mol$^{-1}$. $A_{HAA}$: mean peak area of carbons of each form. $m_C$: mass (mg) measured by $^{13}C$ NMR for each form and calculated according to formula (1). Total $m_C$: calculated mass (mg) of hydroxyacetaldehyde as the sum of $m_C$'s. $m_W$: weighted amount (mg) of HAA. RE%: relative error expressed as a percentage.

intensities, were also observed and, as indicated by the areas of the peaks, they obviously belong to minor components. Particularly, two signals at 90.68 ppm and 66.08 ppm, belong probably to a monomeric or dimeric hydrated form of HAA.

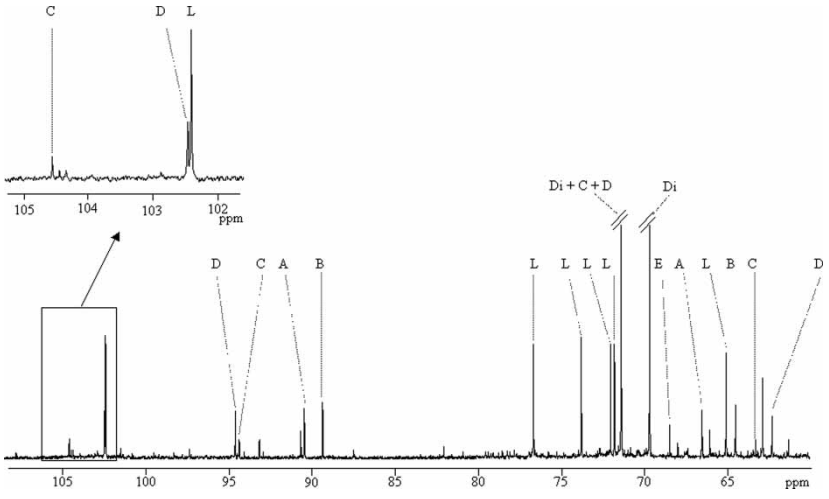


***Figure 5.*** Part of the $^{13}C$ NMR spectrum of the carbohydrate fraction of the biomass pyrolysis liquid. A–E, forms A–E of hydroxyacetaldehyde; Di, diglyme; L, levoglucosan.

The amount of each form (A–E) ($m_C$, mg) was calculated according to formula[1] (Table 4). The investigated sample (76.2 mg) contained 4.6 mg of hydroxyacetaldehyde, which corresponded with 6% of the mass of the carbohydrate fraction. The repeatability measured from four experiments (given at 99%) ensured the precision of the measurements (Table 4). Consequently, hydroxyacetaldehyde accounted for around 3% of the mass of the crude biomass pyrolysis liquid.

***Table 4.*** Quantification of hydroxyacetaldehyde in a biomass pyrolysis liquid

| Hydroxyacetaldehyde | $A_{HAA}$ | $m_c$ | $R$ | $\%m_c$ |
|---|---|---|---|---|
| Form A | 2.395 | 0.9 | $0.9 \pm 0.04$ | 1.2 |
| Form B | 2.992 | 1.1 | $1.1 \pm 0.07$ | 1.4 |
| Form C | 0.841 | 0.6 | $0.6 \pm 0.09$ | 0.8 |
| Form D | 2.297 | 1.6 | $1.6 \pm 0.06$ | 2.1 |
| form E | 1.126 | 0.4 | $0.4 \pm 0.04$ | 0.5 |
| Total | | 4.6 | | 6.0 |

$A_{HAA}$: mean peak area of the carbons of each form. $A_D$: peak area of the methylene of diglyme at $\delta = 69.7$ ppm $= 19.643$. Mass of diglyme: $m_D = 7.8$ mg. Molecular weights: forms A–D $= 120.10$ g mol$^{-1}$, form E $= 60.05$ g mol$^{-1}$ and diglyme $= 134.17$ g mol$^{-1}$. $m_c$: mass (mg) of each form of HAA measured by $^{13}C$ NMR and calculated using formula (1). $R$: repeatability of $m_c$ given at 99% (measured from four analyses). $\%m_c$: mass percentage measured by $^{13}C$ NMR and calculated according to: $\%m_c = m_c \times 100/76.2$.

In conclusion, the content of hydroxyacetaldehyde in a biomass pyrolysis liquid could be determined using a simple fractionation scheme and a $^{13}C$ NMR spectrum recorded with a reasonable occupation time of the spectrometer.

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