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F G Fonseca[1,2], A Funke[1], W Saechua[2] and P Sirisomboon[2]

[1] Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

[2] NIR Spectroscopy Research Center for Agricultural Products and Foods, Agricultural Engineering Department, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand

E-mail: frederico.fonseca@kit.edu

Abstract. Near Infrared (NIR) Spectroscopy is widely employed as a rapid technique for the evaluation of properties of biomass materials. Precision and accuracy of the instruments is an important aspect in order to minimize error in the determination of results. The objective of this publication is to determine scanning repeatability and reproducibility of the NIR spectrometer for wheat straw (*Triticum aestivum* L.), using either a fixed scan or a rotating scan. The former presented marginally better repeatability but worse reproducibility. Samples in equilibrium with the local atmosphere versus samples of controlled and different moisture contents were also compared, and the latter performed better on the precision test but both fixed and rotating scans. As the ultimate objective of this test is the use of this method to determine variations between different moisture content, and as the rotating scan presents better reproducibility, this method was selected as the reference method for further NIR analyses focused on the variation of moisture content.

1. Introduction

The use of biomass as a feedstock for sustainable fuel production has faced controversy in the last years, due to the potential conflict in the use of arable land between food, animal feed and energy crops, and the increased greenhouse gas emissions from changes in land use [1].

Lignocellulosic raw materials, like straws, have a high potential for biorefining while not competing with food production. This enables the use of a secondary product of lower economic value for the manufacture of commodities including fuels, intermediates or fine chemicals, that could theoretically compete in the traditional markets [2].

Straws are crop residues consisting of dry stems and leaves left after the harvest of cereal crops. As they make up over 50% of the harvestable vegetation of each crop, they are available in large quantities. They are coarse and highly fibrous materials, making them unfit for human consumption, but were extensively used as livestock feed and bedding. Other relevant uses include manure production, as well as construction, handcrafting and clothing materials. The industrial revolution brought cheaper and more efficient replacements that stripped straw of most of its commercial value. [3]

Fast pyrolysis is a thermochemical conversion process that has been extensively applied for the degradation of bio-based materials. It features fast heating rates and very short vapor residence times. Fast condensation systems are employed to recover one or more liquid phases, the fast pyrolysis bio-

oils (FPBOs). This process is characterized by a very high liquid production and smaller fractions of solids and non-condensable gases. [4].

In the liquid phase, a fraction of water between 15-35% is expected, which is mostly dependent on the moisture content of the feedstock [5]. Optimally, the water content of the FPBO should be kept as low as possible. A low moisture content promotes stability and energy density while decreasing transportation costs and acidity. It is important to keep in mind that low water content would greatly increase the viscosity of the oil, affecting downstream processing [5,6]. The water content of the FPBO is largely defined by the moisture and ash content of the feedstock. The first is directly carried over within the process if the feedstock is not dried prior to conversion. The latter promotes secondary cracking reactions and thus increases the amount of water formed inside the reactor by pyrolysis.

Near Infrared Spectroscopy is well known as a rapid and accurate technique, widely used both offline and online for determination of dry matter and water content, as well as cellulose and hemicellulose for lignocellulosic materials [7–9]. This non-destructive method presents several advantages when compared to traditional chemical determination methods, such as speed, accuracy, minimal sample preparation, no use of chemical agents, and ease of processing. [8,9]

The repeatability and reproducibility of the scanning method must be determined prior to the development of a predictive model for the determination of water content and/or other parameters. This constitutes the aim of this publication.

2. Materials and Methods

2.1 Sample preparation

Wheat straw (Triticum aestivum L.) was supplied by a farmer (Dörrmann, Kraichtal-Münzesheim, Germany), collected from a harvest of spring wheat, and supplied in large bales (250-300 kg each). Prior to conditioning, the straw was chopped to a particle size of <5 mm using a disintegrator (model HZR 1300, Germany) followed by a cutting mill (model LM 450/1500-S5-2, Germany), both supplied and installed by 'Neue Herbold Maschinen- und Anlagenbau GmbH' (Sinsheim/Reihen, Germany).

The chopped wheat straw is stored in large bags in a controlled environment at Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany. 'As received' it presents a moisture content of 8.9%.

It was dried to 1.1% using a tray batch convection dryer (Memmert Modell 700; Germany) overnight at 105 °C. Batches of around 400 g were then taken from this dried biomass and conditioned through direct spraying of deionized water, followed by leaving the biomass still overnight.

The moisture content of the straw was determined according to the DIN EN 14774-3 during the conditioning process, by drying overnight at 105 °C and employing the following formula (Eq. 1):

$$W\ (wt.) = 1 - \left(\frac{M_{\mathrm{i}} - M_g}{M_{dry} - M_g}\right) \quad (1)$$

In which M_i is the initial mass of the sampling glass plus the original biomass, M_g is the mass of the sample glass and M_{dry} is the mass of the sampling glass plus biomass after drying.

The samples were shipped to the NIR Laboratory of the Department of Agricultural Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand. From those, three samples of different moisture contents (1.1%, 8.9%, and 12.3%) were selected plus three others of the same moisture content (8.9%). The latter was opened and exposed to atmospheric conditions overnight in such a way that the biomass reaches the same moisture content as the environment.

The samples exposed to air overnight are henceforth named Conditioned (C1, C2, C3) and had a starting moisture content of 8.9% prior to conditioning. The ones of different moisture content are named Non-Conditioned (NC1, NC2, NC3), with moisture contents of 1.1%, 8.9%, and 12.3%, respectively. These amount to a total of 6 samples.

2.2 NIR Scanning

Scanning was performed using a NIR Multi-Purpose Analyzer (MPA) Spectrometer (Bruker, Germany) with a scanning resolution of 16 cm^{-1} in absorbance mode, featuring 32 scans per each average spectrum of the sample. Wavenumber ranged from 12500-4000 cm^{-1}.

Each sample was scanned using a rotating cylindrical cup (diameter of 9 cm and height of 9 cm), allowing for a more thorough analysis, as well as a smaller fixed cup (diameter of 5 cm and height of 5.8 cm). This allows one to determine the best method to use in future analyses.

2.3 Repeatability and reproducibility of scanning

The repeatability gives a numeric value of the variation between measurements using the same device and same operating conditions. Reproducibility gives the dispersion of the result after changing conditions, i.e. by reloading the sample. A low repeatability value means a low variation between the measurements, indicating a high precision of the scanning instrument.

Each sample was loaded and scanned 10 times in the same position to account for the repeatability of the method. Similarly, for reproducibility, each sample was reloaded and rescanned 9 times.

After performing the reproducibility test for the rotating cup, a fraction of the sample was loaded into the fixed cup, and both tests were performed again.

For each relevant peak value, we calculated the standard deviation of the adsorption over the 10 repetitions. The average of the standard deviations was taken as a measure of repeatability or reproducibility, respectively.

The final values presented are the averages of the repeatabilities and reproducibilities of each sample and method.

3. Results and discussion

Three relevant wavelengths that represent important NIR peaks for wheat straw were selected: wavenumber 6711.4 cm-1 (1490 nm) for the cellulose peak, 5154.6 cm-1 (1940 nm) for the water peak, and 4739.3 cm-1 (2210 nm) for the hemicellulose peak [10]. All three peaks are contrasted with the whole spectrum in Figure 1.

Table 1: Standard deviation values of the repeatability and reproducibility tests for the Conditioned (C) biomass, using both methods.

	Repeatability	Reproducibility
Fixed	0.00055	0.01162
Rotating	0.00114	0.00243

Table 2: Standard deviation values of the repeatability and reproducibility tests for the Non-Conditioned (NC) biomass, using both methods.

	Repeatability	Reproducibility
Fixed	0.00023	0.00996
Rotating	0.00044	0.00284

Wheat straw is a very heterogeneous material, and each sample contained particles of a wide range of sizes. This fact leads to the observed higher standard deviations observed for the reproducibility when compared to the repeatability, as on the former the position of each particle is randomized when performing each measurement.

Using the smaller, fixed cup consistently leads to better (lower) repeatability but worse reproducibility when compared to the rotating cup. A smaller scanning area would lead to smaller deviations between consecutive measures, hence lower repeatability. However, a smaller cup size means that randomization brought by emptying and refilling like in the reproducibility tests would play a bigger role.

If one assumes that all C samples reached equilibrium overnight, it would be expected that its repeatability would be better as the same value should be consistently measured. However, the repeatability of the NC biomass shows a lower value for both cups (comparing Table 1 with Table 2). It

would be expected that the NC biomass would change moisture content over the course of the experiments, and therefore the amplitude of the peak. When regarding the reproducibility, the values obtained for the NC biomass are marginally worse than for the fixed one.

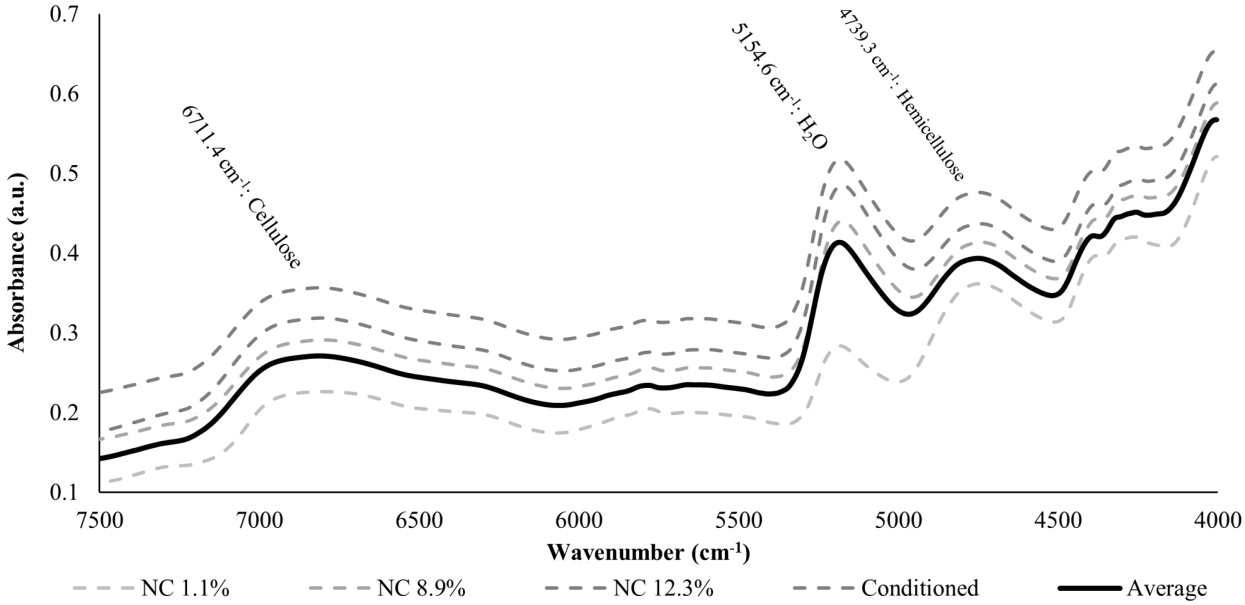

Figure 1: Average NIR spectra of wheat straw focused on the wavelengths relevant to the analysis. NC stands for "Non-conditioned", with the estimated moisture contents; Conditioned biomass is expected to have a moisture content of 8.9%.

The fact that the moisture content of NC biomass would change in measurable amount throughout the course of the measurement can be measured by calculating the Pearson correlation coefficient. This value measures the degree of linear correlation between two variables, where values close to 0 indicate lack of correlation and values close to 1 (or -1) indicate the presence of a linear correlation. In this case, the correlation is estimated between the amplitudes at the relevant wavelengths and the number of the repetition, indicating the passage of time.

Table 3: Pearson correlation coefficient (PCC) and slope of the linear correlation for the Conditioned (C) biomass, using both methods.

	Repeatability		Reproducibility	
	PCC	Slope	PCC	Slope
Fixed	-0.9268	-3×10^{-3}	0.1508	2×10^{-3}
Rotating	-0.8083	-3×10^{-3}	-0.2759	-2×10^{-3}

Table 4: Pearson correlation coefficient (PCC) and slope of the linear correlation for the Non-Conditioned (NC) biomass, using both methods.

	Repeatability		Reproducibility	
	PCC	Slope	PCC	Slope
Fixed	-0.8362	-1×10^{-3}	0.1381	6×10^{-3}
Rotating	-0.8924	-1×10^{-3}	0.2685	2×10^{-3}

According to Table 3 and Table 4, PCC values close to -1 indicate the presence of negative linear correlations for the repeatability tests and the absence of linear correlation for the reproducibility tests. Low absolute PCC values for the reproducibility tests indicate that the effect of time, i.e. the absorbance

of air moisture, plays a negligible effect in the dispersion of the values. This lack of a trend ensures that the time contacting air, under these conditions, does not have a measurable effect on the value obtained.

Compared with the standard deviations (see Table 1 and Table 2), the slopes (Table 3 and Table 4) calculated for all these situations are at least one order of magnitude lower and close to 0, indicating very low dispersion of the values around the average, regardless of the evidence for the presence of linear correlations.

Using these as reference values for subsequent NIR analyses of wheat straw, it must be taken into consideration that the use of the rotating cup allows for a more thorough scanning of the biomass. This stems from the fact that it employs a greater amount of biomass, and scans a higher portion of that same biomass. If other methods of analysis are employed, such as thermogravimetry (TGA), it is important to ensure that the scanned surface area corresponds to an amount of biomass that would give reliable results.

It is important to keep in mind the samples were first tested using the rotating cup, and only afterward the smaller fixed cup. Then, repeatability and reproducibility tests were performed in this order. This situation might have led to minor moisture content variations throughout the fixed cup analyses.

4. Conclusions

This publication focuses on comparing the use of two different NIR methods using the same biomass and the same equipment as a reference method for further analyses for the establishment of a predictive model. The first method employs a large rotating cup, whereas the second uses a small fixed cup.

Repeatability and reproducibility tests were conducted for all four variants. The fixed cup consistently yielded better repeatability results but worse reproducibility, indicating that a smaller sample size is disadvantageous, as the material is very heterogeneous.

The effect of variations in the moisture content of the material was also considered by comparing three samples conditioned at local atmospheric conditions (air-conditioned room kept at 25±2 °C in Bangkok, Thailand) and three samples treated for different moisture contents (stored in sealed containers). In terms of repeatability and reproducibility, conditioned samples performed similarly to samples of different moisture contents.

Low Pearson correlation coefficients observed for all situations indicate that contact time with air was not enough to vary the moisture content appreciably throughout the experiments.

Despite all these remarks, the standard deviations observed were consistently small, when compared to the amplitude at the relevant wavelengths. This indicates the precision of the scanning method, allowing for the development of a predictive method based on NIR experiments.

References

[1] Kamm B, Gruber P R and Kamm M 2005 *Biorefineries-Industrial Processes and Products* vol 1–2, ed B Kamm, P R Gruber and M Kamm (Weinheim, Germany: Wiley-VCH Verlag GmbH)
[2] Basu P 2010 *Biomass Gasification and Pyrolysis: Practical Design and Theory* (Elsevier)
[3] Suttie J M 2000 *Hay and straw conservation for small-scale farming and pastoral conditions* (Rome: Food and Agriculture Organization of the United Nations)
[4] Bridgwater A V 2012 Review of fast pyrolysis of biomass and product upgrading *Biomass and Bioenergy* **38** 68–94
[5] Westerhof R J M R J M, Kuipers N J M, Kersten S R A and van Swaaij W P M 2007 Controlling the water content of biomass fast pyrolysis oil *Ind. Eng. Chem. Res.* **46** 9238–47
[6] Oasmaa A and Czernik S 1999 Fuel oil quality of biomass pyrolysis oils-state of the art for the end users *Fuel Energy Abstr.* **13** 914–21
[7] Xu F and Wang D 2015 Analysis of Lignocellulosic Biomass Using Infrared Methodology *Pretreatment of Biomass* (Elsevier) pp 7–25
[8] Sharma S and Sirisomboon P 2017 Precision Test for Spectral Characteristic of On-line Vis-NIR versus At-line NIR Spectroscopy for Measuring Total Soluble Solids of Mango (Mangifera indica CV Nam Doc Mai) *The 18th TSAE National Conference and the 10th TSAE*

International Conference p 8
[9] Sun D-W 2009 *Infrared Spectroscopy for Food Quality Analysis and Control* (Elsevier Inc.)
[10] Osborne B G, Fearn T and Hindle. P H 1993 *Practical NIR Spectroscopy with Applications in Food and Beverage Analysis* (Singapore: Longman Singapore Publishers (Pte) Ltd.)

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