



Hydrothermal carbonization (HTC): Near infrared spectroscopy and partial least-squares regression for determination of selective components in HTC solid and liquid products derived from maize silage



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HIGHLIGHTS

- HMF and furfural produced during HTC are degraded on HTC 250 after 180 min.
- NIR spectroscopy can be applied for both solid and liquid products of HTC.
- NIR accompanying with PLSR can be applied for quantitative prediction of HTC products.

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ABSTRACT

Near-infrared (NIR) spectroscopy was evaluated as a rapid method of predicting fiber components (hemicellulose, cellulose, lignin, and ash) and selective compounds of hydrochar and corresponding process liquor produced by hydrothermal carbonization (HTC) of maize silage. Several HTC reaction times and temperatures were applied and NIR spectra of both HTC solids and liquids were obtained and correlated with concentration determined from van-Soest fiber analysis, IC, and UHPLC. Partial least-squares regression was applied to calculate models for the prediction of selective substances. The model developed with the spectra had the best performance in 3–7 factors with a correlation coefficient, which varied between 0.9275–0.9880 and 0.9364–0.9957 for compounds in solid and liquid, respectively. Calculated root mean square errors of prediction (RMSEP) were 0.42–5.06 mg/kg. The preliminary results indicate that NIR, a widely applied technique, might be applied to determine chemical compounds in HTC solid and liquid.

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1. Introduction

The world is facing two large challenges in energy sector, e.g., renewable sources and their sustainability. According to the United Nations report, up to 77% of the world's energy in 2050 could come from renewable sources [UN report, 2007]. Lignocellulosic biomass like primary (straw, grasses) and secondary agricultural residues

(rice hulls, corn cobs, straw-manure mixtures) have no conflicts with the food versus fuel issue. Moreover, biomass is the third largest source of energy after petroleum and coal. This is the only renewable energy source with carbon in the structure, compared to wind, solar, and water [IPCC, 2011]. However, the handling characteristics, lower bulk density, high ash content, and lower energy content hindered the usage of lignocellulosic biomass for energy production [IPCC, 2011]. An efficient method of producing renewable, sustainable energy from lignocellulosic biomass is beneficial to overcome the current crisis.

Hydrothermal carbonization (HTC) is one of the promising thermochemical processing of biomass for producing hydrochar and value-added chemicals. The history of HTC goes back to 1913, when Bergius made an attempt of producing synthetic coal from cellulose. However, the similar concept was rediscovered recently aiming to mitigate the emission of green-house gases, to improve energy, and food security, and to use the most abundant form of

Abbreviations: HTC, hydrothermal carbonization; NIR, near infrared spectroscopy; HHV, higher heating value; HMF, hydroxymethyl furfural; PLS, partial least squares; PLSR, partial least squares regression; OSC, orthogonal signal correction; JK, Jack Knifing; VN, vector normalization; KM, Kubelka–Munk; EMSC, extended multiplicative scatter correction; RMSEC, root mean square error of calibration; RMSECV, root mean square error of cross validation; SNV, standard normal variate; PCA, principal component analysis; PC, principal component; DI water, de-ionized water; PID controller, proportional-integral-differentiate controller.

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carbon to value-added products. Recent studies mentioned that HTC is a promising technology for converting biomass into lignite-type coal [Parschetti et al., 2013], into liquid biofuel [Hoekman et al., 2011], into a soil amender [Libra et al., 2011; Rillig et al., 2010], into a carbon material for liquid contaminant adsorption [Regmi et al., 2012], into nanostructure carbon material [Cui et al., 2006], into a carbon catalyst [Hu et al., 2010; Yu et al., 2012], or into carbon material for increasing fuel cell efficiency [Titirici and Antonietti, 2010].

Subcritical water has the ionic product maximum in the temperature range of 200–280 °C [Bandura and Lvov, 2006]. When biomass is treated with subcritical water, organic components, e.g., lignin, cellulose, hemicelluloses degrade to some extent. During HTC, first hydrolysis of the extractives, hemicellulose, and cellulose followed by dehydration, and followed by decarboxylation, condensation, polymerization, and aromatization take place in the liquid phase [Funke and Ziegler, 2010; Reza et al., 2014]. Although the overall reaction chemistry follows mainly the stated reaction paths, each of the individual HTC reaction has their own reaction kinetics and probably catalyzed by one another [Reza et al., 2013b]. The HTC reactions in the liquid phase are mainly responsible for the production of so-called liquid biocrude [Kruse et al., 2013], which considers as the main precursor of solid hydrochar. Thus, the quality of hydrochar depends on the composition of process liquor and which makes the HTC process more unique compare to other thermochemical conversion processes [Libra et al., 2011]. Besides HTC reaction temperature and reaction time, the liquid phase reactions as well as the formation of the hydrochar also depend heavily on the feedstock [Wiedner et al., 2013]. HTC process liquor is often defined as the waste water and requires proper treatment prior to discharge into the environment, even after successive recycling [Uddin et al., 2013]. However, the high strength HTC process liquor can be an effective feedstock for biogas production via anaerobic digestion [Wirth and Mumme, 2013], which can potentially contribute to the overall economics besides treating waste water. So, the knowledge about the chemistry and kinetics of liquid phase as well as solid phase of specific feedstock are necessary for comprehensive HTC process and product optimization.

Optical spectrometry is a universal tool for characterization of solid and liquid products. The signature spectra can reveal the chemical information, which will reduce the extensive, tedious laboratory analyses. A successful optical technique is often necessary for designing in-line or on-line process control, thus helps to scale up processes from batch to continuous, and from small to large scale. For instance, NIR spectroscopy has proved to be a valid analytical tool for food products quality assurance [Blanco and Villarroya, 2002; Chen and He, 2007]. As a multivariate and rapid technique NIR spectroscopy offers the possibility to determine concentration of selective substances. The solid as well as the liquid phase can be measured with adjusted probes and measurement configurations. Several applications of the use of NIR spectroscopy to construct models for evaluating components content can be found in the literature. For example, it has been employed to analyze carotenoids content in maize [Brenna and Berardos, 2004], organic matters in soil [Fidencio et al., 2002], arachidonic acid in powdered oil [Yang et al., 2010], and α -tocopherol in vegetable oils [Szyk et al., 2005]. However, by far the author's knowledge, NIR was conducted for neither hydrochar nor HTC process liquor yet.

The main goal of this work was to investigate the use of NIR for the detection of selected HTC products by means of Partial least-squares regression. Further objectives were to determine quantitatively the concentration of selective soluble organic products, to describe the physical and chemical changes of both hydrochar and process liquor with different HTC temperature and time, and correlate the chemical analyses with the NIR spectra.

2. Methods

2.1. Hydrothermal carbonization

Maize silage was acquired from a locally grown test site at Leibniz Institute for Agricultural Engineering (ATB), Potsdam, Germany. The feedstock's size was reduced to 5 ± 3 mm. Moisture content of the feedstock was 13 ± 1 wt%. Around 50 g of maize silage was weighed in a beaker, transferred into a 1 L Parr reactor stirred reactor (reactor series 4520, IL, USA). DI water of 600 ml was weighed by same balance (maintain 1:12 maize silage, water ratio) and poured into the reactor. The experimental condition was set either 200 or 250 °C for holding time 20, 60, 180, and 300 min with the 3 K min^{-1} heating rate. There was one additional experiment performed at 230 °C for 1 h. The reaction temperature was controlled by a Parr PID temperature controller (4520 series). The accuracy of the controller was set at ± 1 K. The pressure was not controlled, rather monitored during the reaction. The content was stirred continuously during the hydrothermal treatment at 180 rpm. After the end of reaction period, the heater was turned off and let the reactor cooled down naturally. It took 3–4 h to cool down from 250 to 25 °C (about 20 min from 250 to 180 °C), while pressure drops from 4–4.5 to 0.2–0.5 MPa. The gaseous product was purged in the hood; the solid product was filtered using a folded filter paper (ROTH Type 113 P filter) for 20 min. The process liquid was stored into a 4 °C refrigerator for further analyses. The solid product was dried in a heating oven for overnight at 105 °C. Dried solid product was placed into a zip-lock bag and stored for further use. Each individual experiment was carried at least three times and the solid products and process liquors were mixed prior to further analyses for minimizing experimental errors.

2.2. Chemical analyses

A modified van-Soest method using the ANKOM A200 Filter Bag Technique (FBT) was used to determine the contents of hemicellulose, cellulose, lignin, and aqueous soluble compounds in solid samples [Reza et al., 2014]. The solid samples are first crushed and sieved to the desired particle size (20–65 mesh) and were dried at 105 °C for 24 h prior to the analysis. The contents of hemicellulose, cellulose, and lignin were calculated from the difference of neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent liquid (ADL), and ash as shown following;

$$\text{Extractives (\%)} = 100 - \text{NDF (\%)}$$

$$\text{Hemicellulose (\%)} = \text{NDF (\%)} - \text{ADF (\%)}$$

$$\text{Cellulose (\%)} = \text{ADF (\%)} - \text{ADL (\%)}$$

$$\text{Pseudo-lignin (\%)} = \text{ADL (\%)} - \text{Ash (\%)}$$

According to modified van-Soest method, biomass and hydrochar are divided into five components only in this method and any change of one component will affect the others. The method is based on extraction of fibrous substances using NDF, ADF, and ADL. The method is well-established for raw biomass, however, several scientists were adopted this technology for hydrochar analysis as well [Parschetti et al., 2013; Reza et al., 2013b, 2014; Uddin et al., 2013]. The solid residue left after ADL is pseudo-lignin and ash. Ash, determined separately by muffle furnace according to ASTM D2974, subtracted from lignin and ash weight from fiber analysis, to find lignin content. So, pseudo-lignin is not measured directly and this is one of the main shortcomings of this method. The higher heating value (HHV) was calculated using the correlation of Boie and presented as dry-ash-free basis (Boie, 1953).

Liquid phase pH was measured directly after filtration using a WTW inoLab pH/Cond 720 with a Sen Tix probe. Solid pH was measured after drying the solid residue and then mixing with water in

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