APPLICATION NOTE

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EXCELLENCE IN ELEMENTS

Characterization of biomass and biochar

CHALLENGE

Determination of the elemental composition of biochar and its biomass feedstock

According to the U.S. Department of Agriculture, "biochar is black carbon produced from biomass sources for the purpose of transforming the biomass carbon into a more stable form (carbon sequestration)". This carbon-rich material is derived from thermal conversion (including pyrolysis) of biomass under oxygen-limited conditions[1]. Biochar is on the one hand a carbon negative soil amendment as it captures carbon which is then not released back into the atmosphere. On the other hand, biochar possesses huge potential to combat climate change in non-soil applications, such as e.g. road building, construction materials, polymer composites, filters and purifiers, or batteries. This is why biochar can play a pivotal role in the concept of circular economy. It contributes through resource use efficiency, material recycling/upcycling, and cascade uses[2]. Biochar can potentially remove up to 6% of global emissions annually and biochar production via biomass pyrolysis is one of the few carbon dioxide removal technologies that can be deployed at scale[3].

Various biomass feedstocks such as plants, wood residues, organic biowaste, landscaping materials or animal manure can be turned into value by producing biochar. Depending on the feedstock and processing conditions various types and qualities of biochar with different characteristics can be produced. Next to the structural characterization of biochar the determination of the elemental composition (CHNS+O) is of

1 IBI (2015) Standardized product definition and product testing guidelines for biochar that is used in soil. Int Biochar Initiat 2:1–61

2 Kua, H. W., Masek, O., Gupta, S. "Biochar-based circular economy" in "Biochar – Emerging Applications"

3 Lefebvre et al, 2023, "Biomass residue to carbon dioxide removal: quantifying the global impact of biochar", https://doi.org/10.1007/s42773-023-00258-2

INSTRUMENTS:

- vario MACRO cube CHNS, O-TCD option
- soli TOC® cube

SAMPLES:

Rice husk biomass:
- 35 to 50 mg for CHNS
- 2-3 mg for O determination

Rice husk biochar:
- 35 to 50 mg for CHNS
- 2-3 mg for O determination

Soft wood pellet biomass:
- 35 to 50 mg for CHNS
- 2-3 mg for O determination

Soft wood pellet biochar:
- 35 to 50 mg for CHNS
- 2-3 mg for O determination

high importance for the characterization of the biochar and especially for its suitability for specific applications. For example, the stability of biochar, which is important for the long-term carbon sequestration potential, is determined by its O/C and H/C elemental ratios, and C/N is a parameter for degradability of organic matter. To be able to industrialize biochar production on a large scale, major efforts in research & development must be made, and a classification of different standardized biochar products is required. CHNS+O analysis is a key analytical method for this task.

SOLUTION

Simultaneous CHNS determination + O option with highest precision and accuracy

Two types of commercial biochar and their biomass feedstocks from "UK biochar research centre" were analyzed: firstly, rice husk and its pyrolyzed porous silicon-rich carbon material, which can be applied to water and air purification or cement composites, besides its benefits for environmental restoration. Around 510 million metric tons of milled rice are produced annually. Due to its tough fibers, natural decomposition lasts very long and its use as animal feed is complex due to its low nutritional value. That is why rice husk is considered as biochar feedstock at commercial scale. Secondly, soft wood pellets biomass and biochar, typically applied as soil amendment for agricultural purpose, were analyzed. Both biochars were produced at a nominal peak temperature of 700 °C in a rotary kiln pyrolysis unit.

For the elemental analysis of these samples the vario MACRO cube was applied. It is designed for simultaneous determination of CHNS in a single, fully automated step. It guarantees blank-free sample transfer thanks to the patented ball valve sample introduction, resulting in analysis results with highest precision and accuracy. The use of the Advanced Purge and Trap (APT) technology enables the instrument to measure samples with even the most challenging C:N elemental ratios. The inhomogeneous samples were weighed in without time-consuming sample preparation like grinding or milling. Calibration and standard factors were carried out with the Elementar LNS standard for low nitrogen and sulfur. The samples were measured in a six-fold determination.

The oxygen content of the biomass and biochar samples were measured with the O-TCD option in a six-fold determination. Benzoic acid was used for calibration and daily factor. This oxygen option is available as upgrade kit for vario MACRO cube, vario EL cube and UNICUBE®.

Flexible temperature-dependent differentiation of carbon in biomass and biochar

The determination of total organic carbon (TOC), total inorganic carbon (TIC) and residual oxidizable carbon (ROC) was performed on the soli TOC® cube. Sample preparation was simple due to the advanced crucible technology that reduces time-consuming homogenization steps.
The soli TOC® cube offers an unmatched measurement range of 0.001 – 100 % carbon. For the determination of temperature-dependent carbon fractions, a precise, adjustable temperature with fast heating rates is required for reproducible measurements. This is achieved by the dynamic heater of the soli TOC® cube, which controls the temperature directly at the crucible position. This eliminates any possible thermal interferences and

guarantees stable combustion conditions. Additionally, the use of a post-combustion catalyst ensures that even high carbon-content samples are quantitatively oxidized and achieve equally high measurement quality.

Did you know?

There are a variety of analytical methods for biochar characterization: these include X-ray µ-tomography, SEM/EDX or Raman spectroscopy for structural characterization. NMR spectroscopy, FTIR or analysis of electric conductivity, pH or magnetic properties reveal further key characteristics of biochar. However, CHNS+O compositional analysis of biochar is indispensable in terms of mass concentration determination. The most accurate results can be obtained by CHNS bulk analysis of the whole compound and by measuring the oxygen content rather than calculating it. The elemental concentration is also the starting point for determining the stability of biochar. More recently, the van Krevelen diagram, which compares elemental ratios of H/C with O/C to assess structure and reaction processes of coal, has been applied to biochar. A potentially high concentration of inorganic carbon in the biochar can be an issue. This is avoided by measuring TOC and using this value to elaborate on the long-term stability of biochar.

RESULTS

As the results in table 1 show, the carbon content of the biochar samples is higher than that of their biomass feedstock, due to the pyrolysis process. Especially the soft wood pellet biochar shows a high carbon content of > 88%, indicating a high carbon capture capacity. The rice husk biochar contains silicium oxide SiO_2, incorporated as silicate crystals. Its carbon content is about 45%. While the carbon and nitrogen content accumulates during the pyrolysis process from biomass to biochar, oxygen and hydrogen are removed from the material.

Table 1. CHNS+O results of rice husk and soft wood pellets biomass feedstock and pyrolyzed biochar.

SAMPLE		C [%]	H [%]	N [%]	S (IR) [%]	O [%]
RICE HUSK BIOMASS	**Mean value**	**37.36**	**4.91**	**0.33**	**0.027**	**37.47**
	Standard deviation (abs.)	0.27	0.10	0.06	0.003	1.06
RICE HUSK 700 BIOCHAR	**Mean value**	**45.39**	**0.92**	**0.60**	**0.029**	**3.44**
	Standard deviation (abs.)	0.84	0.05	0.05	0.003	0.21
SOFT WOOD PELLETS BIOMASS	**Mean value**	**45.80**	**5.96**	**0.05**	**0.040**	**44.66**
	Standard deviation (abs.)	0.10	0.13	0.00	0.012	0.30
SOFT WOOD PELLETS 700 BIOCHAR	**Mean value**	**90.36**	**1.93**	**0.27**	**0.007**	**4.64**
	Standard deviation (abs.)	0.14	0.05	0.03	0.004	0.09

Table 2. Measurement results for rice husk and soft wood pellets according to DIN 19539 method for the differentiated determination of the content of total organic carbon (TOC_{400}) released up to 400 °C.

SAMPLE		TOC_{400} [%]	ROC [%]	TIC [%]	TC [%]
RICE HUSK BIOMASS	**Mean value**	**35.66**	**0.359**	**0.286**	**36.30**
	Standard deviation (abs.)	0.46	0.095	0.125	0.50
RICE HUSK 700 BIOCHAR	**Mean value**	**44.60**	**0.401**	**0.117**	**45.12**
	Standard deviation (abs.)	1.52	0.252	0.023	1.72
SOFT WOOD PELLETS BIOMASS	**Mean value**	**44.20**	**0.310**	**0.217**	**44.72**
	Standard deviation (abs.)	0.20	0.019	0.020	0.21
SOFT WOOD PELLETS 700 BIOCHAR	**Mean value**	**88.98**	**0.314**	**0.177**	**89.47**
	Standard deviation (abs.)	0.53	0.248	0.149	0.49

Table 3. Relevant elemental ratios of rice husk and soft wood pellets biomass feedstock and pyrolyzed biochar.

SAMPLE		H:C	O:C	C:N	H:TOC
RICE HUSK BIOMASS	**Mean value**	**0.131**	**1.003**	**115.2**	**0.134**
	Standard deviation (abs.)	0.008	0.005	8.0	
RICE HUSK 700 BIOCHAR	**Mean value**	**0.020**	**0.076**	**75.9**	**0.020**
	Standard deviation (abs.)	0.001	0.005	5.9	
SOFT WOOD PELLETS BIOMASS	**Mean value**	**0.130**	**0.975**	**1030.5**	**0.135**
	Standard deviation (abs.)	0.011	0.006	8.0	
SOFT WOOD PELLETS 700 BIOCHAR	**Mean value**	**0.021**	**0.051**	**333.2**	**0.022**
	Standard deviation (abs.)	0.011	0.007	10.0	

From left to right: Rice husk biomass, rice husk biochar, soft wood pellets biomass, soft wood pellets biochar.

The H/C and O/C ratios are the most relevant for characterizing biochar, e.g. they indicate the quality of the pyrolytic conversion and the stability (half-life) of the material as a carbon sink. Moreover, the ratios make different biochars comparable, which is important for scaling up global biochar production as customers require stable supply chains and quality of their biochar for different applications. The C/N value is interesting for the nutrient content of biochar when used in soil / fertilizer applications. Both rice husk and soft-wood pellets biochar show an O:C ratio <0.2, indicating a biochar half-life of more than 1,000 years and the H/C ratio <0.7 represents pyrolytic chars without pyrolysis defiancies.

SUMMARY

Biochars are finding their ways into non-soil applications where carbon sequestration is an objective. The increased research and production for a wide variety of applications lead to new opportunities[1]. As research will lead to new production processes and new biochar-based products, elemental analysis is of great importance. Both CHNS + O and TOC analysis are crucial for a complete characterization of biochar. A reliable detection of H/C, O/C and C/N ratios, as well as differentiation of TOC, ROC and TIC is best accomplished by bulk elemental analysis of the samples rather than only analyzing the surface of the material. This Application Note shows results for the accurate and precise determination of carbon, hydrogen, nitrogen, and sulfur as well as oxygen with the vario MACRO cube elemental analyzer. In addition, the carbon fractions were determined on the soli TOC® cube with its temperature-dependent differentiation of carbon. Both instruments are ideally suited for a reliable and effortless determination of the elemental composition of biochar with high precision and accuracy.

1 Tagiaferro, A., Rosso, C., Giorcelli, M. "Introduction to the biochar world with a focus on new possible applications" in "Biochar – Emerging Applications"

This Application Note was created in collaboration with Mauro Giorcelli, electronic engineer with a PhD in physics. He is co-founder of the Carbon Group of Politechnico di Torino (Italy) and board member of ICHAR (Italian Biochar Association). With his world-wide cooperations he has published over 100 articles which have garnered over 1,500 citations.

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