



UNIVERSITY OF LEEDS

This is a repository copy of *Biocoal - Quality control and assurance*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/160334/>

Version: Accepted Version

Article:

Pawlak-Kruczek, H, Arora, A, Gupta, A et al. (7 more authors) (2020) *Biocoal - Quality control and assurance*. *Biomass and Bioenergy*, 135. 105509. ISSN 0961-9534

<https://doi.org/10.1016/j.biombioe.2020.105509>

© 2020, Elsevier. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>



Review

Biocoal - Quality control and assurance



Halina Pawlak-Kruczek ^a, Amit Arora ^b, Ashish Gupta ^b, Muhammad Azam Saeed ^c,
Lukasz Niedzwiecki ^{a,*}, Gordon Andrews ^d, Herodotos Phylaktou ^d, Bernard Gibbs ^d,
Anna Newlaczyl ^e, Penelope M. Livesey ^e

^a Department of Boilers, Combustion and Energy Processes, Faculty of Mechanical and Power Engineering, Wrocław University of Science and Technology, Poland

^b Department of Chemical Engineering, Shaheed Bhagat Singh State Technical Campus, Ferozepur, Punjab, 152004, India

^c Department of Chemical Engineering, University of Engineering and Technology, Faisalabad Campus, Lahore, Pakistan

^d School of Chemical and Process Engineering, University of Leeds, United Kingdom

^e University of Liverpool, United Kingdom

ARTICLE INFO

Keywords:

Biocoal
Torrefaction
Carbonization
HTC
FTIR
NIR
NMR
Solid biofuels
REACH

ABSTRACT

Torrefied biomass is said to have potential as a replacement for coal. One of the main goals of torrefaction is to make biomass resemble coal more in terms of its properties as a solid fuel. As a fuel, a novel fuel that is produced by thermal treatment of raw biomass, biocoal has to comply with the regulations of solid fuels from different regulatory bodies. The production regime is different in comparison to the thermally treated fuel already established on the market, such as charcoal. This might raise an issue with the bodies controlling the circulation of chemical substances in the market, such as ECHA in Europe. The aim of this paper is to recommend suitable analytical techniques in order to enable effective quality control. This is necessary if biomass of low and highly variable quality is supposed to become more uniform and turn into a commodity. Information given in many published studies seems sufficient to use of FTIR and NIR as quality control techniques. The use of NMR can be complementary but is limited due to the high cost of the analytical equipment and time-consuming sample preparation. Rapid testing techniques, such as FTIR ATR or NIR, might prove feasible for quality control of solid biofuels, such as biocoal, especially for in-house quality control purposes. This way proper quality assurance and compliance with various novel regulations, such as REACH, could be assured. Further research could be helpful, especially if results would be available in publicly available databases, such as Phyllis.

1. Introduction

1.1. Energy from renewable sources

Renewable Energy Sources are effective solutions on the way towards a low carbon future. Emissions of CO₂ from the consumption of energy exceeded 33 Gt in 2011 [1]. There is an ongoing international effort to reduce these emissions. On the European level, the EU Directive (2009/28/EC) specified targets for the share of consumed (final) energy coming from renewable energy sources that should be achieved by 2020 [2]. It is 20% of renewable energy in total energy consumption, which splits into 21% renewable share of heating and cooling, 10% share of transport, and 34% share of electricity consumption [3]. In 2014 in the European Union, 46% of final energy was consumed as heat and cold, 24% was consumed as electricity and 30% was consumed by transport

[3]. In total, a 15.3% share of final energy is coming from renewable sources [3]. Each of the EU member countries, as well as Norway and Iceland, has its own target to be achieved [2].

1.2. Biomass as an energy source and material

Biomass is considered as an energy source that is neutral in terms of CO₂ emissions [4,5]. Thus the rate of absorption of atmospheric CO₂ is correlated with the rate of growth of biomass. It is possible to obtain biomass on a long term, sustainable basis, and this practice is well known [6]. In some of the cases leaving the biomass unused might lead to diminished capability to absorb CO₂ by the ecosystem, e.g. the threat is real for the European forests in the near future [7,8]. Moreover, accumulation of unused residual biomass might lead to pest infestation [7] and wildfires [9,10], which in itself can be significant source of

* Corresponding author.

E-mail address: lukasz.niedzwiecki@pwr.edu.pl (L. Niedzwiecki).

<https://doi.org/10.1016/j.biombioe.2020.105509>

Received 25 May 2019; Received in revised form 1 February 2020; Accepted 13 February 2020

Available online 26 February 2020

0961-9534/© 2020 Elsevier Ltd. All rights reserved.

harmful emissions. From an energy point of view, this seems to be an enormous waste, since CO₂ is being emitted anyway, without any useful energy recovered from that process.

Carbon, oxygen, and hydrogen are the three main elements present in biomass and their respective contents are correlated with various effects on the energy conversion processes, utilizing this renewable energy source. Biomass is composed of the three main polymers: cellulose, hemicelluloses and lignin, which form the orthotropic, composite organic structure of plants, wood serving as a good example [11].

Cellulose is a glucose polymer that typically consists of repeating units of β 1–4 linked D-glucose [12]. The degree of polymerisation, which is a number of glucose units, is variable and depends on the region of the cell [11]. In secondary cell walls, cellulose consists of 8,000–10,000 units, while in primary cell walls its degree of polymerisation varies between 2,000 and 4,000 units [11]. Wood typically consists of 40 to nearly 47% of cellulose [11]. Hemicellulose is a heterogeneous class of polymers containing glucose, galactose, mannose, xylose and other sugars [12,13]. Both the degree of crystallisation and the degree of polymerisation (approx. 200 units) of hemicellulose are generally low [11,14]. Wood typically contains 25–35% of hemicellulose [11].

Lignin is a complex, amorphous, three dimensional, aromatic molecule that consists of phenyl groups [14]. It is non-crystalline, hydrophobic and is the main constituent of a composite matrix of woody biomass. Lignin is a brittle material, and its presence in middle lamella provides adhesion between the cells [11]. Wood typically contains 20–31% of lignin. Plants also contain some amounts of compounds that are not polymers (saps/extractives) that usually add up to less than 10% of dry mass [11].

Content of these respective polymers can have influence on the subsequent conversion processes, such as densification [15,16], pyrolysis [17,18], gasification [19,20] as well as combustion characteristics [17,21,22] and emissions [23,24].

1.3. Production of biocoal using dry and wet torrefaction

Torrefaction (sometimes called roasting, slow, or mild pyrolysis [25]) is a process in which biomass is heated up to approximately 200 °C–300 °C [25–32]. Depending on the severity of the process, fibrous, tenacious and hydrophilic biomass is transformed into more hydrophobic material, which is also more brittle and contains less volatile matter. During torrefaction, the processed feedstock is heated up, dried and then kept under an elevated temperature inside of the reactor. During drying, free and physically adsorbed water is removed first. As the temperature of the particle becomes higher, chemically bound water is also removed [27]. This is called by some authors a “reactive drying” [27]. While being in the reactor, a devolatilisation process occurs and the feedstock becomes subject to decomposition. Some authors call this step “destructive drying” [27]. Most of the process product is solid, but some of it is gaseous and some liquid (condensable volatiles). Process gas (called torgas) is typically used as a source of heat for the process, therefore it is combusted. In many cases, torgas itself is not sufficient and a part of the feedstock has to be burned to obtain the necessary amount of heat. Among condensable volatiles, acetic acid and water are dominant [29], while other compounds like furfural, formic acid etc. are formed in different concentrations depending on process conditions and feedstock [25–32]. Non-condensable volatiles consist mainly of carbon dioxide and carbon monoxide [25–32]. At present torrefaction is a widely discussed technology due to its potential to enable the use of additional biomass resources and make it a tradable commodity, which could enable broader use of biomass as one of the energy sources that are not intermittent [25].

There are many different designs of torrefaction reactors existing nowadays [25,30]. The torrefaction process improves various properties of biomass, not only those that enable more efficient transport (energy density) but also those that enable easier handling (hygroscopic/hydrophobic nature).

However, some crucial properties, important at the power plant (or other energy conversion technology facility), are also subject to change [28]. Grindability increases, as an effect of torrefaction, which offers potential savings in both energy consumption for grinding equipment and investment costs of auxiliary devices in co-firing power plants. Torrefaction, especially along with the densification stage, allows one to handle reduced volumes of material, containing a majority of its original chemical energy. Moreover, the hydrophobic character of the torrefied product might provide a possibility to avoid weather-protected storage. During torrefaction –OH groups are substituted by non-polar groups. As a result, water-absorbing capacity is significantly reduced. This makes the fuel less sensitive to biodegradation, self-heating and moisture uptake [25–32]. Reactivity of torrefied biomass is typically increased, in comparison to the original feedstock, which is important in terms of subsequent use of torrefied material as a fuel in combustion and gasification processes [33,34].

Torrefied biomass is said to have potential as a replacement for coal [25–32]. One of the main goals of torrefaction is to make biomass resemble coal more in terms of its properties as a solid fuel [25–32]. Due to these factors, torrefied biomass is often called biocoal. The term biocoal is also used for biomass valorised thermally using other processes, such as hydrothermal carbonization (HTC) [35–41]. Hydrothermal carbonization (HTC) is a thermal valorisation process, typically performed at 200 °C up to 260 °C, in subcritical water under saturation pressure [37,42]. Between 200 °C and 280 °C, the ionic constant of water is a subject of significant increase and water behaves as a non-polar solvent [43]. The process involves a multitude of concurring reactions, with many different products, especially when it is performed using biomass [37,42]. Hydrolysis is the first stage of the HTC process. During these stages, biomass is degraded to monomers and oligomers [37], with some intermediates, such as 2-furfural, 5-hydroxymethylfurfural (5-HMF) being subsequently produced [35,37]. The rate of hydrolysis is said to be diffusion controlled and thus limited by transport phenomena within the fibrous structure of biomass [44]. Therefore, the hydrolysis rate rises if the process temperature increases [45–47]. Dehydration and decarboxylation follow the hydrolysis [35,37,48]. Dehydration decreases the amount of hydroxyl groups (OH) [37]. Colloidal structures are destroyed, thus decreasing the amount of hydrophilic groups and promoting the formation of gases (mainly CO₂) [42]. Other gases such as CO, CH₄ and H₂ (in case of a catalytic process) can also be detected [45,47]. The decrease in the amount of OH groups also causes a lower O/C ratio. Decarboxylation decreases the amount of carboxyl (COOH) and carbonyl (C=O) groups, also slightly decreasing the O/C ratio of the solid product [37]. Subsequently, polymerisation and aromatization take place [35,37]. Hydrothermal carbonization is also capable of removing a part of the inorganic fraction of the biomass [42,49,50]. This can be typically observed as the ash yield lower than 100% [42,49]. Hydrothermal carbonization can also result in an increase in a specific surface area [49] and differential pore volume [51]. HTC of the digestate has significant potential due to possible improvements in terms of the subsequent dewatering [52–54]. This process partially removes organic fraction, which could also be used as a feedstock for anaerobic digestion [55–63]. The potential advantages of the use of HTC for the digestate include a decrease in the overall solid mass, sanitization of the digestate and elimination of the problems related to emissions of odours from the installation, improvements of its fuel properties.

Published literature suggests that thermal valorisation of biomass might lead to the presence of condensable compounds on the surface of the solid product. Some works focused on biochar, mention condensed tars as a potential factor relevant in terms of the hydrophobic behaviour of thermally treated solids [64,65]. Published studies indicate that volatile organic compounds, including PAH, can be produced during the carbonization process and stay within the porous structure of the material [64–67]. This claim can be extended on torrefied biomass, as some hypothesized that condensed tars could be responsible for blocking the

active oxidation sites on the particle surface [68]. Particularly, the potential formation of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) could be potentially problematic for the torrefaction process. It has been shown that especially torrefaction of poor quality woody biomass, such as wood from a discarded telephone pole, demolition wood or particleboard, may lead up to a significant increase of PCDD concentration in the torrefied product, in comparison to feedstock [69,70]. Moreover, significant amounts of phenols and furans were found in torrefaction condensates from the torrefaction of wheat straw [71]. The creation of chlorinated compounds could be attributed to the fact that chlorine can be relatively easily released in torrefaction conditions [72,73]. Typically torgas, along with these compounds, are burned in sizeable, refractory-lined combustion chambers with sufficiently long residence time. However, compounds condensed on the surface may potentially become problematic, from the environmental point of view, due to hazards related to leaching.

1.4. Objectives of this paper

To date, many articles have been published on biocoal, which included results describing many different parameters important for its use as a solid fuel. Some publications already discussed a practical reality of introducing biocoal into the market [74]. However, there is still a knowledge gap, regarding possible introduction of novel, quick and effective analytical techniques, that in the long term could both ensure compliance of the produced biocoal with various regulations and in the same time ensure frequent testing that could be a safeguard against problems caused by relatively high variability of the feedstock. This is a practical obstacle for the introduction of biocoal to the wide market. Customers would have to be assured that by purchasing a novel type of fuel, they will not become a subject of an investigation of various enforcement institutions. This can be achieved by proper quality control, targeting the following aspects:

- Compliance with various regulations (e.g., REACH)
- Performance of the fuel in the combustion systems:
 - o Certain quality of the fuel would make it possible to maintain emissions beyond certain limits (e.g., emission limits for a particular class of small scale boilers as defined in EN 303-5 [75])
 - o Certain quality of the fuel allowing to stay below emission limits that presently are not regulated, but might be in the future (e.g., formaldehyde)
 - o Load flexibility – the capability of lowering load without extinguishing of the combustion process
- Performance in the novel energy conversion systems, based on solid fuels (e.g., gasifiers)

The aim of this paper is to recommend suitable analytical techniques in order to ensure an effective QC (Quality Control). The quality control tools can be regarded as effective if they:

- enable compliance with existing regulations
- enable determination if produced solid fuel fits within the boundaries outlined by the industry's standards
- give binary (pass/fail) result, based on certain, required parameters
- enable testing in a cost-effective manner (both in terms of the equipment cost and labour intensiveness of the technique)
- enable sufficiently fast testing (i.e., it is possible to perform tests quick enough to make up for the variability of the feedstock, thus limiting losses).

This is necessary if biomass of low and highly variable quality is supposed to become more uniform and turn into a commodity, as the effect of the thermal valorisation process.

2. Standardisation, compliance issues and other market barriers for biocoal to become a fully tradable commodity

2.1. REACH registration – additional compliance requirements

The abbreviation REACH stands for Registration, Evaluation, Authorisation, and restriction of CHEMicals [76]. REACH is a pan-European control mechanism for chemicals introduced into the European market. The existence of the mechanism is based on the regulation of the European Parliament and the European Council from 2006 (EC 1907/2006) [76].

Administration of REACH registration is one of the key roles of the European Chemicals Agency (ECHA) [77]. REACH is not limited to fuels, and its scope is much broader. It has been adopted and implemented to improve the safety of customers in Europe by reducing hazards posed by different chemicals produced and imported to Europe. This is done by obtaining the knowledge necessary to ascertain the potential risks assessed with usage, handling and storage of different chemicals. By January 2016, information on up to 120,000 different substances has been collected [77]. Enforcement of the REACH provisions, according to the article 126 of the regulation, is within the responsibility area of EU member states [76]. Enforcement varies across the states and its nature can be administrative or criminal [78]. E.g., in the United Kingdom enforcement is under the responsibility of Health and Safety Executive [78], whereas in Poland, various bodies, such as State Sanitary Inspectorate, Inspectorate for Environmental Protection, State Labour Inspectorate can be involved, within their respective field of competences [78].

2.2. Situation of different solid fuels under REACH

All the information required for REACH registration relates only to the effects caused by a particular product itself [76]. It does not take into account any effects induced by its use, e.g., emissions from energy conversion processes (such as combustion).

Coal is exempt from REACH registration according to ANNEX V point 7 of REACH regulation [76] as a mineral substance occurring in nature, under the condition that it has not been chemically modified. Substances which occur in nature are defined in Article 3.39 as “naturally occurring substances as such unprocessed” or processed by Ref. [76]: manual, mechanical or gravitational means; dissolution in water; flotation; extraction with water; steam distillation; extracted from the air by any means; heating solely to remove water.

A non-chemically modified substance is defined in Article 3.40 as “a substance whose chemical structure remains unchanged, even if it has undergone a chemical process or treatment, or a physical mineralogical transformation” [76].

Pellets, briquettes, chips, log, and any other form of raw solid bio-fuels seems to fulfil the criteria set by ANNEX V of REACH regulation since they can be deemed as naturally occurring substances and they are not classified as dangerous (ANNEX V point 8 and 9 [76]). This is due to the fact that they are processed by mechanical means. Any additives have to be registered unless they are exempt (for example, Starch is exempt since it is named in ANNEX IV of REACH regulation [76]).

Charcoal is the most widely known solid fuel that is produced under elevated temperatures. It is characterised by proximate analysis, with its unique testing procedures specified in the European Standard [79]. Some details are different in comparison to the standard for solid bio-fuels, e.g., the temperature for determination of ash content is in this case, 710 °C. However, the temperature for the determination of volatile matter content is exactly the same as in the standard for solid biofuels [80] (900 °C). This gives the basis for clear comparison. There is also a strict limit for fixed carbon content, which is a minimum of 75% for charcoal and 60% for charcoal briquettes [79] (probably due to necessary additives - binders). There is no test defined for fixed carbon content and it is calculated using the results of volatile and ash content tests [79] (therefore expressed on a dry basis).

Charcoal (CAS number 16291-96-6) is registered under the EC/List number 240-383-3 as a UVCB substance (substances of unknown or variable composition, complex reaction products, or biological materials [76]) of organic origin [77]. It has been a subject of the full registration process [77].

Another form of carbonised plant material is called biochar. Since it is used as a fertiliser, it is not defined exactly the same way as charcoal. International Biochar Initiative (IBI) deems the H/C_{organic} molar ratio as a property that correlates with the degree of thermal alteration [81]. IBI sets criteria for H/C_{organic} molar ratio to be lower than 0.7 for materials that are thermochemically converted, whereas products with higher H:C_{organic} molar ratio are considered thermochemically altered, but not converted [81]. Armeccin and Gabon assessed the content of organic carbon indirectly using organic matter content and van Bremellen factor [82]. However, the value for H/C_{organic} molar ratio is arbitrary and it has been established based on the stability of biochar in the soil, which is correlated with the presence of fused aromatic rings in the material [81].

2.3. Mechanism of REACH registration

Mechanism of REACH registrations can have important implications on quality control requirements, depending on the choices made by applicants. All chemical substances to be sold in the EU in quantity of more than 1 ton per annum have to be REACH registered [76]. There are a couple of different categories that substances can be assigned to. Some products require full registration, whereas others are simply exempt from the expensive and time consuming full registration process. In order for a particular substance to be the subject of exemption, the lead registrant has to perform tests to obtain evidence that will support the claim for a particular exemption [76].

If a substance is to be produced in quantities that exceed 1 ton per year, but for the purpose of developing a new process/product, there is a special mechanism called PPORD (Product and Process Orientated Research and Development) [83]. This allows compliance to REACH and gives the possibility of performing tests on a big enough scale.

Products that do not qualify for the exemption have to perform a full suite assessment that, according to Article 44 (Title VI, Chapter 2) of the REACH regulation, is defined as a “risk-based approach” [76]. This assessment is meant to give full details on health risks involved with exposure to the tested substance as well as the potential of bio-accumulation [76]. The complexity of information depends on the amount of product introduced to the European market per year and it grows with the growing amounts of the product (as described in Annexes VII to X) [76]. For example, substances to be sold in quantities between 1 and 10 tons/annum, under a full REACH registration, need to be tested for [76]:

- a range of physicochemical properties (e.g., water solubility, self-ignition temperature, explosive properties, etc.)
- toxicological properties (skin irritation, eye irritation, mutagenicity, acute toxicity, etc.)
- ecotoxicological properties (aquatic toxicity and degradation)

On the other hand, registration of substances to be sold in quantities of 1000 tons and more (per annum) extends the ecotoxicological properties to be reported, to properties such as effects on terrestrial organisms, long-term toxicity to sedimentary organisms and long-term reproductive toxicity for birds [76].

Polymers are exempt from the full REACH registration, according to article 2(9) [76,84]. Criteria for a polymer to be exempt are as follows [76,84]:

- the amount of the polymer molecules of the same molecular mass must be less than 50% by mass of the substance
- over 50% of the mass of the substance consists of polymer molecules

A polymer molecule is defined further as a molecule that contains a sequence of at least 3 monomer units that are covalently bound to at least one other monomer unit or another reactant [76,84]. Under REACH regulations, polymers may not only be synthesized by polymerisation of monomers but also by post-modification of polymer substances, which includes “controlled polymer degradation” [84]. Obviously, degraded polymer still needs to fall into the polymer criteria to be exempted from full registration. One substance that is subjected to a very similar thermal process as biochar is roasted coffee beans, registered under the EC/List number 272-823-5 (CAS no. 68916-18-7) [77]. The substance information card states that “According to the majority of notifications provided by companies to ECHA in CLP notifications, no hazards have been classified.”

2.4. ISO standard for thermally treated biofuels - market barriers

Market introduction of torrefied biomass has been recently discussed by D. Thran et al. [74], identifying co-firing in power plants as well as the use in small and middle scale appliances as main market opportunities for biochar. Few experimental works on the explosibility data of torrefied biomass are described in the literature [85,86] and need extensive work in order to standardise the procedure. The lack of standardisation was also discussed and this was named as one of the major issues in terms of the successful introduction of Biochar into the market [31].

Recently, a draft standard for “Graded, thermally treated and densified biomass fuel” has been issued for comments [87]. This draft version of the standard is supposed to become part 8 of the set of EN/ISO 17225 standard for Solid biofuels. This standard is an important step towards making Biochar a tradable commodity. However, it seems like some small amendments could contribute towards its further improvement.

As mentioned above, the new draft is supposed to cover all thermally treated materials, which implies a wide variety of technologies. Only drying is excluded, as stated in Note: 1 of the definition of thermally treated biomass [87]. It seems a difficult task to accommodate all thermal treatment technologies into one standard, especially taking into account the fact that EN/ISO 17225 consists of separate parts dedicated to raw woody and agro biomasses, as well as separate parts dedicated to briquettes and pellets exclusively [88–94]. This standard, same as all the others from the 17225 group, names the acceptable ranges of values for basic parameters from the solid fuel point of view and states the origin of feedstock. It defines acceptable ranges for proximate and ultimate analysis results. It also defines an acceptable Net Calorific Value range, as well as parameters important from the perspective of handling of densified forms of the fuel (pellets and briquettes). The standard also sets ranges for chlorine content as well as for heavy metals, which is feedstock dependant. Ash melting behaviour is not normative but needs to be stated.

Attempts to accommodate too many different processing technologies in one standard evidently yield some problematic results. One needs just to compare the results of Net Calorific Value (as received basis) stated for the thermally treated woody biomass with typical values for wood pellets to notice the problem. Three of the six values in the draft (TW1b, TW2b, TW3b) have a requirement for minimum Net Calorific Value (as received) set at a level slightly below 17 MJ/kg, which is similar to unprocessed wood pellets as stated in EN ISO 17225-2 standard [89] or EN + pellet quality requirements [95]. This brings up the question - if the processing of the material that yields such values is anything more than drying.

Another question is brought up by the lack of any mention of grindability and hydrophobic behaviour in the standard, which would be an important piece of information for utility-scale customers. Grindability seems to be simple enough, as there is a standard value, namely Hardgrove Index [96], which allows a comparative assessment of the grindability of the solid fuel. Many published articles suggest

improvement in the grindability of torrefied material [97–101].

Hydrophobic behaviour is more problematic to assess as there is no standard test procedure for solid fuels at present. However, efforts have been made by participants of the SECTOR programme to develop such a method [102]. The development of MSDS sheets for Biocoal has been attempted, with some proposed documents, created as a part of the SECTOR program [103] and by Dutch Torrefaction Association [104].

3. Quality control tools to determine product compliance with existing standards and registrations

3.1. Established techniques of quality control for solid biofuels

Quality control of solid fuels typically is focused on its fuel-related properties. Thus, usually proximate and ultimate analysis of the fuel is performed. The proximate analysis determines the moisture content of the fuel, its ash content, respective content of volatile matter and fixed carbon. Moreover, determining the calorific value of the sample is critical. The ultimate analysis is used to determine the content of elements fundamental for fuels (C, H, N, S and O). There are existing standards that can be readily used. Moisture content can be analysed using a method outlined by EN ISO standard (EN ISO 18134) [105]. Drying takes place in the appropriate lab oven with a controlled temperature of 105 °C (± 2 °C). Mass of the tray is checked every hour until a constant mass is achieved. Constant mass is defined as the change of the mass between two consecutive measurements not exceeding 0.2% of the absolute mass of the test portion.

The content of volatile matter can be tested according to EN standard (EN15148) [80]. Crucibles covered with lids are put on a stand that is then transferred to a laboratory furnace heated up to 900 °C (± 2 °C) for 7 min (± 5 s) and subsequently placed in a desiccator to cool down before weighing. It seems prudent to note that the choice of the temperature and residence time is arbitrary, which in fact enables the determination of a generation of the volatile compound in that typical regime. It is based on the vast experience with the combustion of other solid fuels, such as coal, and gives some data for comparative analysis of different solid fuels.

Ash content of biofuels is typically tested according to EN (EN 18122) [106]. Ashing takes place at 550 °C (± 10 °C) for at least 120 min. Dishes are subsequently placed in a desiccator to be cooled down before weighing. The temperature is specific to biomass and substantially different in comparison to fossil fuels as it is typical for some types of biomass to release significant amounts of inorganic compounds in the temperatures above the threshold set in the standard [107]. There are some indications in the published literature that the release of inorganic compounds might take place in the temperatures much lower than 550 °C and take place even during the torrefaction process itself [72,108,109]. On the other hand, the temperature during the test has to be high enough to achieve ignition and complete combustion of the sample.

Test protocols for the determination of fundamental properties of solid fuels are well established. However, the situation is different regarding test protocols for compliance with REACH registration. The preferred method to determine if a product falls under the definition of polymer, according to ECHA, is the determination of molecular weight distribution with gel permeation chromatography [84]. However, it seems reasonable to suspect that Quality Control would require a simpler, more rapid and more cost-effective technique to analyse different samples of the product from commercial-scale production frequently.

Yan et al. used the Van Soest method to perform fibre analysis by determining the content of cellulose, hemicellulose and lignin in the product [110]. As mentioned before, cellulose, hemicellulose and lignin vary in terms of their degree of polymerisation. Also, digestion might not be preferable as it is a slow process and, therefore, does not fulfil the requirement of rapid analysis.

3.2. Fourier transform infra-red

FTIR analysis is a technique used in the analysis of biomass and pyrolysis products, as indicated by Kan et al. [111]. Xu et al. [112] reviewed the use of infrared techniques to characterise lignocellulosic biomass, as an opposite to labour intensive digestion techniques. The ability of ATR to provide spectra free of the influence of background water (humidity of the air) was mentioned as one of the advantages of this technique [111,112].

ATR (Attenuated Total Reflectance) makes use of a difference in the refractive index of the sampling crystal and refractive index of the sample. The infrared beam enters the sampling crystal at an angle greater than a critical angle of the crystal [113]. As the light bounces off the inside surface of the crystal, a small amount of radiation, called evanescent wave, penetrates the sample up to a certain depth [113].

FTIR ATR seems to be a potential technique of interest due to its capability to perform rapid testing, with a typical test for one sample taking just a couple of minutes. ATR obtains as a result absorbance of the sample for a selected spectral range of wavenumbers, which depends on the type of crystal used and range defined in experimental settings and Refractive Index of the tested sample [113]. Typically software can use its correction algorithm to obtain peak positions more closely matching transmission data from its spectral library since positions of peaks collected using the absorbance of the sample might not necessarily match positions of peaks collected using transmittance (by another type of FTIR analysers) [113,114]. Most organic materials have refractive indices within a range of 1.3 up to 1.7 [113].

Bui et al. used FTIR along with acid hydrolysis to characterise solids after another thermochemical conversion process of biomass called liquefaction [115]. Solid residues, obtained after this process, were hydrolysed in sulfuric acid to perform HPLC (High-Performance Liquid Chromatography) analysis further to obtain the content of simple sugars that allowed determination of cellulose and hemicellulose content [115]. FTIR was used, in conjunction with wet chemical methods, for the quantitative determination of lignin content [115]. Brewer et al. used FTIR as a qualitative method to assess the “progress of the pyrolysis reaction” [116]. It was also determined that chars contain little functional groups present in lignocellulosic materials [116].

Fabiya and Oguleny investigated the thermal treatment of wood as a material as an alternative to chemical treatment. Temperatures used (160 °C–200 °C) were a bit lower than the typical torrefaction range. ATR-FTIR was used as one of the techniques to characterise treated wood. The study confirmed that under the conditions mentioned above Relative Crystallinity index of Cellulose increases along with the Relative Lignin Content as a consequence of the treatment. The study concluded this type of thermal treatment promising due to improvements in dimensional stability and stiffness of heat-treated wood [117]. Poletto and Zatera [118] used the FTIR technique along with TGA to characterise Klason lignins from *Eucalyptus grandis* and *Pinus taeda*.

Wilk et al. [119]. studied the effect of Torrefaction on woody biomass and sewage sludge using FTIR. The decrease in OH group peak was observed with increasing temperature of torrefaction. Torrefaction effect on the chemical structure of sewage sludge was assessed as much lower than in the case of woody biomass.

Some comparisons between the Raman spectroscopy and FTIR techniques, state that the spectra generated by the latter are more intensive [120,121]. Moreover, the former is very much sensitive with respect to the presence of water [120,121]. FTIR is an important technique for the analysis of the structure of biomass and this can also be used for analysing the change of the aforementioned structures, which may occur because of certain physical and chemical treatments [122–126]. Lignin/cellulose content was calculated using the ratio of the peak areas in the bands ranging from 1500 to 900 cm^{-1} [127]. Tropical hardwoods can be classified using the FTIR technique [128]. FTIR technique was shown to identify the structure of lignin [126,129–132].

Garrido et al. [133] observed no significant changes in the chemical structure of Flexible polyurethane form briquettes (FPUF) during the briquetting process. The FTIR spectra were acquired in the range of 4000–500 cm^{-1} . The wavenumbers (1013, 1085 cm^{-1}) at the absorption bands signified the stretching vibration of the C–O–C group. The peak at 3367 cm^{-1} , caused by the stretching vibration of the NH group, was also observed in the IR spectra and this was also contributed because of urethane bond present in FPUF. Another stretching because of the C–O–C bond at 1107 cm^{-1} was observed signifying the urethane bond present in FPUF which got fractured while homogenous and heterogeneous briquetting [133]. The temperature of 180 °C and pressure of 35 MPa is sufficient to break the urethane bond present in FPUF, leading to the mobility of long polymeric change, which resulted in the bonding of different materials.

Blesa et al. [134] have synthesized fuel briquettes with carbonaceous materials with the help of the binder and calcium additives have been added in order to decrease sulphur emissions during combustion. It was also revealed that these briquettes were waterproof. The FTIR spectra were obtained in the range 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . When the temperature of the blend of humates with calcium hydroxide was increased, it was observed that the broadband at 3400 cm^{-1} decreases, and it is because of the release of hydroxyl groups. It was revealed that Micro FTIR spectroscopy was an effective technique to follow the evolution of the structural changes, which take place between humates, calcium hydroxide and the carbonised materials at various temperatures.

Blesa et al. [135] have synthesized smokeless fuel briquettes using low-rank coal and olive stone as biomass with a binder as molasses. The FTIR spectroscopy was used to study the effect of curing temperature on these briquettes. The curing led to a decrease in the hydrogen bonds as well as aliphatic structures and methoxy groups, while carboxylic groups increased during curing because of oxidation. Moreover, the briquettes cured at 200 °C for 2 h revealed the highest mechanical strength. The curing also led to the production of waterproof briquettes. The FTIR spectroscopy ranges between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1} . It helped in finding structural changes produced during the curing process. The briquettes have been prepared with molasses as a binder and investigated by varying the temperature from 150 to 200 °C for 4 h. The hydroxyl groups appeared at 3400 cm^{-1} , with a relatively broad peak. The height of the peak decreased with increasing treatment temperature. The curing, lasting more than 2 h, did not produce any relevant molecular changes. Moreover, the treatment at 200 °C (4 h) did not produce any additional stabilisation. The briquettes cured at 200 °C for 2 h showed the best mechanical resistance and water repellence. Some of the FTIR bands/peak values, potentially useful for the Quality Control of thermally treated biofuels, are presented in Table 1.

3.3. Near Infra-Red spectroscopy

NIR technique is considered useful in the determination of the chemical structure of solid and liquid fuels. It is one of the speedy characterisation techniques with a simple methodology [146–149]. The infrared region consists of three regions according to wavelength range: near-infrared (780–2500 nm), mid-infrared (2500–25000 nm), and far-infrared (25000–1000000 nm) [146–149]. In general, two types of spectrophotometers are in use, with respect to wavelength selection, namely discrete wavelength and whole spectrum. Discrete wavelengths photometers are simpler as only a few wavelengths are used to irradiate samples. Thus, their application is limited to materials absorbing in specific spectral zones [146–149]. Detection in NIR spectroscopy uses devices comprising semiconductors (PbS or InGaAs). In multi-channel detectors, several detection elements are arranged in rows (diode arrays) or planes (Charged Coupled Devices CCDs) in order to record many wavelengths at once, so as to increase the speed at which spectral information can be acquired [146–149].

Table 1

FTIR bands/peak values, identified in literature sources studying various aspects of biomass (Ref. – Reference).

Wavenumber, cm^{-1}	Peak assignment	Corresponding compound(s)/ polymer(s)	Comments	Ref.	
875	–	Glycosidic linkage	Hemicellulose	–	[122, 136]
–	895	Glycosidic bonds symmetric ring-stretching mode	Cellulose	Determination performed for raw, de-waxed, and de-lignified pine wood. Peak attributed to polysaccharides.	[137, 138]
–	898	β -glucose bond ($\text{C}_1\text{--O--C}_4$)	Cellulose	CEAL (reference cellulose)	[139]
987	995	C–O valence vibration	Cellulose	Spruce wood and spruce holo-cellulose, before and after milling	[140]
1214	1215	C–C + C–O stretch	Lignin	Kraft Lignin in both softwood and hardwood	[141]
1200	–	O–H bending	Cellulose, Hemicellulose	–	[136]
1682	–	C=O stretching	Lignin	Kraft Lignin in hardwood	[141]
1704	–	–	–	Kraft Lignin in softwood	[141]
2840	2937	C–H stretching	Lignin	Kraft Lignin in hardwood	[141]
2840	2934	–	–	Kraft Lignin in softwood	[141]
897	–	$\text{C}_1\text{--H}$ deformation of glucose ring	Cellulose	Could be used for determination of the cellulose crystallinity index	[117]
1421	–	C–H in-plane deformation, with aromatic skeletal vibrations	Lignin	–	–
1506	1507	Aromatic skeletal vibration $\text{C}\equiv\text{C}$	Lignin (guaiacyl and syringyl)	Could be used for the determination of relative (to cellulose) lignin content, being divided by the height of the peak for 897 cm^{-1}	[117]
1507	–	C=C aromatic symmetrical stretching	Lignin	Determination performed for raw, de-waxed and de-lignified pine wood	[138]
–	1510	–	Lignin	Cell wall of <i>Zinnia elegans</i>	[142]
720	1450	Methylene group	Long aliphatic chains.	Briquettes synthesized from torrefied SPF (Spruce, Pine, Fir), coal with binders, such as coal tar, coal tar sludge, paraffin, and molasses.	[143]
3386	–	N–H Group	Polyurethane	(a) FPUF	[133]
1107	–	C–O–C bond	–	(Flexible polyurethane foam)	–
1720	–	C=O Group	–	(b) Viscoelastic Memory foam (VMF) with FPUF	–
				(c) Latex foam with FPUF.	–

(continued on next page)

Table 1 (continued)

Wavenumber, cm^{-1}	Peak assignment	Corresponding compound(s)/ polymer(s)	Comments	Ref.	
–	1734	Non-conjugated carboxyl group C(=O) OH	Lignin	Effluent treatment waste after kraft pulping of Eucalyptus	[139]
1730	–	C=O stretching of p-coumaric acids of lignin	Lignin	Determination performed for raw, de-waxed and de-lignified pine wood	[138]
1730	–	C=O stretching of acetyl groups	Hemicellulose		
1730	–	C=O stretching vibration	Hemicellulose	Characteristic to carbonyl band due to the presence of hemicellulose in Sugarcane Bagasse	[144]
1732	–	C=O unconjugated stretching	Xylans (Hemicellulose)	Hemp fibres	[137]
–	1737	C=O stretching of carboxylic acid	Hemicellulose	Alkali treated Indian grass (<i>Poaceae</i> family)	[145]
–	1738	–	Hemicellulose	The cell wall of <i>Zinnia elegans</i>	[142]
2860	2940	Aliphatic C–H structure	Humates	Briquettes with the blend of humates with calcium hydroxide	[134]
1600	–	Aromatic ring stretching			
1578	–	Stretching of C=O bond of carboxylates			
1240	–	C–O aryl group	Lignin	Hemp fibres	[137]
1254	–	C–O aryl group	Lignin	Alkali treated Indian grass (<i>Poaceae</i> family)	[145]
–	1255	C–O aryl group	Lignin	Determination performed for raw, de-waxed and de-lignified pine wood	[138]

The use of NIR analytical techniques has both advantages and disadvantages. Among the advantages, one can count [147–149]:

- The fact that the technique is non-invasive and non-destructive.
- Minimal sample pre-treatment requirements (in some of the cases no pre-treatment needed)
- Rapid measurement, resulting in a high throughput of a single analytical device (many samples per day).
- No need for reagents.
- Easy maintenance of the analytical equipment due to no moving parts.

Following disadvantages can be stated [147–149]:

- It is not a selective technique.
- Insufficient amount of robust models connecting the results of NIR analysis with specific target parameters.
- The need for reference methods, in order to enable calibration of the models, that translate the results, obtained by NIR, into the values of target parameters.
- Relatively low sensitivity, limiting the use of the technique only to the determination of major components.

- Lack of robust calibration methodology for solid fuel analysis, using NIR.

Near Infra-Red (NIR) Spectroscopy is getting attention recently as an economical and fast technique, which permits simultaneous assessment of many parameters for biomass composition [147,150]. NIR is a modern spectroscopic technique, which finds application in many areas, including agriculture, food, medicine, environment, etc. [151]. This technique is simple as well as non-destructive. NIR spectroscopy can give valuable information about carbon, hydrogen, oxygen, volatile matter, fixed carbon and energy contents of various biomasses. Lestander et al. stated in his study that a combination of NIR spectrometry with multivariate calibration modelling can lead to developing a rapid method for characterizing thermally treated biomass, thus reducing the requirement of costly wet chemical analysing methods [152]. Covalent C–O, C=O and C=C bonds are found in torrefied biomass. Moreover, in addition to O–H and C–H bonds, these vibrations interfere with near-infrared radiation [153], i.e., overtones from fundamental vibrations in the IR region. Hence overtone vibrations in the IR give valuable chemical information about the state of carbonised biomass [154]. The simplicity of the sample preparation cause NIR, to be deemed as a potential quality control technique for biomass conversion processes, such as torrefaction [153,154].

Kelley et al. [155] investigated the typical NIR spectra of wood. The major vibrations were in the range of 400–500 nm including the yellow-brown colour of wood due to lignin and extractives. The first overtone of cellulose and hemicellulose hydroxyl is found between 400 and 1600 nm and moreover, the interaction between the water and carbohydrate hydroxyl is between 1890 and 2020 nm. Another strong vibration is seen between 2020 and 2250 nm confirming the cellulose hydroxyl vibration.

He et al. studied the NIR in the spectral range of 12500–3600 cm^{-1} with a resolution of 8 cm^{-1} [156]. The two highest peaks were observed in the wavenumber at 6900 cm^{-1} , and 5150 cm^{-1} and these are because of the absorption of water. O–H deformation and the combination band of O–H stretching are giving a peak at 5150 cm^{-1} [157]. The spectra of the two kinds of wood can be distinguished between the wavenumbers 7300 cm^{-1} and 6800 cm^{-1} and, moreover, also in between 6250 cm^{-1} and 4200 cm^{-1} . The second and third overtones are giving the band between 12500 and 7500 cm^{-1} [158]. Moreover, the NIR model of hot water soluble extracted content was also developed and in the spectra, the absorbance band in the region of 7211 cm^{-1} is arising because C–H stretching and deformation of CH_3 at 7353 cm^{-1} and 7194 cm^{-1} . C–H stretching and C=O group frequencies of carbohydrates are exhibited at 4545 cm^{-1} . The best pentosan prediction model was established with the wave number in the regions 7502.1–5446.3 cm^{-1} and 4601.6–4246.7 cm^{-1} . The spectral regions in the range 6000 cm^{-1} and 4246 cm^{-1} are related to C–H stretching of ROHCH_3 (5885 cm^{-1} and 5773 cm^{-1}), $-\text{C}=\text{OCH}_3$ (5960 cm^{-1} and 5898 cm^{-1}), $\text{R}-\text{OHCH}_3$ (5880 cm^{-1} and 5770 cm^{-1}), and C–H stretching (1st overtone) of CH_2 (5787 cm^{-1}), as well as C–H stretching and C=O group frequencies (4545 cm^{-1}) of carbohydrates, and O–H stretching and C–H stretching group frequencies (4412 cm^{-1}) of cellulose (4405 cm^{-1}). Moreover, the absorbance band in the region of 7168 cm^{-1} is present because of the group frequencies of $-\text{CH}_2$. Hence the important structure of pentosan can be analysed with the help of NIR spectroscopy. The prediction model for the cellulose was developed in the wavenumber regions of 7502.1–4297.7 cm^{-1} . The region 5685 and 4300 cm^{-1} is related with C–H stretching 1st overtone (5612 cm^{-1}) of CH_2 (1st overtone) (5262 cm^{-1}) and O–H stretching (6025 cm^{-1} , 5657 cm^{-1} and 4405 cm^{-1}) and C–O stretching group frequencies of cellulose (6024 cm^{-1} , 5667 cm^{-1} and 4405 cm^{-1}) and also C–H stretching and C=O group frequencies (4545 cm^{-1}) of carbohydrates. Therefore, the main chemical structure of cellulose can be identified using the NIR technique.

Rambo et al. reported that the significant absorption bands in the

NIR spectra are found at 1450/1470 nm, 2090 nm and 1920 nm [159]. The bands in the range of 1450–1470 nm are present because of the first overtone of the O–H groups with H bonds of intermediate strength [160]. The less intense band in the range of 1170–1270 nm are appearing because of C–H stretch 2nd overtone from lignin. C–H stretching in the aromatic structure is also confirmed at 1672 nm and bands in the region of 2150–2460 nm confirm the presence of lignin [161].

Rambo et al. have applied partial least square (PLS) regression for the banana, coffee and coconut samples in order to analyse various chemical constituents [162]. A total of 104 samples of banana, 101 samples of coffee and 28 samples of coconut residues was collected. The VIS-NIR spectra in the range of 400–2500 nm were analysed. The bands at 460 nm and at 670 nm confirmed the presence of lignin and chlorophyll structure, respectively. At 2090 nm, a combination band of O–H of carbohydrates was found. The study showed that NIR could be successfully used for the rapid analysis of many samples of different biogenic materials.

Yue et al. used NIRS technology for the quantitative analysis of biochar [163]. Biochar was produced using low-temperature pyrolysis through anaerobic conditions of organic material and 163 samples were analysed. The study determined that NIR can give reasonably good predictions of fixed carbon and volatile content, with Partial Least Square empirical model [163]. The whole spectra range of biochar samples can be divided into three sections in the NIRS regions: 10000–7000 cm^{-1} , 7000–5000 cm^{-1} and 5000–3000 cm^{-1} . The FC and VM of all samples of biochar can generate NIR information in the range of 7000–3800 cm^{-1} [152,164]. As the ash is an inorganic compound so it does not have a characterised spectra in NIRS but still exhibits a correlation with organic components, which can be used for the quantitative analysis for the ash content in samples [165]. The spectral band for ash in biochar samples is in the range of 10000–5000 cm^{-1} [163]. Some of the NIR bands/peak values, potentially useful for the Quality Control of thermally treated biofuels, are presented in Table 2.

3.4. Nuclear Magnetic Resonance spectroscopy

NMR technique is used for detailed analyses of the structure and features of the organic compounds. It is a non-destructive method that is based on bringing the nuclei in resonance with the external magnetic field and determining the different amounts of energy for the shielded and de-shielded environment. The presence of a more electronegative atom near the nuclei attracts electrons towards it and creates a de-shielded environment for the neighbour nuclei. It then requires more external energy to bring the nuclei in resonance with the external magnetic field. However, if there are atoms with less electron affinity, then there will be a shielded environment for the neighbour nuclei requiring less external energy to bring it in resonance with the external magnetic field. NMR spectroscopy helps to draw the spectrum of energy needed for the shielded and de-shielded nuclei to bring them into resonance. NMR is very much suitable for analysing complex chemical structures such as plant cell walls etc. [169]. Traditional Solid-state NMR such as ^{13}C cross polymerisation magic angle spinning (CP/MAS) of biomass is having the disadvantage of poor resolution and overlapping resonance [170] but it has advantages like Solid-state NMR is a non-destructive technique, not limited by sample insolubility and moreover, it gives the detailed structure information [171]. The solid-state ^{13}C NMR has been widely used to examine the structure of char and many other aromatic compounds [116,172–175].

The results of the qualitative analysis have been confirmed by quantitative analysis using NMR spectroscopy (Nuclear Magnetic Resonance) [116]. Sharma et al. also used an FTIR technique, along with NMR to characterise char from pyrolysis of lignin [176]. They reported an increase of aromatic hydrogen and loss of oxygen-containing functional groups between 400 °C and 500 °C [176]. Similar defunctionalisation was observed in chars from pyrolysis of cellulose above 330 °C by

Table 2

NIR bands/peak values, identified in literature sources studying various aspects of biomass (Ref. – Reference).

Wavenumber, nm	Peak assignment	Corresponding compound(s)/ polymer(s)	Comments	Ref.	
2252	–	Cellulose	Stepwise forward	[166]	
1754	CH ₂	Lignin	multiple linear regression model for the description of degradation of foliage.	[167]	
1438	CH ₂		Stepwise multiple linear regression model for determination of lignin, holocellulose, and organic solvent extractives in fresh leaf, litterfall, and organic material on the forest floor		
1708	CH ₃		Partial least square model for determination of α -Cellulose in woody biomass.		[168]
1960	C=O stretch bond		Lignin		This is confirming the first and second overtone of the lignin aromatic and aliphatic carbon/hydrogen vibrations giving the information of the chemical structure present in the material, but the overlapping limits the information.
1400	2500	–	α -Cellulose	[168]	
1635	1825	Aromatic C–H stretching	Lignin	[155]	
1075	1250	Aliphatic C–H stretching			
6900	–	The 1st overtone of O–H structure	Softwood	[156]	
5200	–	O–H and $-\text{C}=\text{O}$	Hardwood		
1920	–	O–H stretching from water	Coconut residues	[159]	
2090	–				

(continued on next page)

Table 2 (continued)

Wavenumber, nm	Peak assignment	Corresponding compound(s)/ polymer(s)	Comments	Ref.
	O–H stretching from polysaccharides		lignocellulose constituents: Glucose (Glu), total lignin (TL), and total sugar (TS); of coconut husk samples through their dried spectra and the wet spectra gave useful reasons for sugar models but not for lignins.	

Boon et al. [177].

Park et al. used NMR as a technique for comparative characterisation of torrefied biomass along with a comparative TGA study [178]. Using solid-state NMR spectroscopy, it was proven that torrefaction leads to increase in the aromaticity from 36 to 60%. NMR spectra of both untorrefied (raw) and torrefied biomass were examined. Three torrefied samples having different treatment temperature were synthesized, namely lightly torrefied biomass (TA) at 270 °C, moderately torrefied biomass (TB) at 300 °C and severely torrefied biomass (TC) at 330 °C. Fu et al. have revealed that solid-state NMR is one of the most effective techniques for the quantification of lignin in biomass [179]. In his study on the treatment of Kenaf, the ¹³CP/MAS spectrum of Kenaf biomass revealed the presence of an aromatic signal at 142–157 ppm, which was observed because of the presence of lignin [179]. In the untreated biomass samples of Kenaf, the lignin content was found to be 32% [179]. Samuel et al. successfully used NMR to determine the influence of the dilute acid pretreatment, performed at 190 °C using sulfuric acid (50 g per kg of switchgrass), on the ultrastructure of cellulose the material [180]. The study determined that such pre-treatment can increase the crystallinity index of cellulose by 18% [180].

4. Discussion and conclusions

Biocoal is a thermally pre-treated solid fuel that is supposed to be more uniform than the initial feedstock. This way, through torrefaction, low-quality fuel can become a tradable commodity, with improved properties [25,42]. This ideal can be fully realised only up to a certain extent. The choice of optimum quality control technique should take this potential variability into account. Probably non-uniform feedstock would require quality control, every time the quality of the feedstock changes dramatically. Due to this anticipated frequency of testing, analytical techniques for QC of Biocoal should not only give reliable results, but also be fast, both in terms of the test itself and the time necessary for sample preparation.

The preferable analytical technique would be quantitative (NMR) as the interpretation of such a result is more straightforward, and a significant amount of knowledge could be gained, with little need for additional tests. However, the price of the equipment, as well as labour intensive sample preparation, introduces some complications as the amount of tests, possible to do during a single day might not be able to meet the needs of the industrial environment. On the other hand, qualitative techniques, such as FTIR or NIR, could also be a sensible solution, when prior calibration takes place. This one would typically involve the determination of the peaks in the bandwidth, within the range of the used spectroscopy technique, that correlates well with the properties of the fuel, that is of typical concern. In terms of REACH compliance, this would be the change in the content of different

polymers, as detailed in paragraph 2. From the practical perspective, having the effective mean of quality control that could guarantee the compliance with REACH and in the same time provide additional useful information on the product would be useful from the point of view of both investors and consumers, as it could add some assurance, regarding the use of the biocoal (as a commercial product and a commodity). This in turn could be important step towards wider introduction of biocoal into the markets. Any solid fuel is ultimately used for other energy conversion processes (predominantly combustion). Therefore, it would be useful if some peaks, corresponding to established parameters for solid fuels, were determined. This is because often performance of the fuel in a particular end-use process can be assessed by using traditionally established results of proximate and ultimate analyses. As shown in Table 3, stoichiometry is extremely important in combustion [181,182], whereas the content of N and S is important in terms of respective emissions of NO_x and SO_x [183–190]. For the fast pyrolysis processes, the O/C ratio is significant and has a profound influence on the quality of the obtained bio-oil [191,192].

Moreover, results of proximate and ultimate analyses, with special emphasis on the result of the calorific value of the fuel, are the values that are widely recognized parameters in terms of various certifications and standards. An extensive amount of data is needed for various materials in order to make qualitative analytical techniques feasible, form that point of view. To some extent, it has already been done, as shown by this manuscript.

To some extent novel techniques can give a lot of valuable information, which could be either supplementary or to some extent, replace the existing methods, as shown in Table 3. Knowledge about the presence of the particular functional groups and qualitative assessment of their abundance might not necessarily be a straight predictor of performance. However, it is well known that the content of the polymers present in biomass (cellulose, hemicellulose and lignins) plays a significant role in pyrolysis and combustion (see Table 3). This might not be enough for gaining in-depth knowledge of the energy conversion process that ultimately uses solid biofuel. Nonetheless, this might be enough for quality control, especially taking into account the rapid character of these tests. In the beginning, one would need to perform extensive suite of tests in order to determine performance of the biocoal of particular origin (feedstock, torrefaction temperature and residence time) in the specific end-use process (pyrolysis/gasification/combustion), including detailed fibre analysis as well as analysis of functional groups in order to find groups giving some correlation with performance of the end-use process (Fig. 1 – route A). One could build on existing knowledge by focusing the search on functional groups reported so far in the literature taking into account the reported connection between the abundance of a particular polymer and the abundance of a certain functional group. Following with establishing of the relationship between the abundance of particular functional group(s) and the performance of the fuel in a certain end-use process would reduce the necessary amount of work (Fig. 1 – route B). This would limit the need for quantification of the content of the aforementioned polymers by time-consuming “wet chemistry” methods. Understanding the relationship between the content of certain functional group(s) in an end-use process would subsequently allow setting minimum and maximum levels of the content of these groups in the particular fuel. Using that could consequently allow using relative sizes of certain peaks as indicators for quality control purposes (Fig. 1 – route C), especially in-house QC (see Fig. 2). The use of published data should be treated with caution and preferably relevance of a particular peak should be confirmed by more than one source as some peaks might overlap. One such example is shown in Table 1, where C=O stretching appearing at approx. 1730 cm⁻¹ for FTIR is attributed by several authors both to lignin and hemicellulose [137–139,144,145]. This issue could be mitigated by not focusing on a single peak but instead finding a couple of peaks to be used as performance indicators. Although using peaks exclusively from one spectrum would be sensible from the cost efficiency perspective, the use of peaks from both FTIR and

Table 3

The advantages of characterizing the Biocoal fuel characteristics and relevant associated parameters.

Characteristics/analysis	Analytical techniques/methods of determination	Advantages, disadvantages and possible use of information
Proximate analysis	<ul style="list-style-type: none"> Gravimetric methods Bomb calorimetry 	<ul style="list-style-type: none"> Possible to perform with only basic laboratory equipment (balance and furnace) Cheap Results necessary to perform mass and energy balance of combustion Allow simple determination of mass yield of biocoal by an indirect method [193] Time-consuming Allow calculation of the stoichiometric amount of oxygen/air [181,182] Allow estimation of the change of NO_x emissions ("fuel NO_x") and SO_x depending on the used fuel ** [183–190] Parameters necessary for ATEX assessment and risk prevention (fire and explosion safety) [194] Assessment of reactivity [33,85,195–197] Knowledge about ignition and flame propagation [34,197–199] Time-consuming
Ultimate analysis	<ul style="list-style-type: none"> Dedicated (CHNS*) analysers 	<ul style="list-style-type: none"> Allows determination of ash composition Allows estimation of slagging/sintering/fouling behaviour of a particular fuel in combustion or gasification [43,200–205] Allows to estimate the severity of high-temperature corrosion in boilers [206,207] Time-consuming (especially AAS due to the use of different lamp for each element) Characterisation of solid fuel for combustion [119,208–210]: <ul style="list-style-type: none"> Kinetics Ignition Characterisation of solid fuel for pyrolysis [138,208,211]: <ul style="list-style-type: none"> Kinetics Reactivity
Fire and explosion characteristics	<ul style="list-style-type: none"> 20 L or 1 m³ spherical vessel Hartmann apparatus Layer Ignition Temperature Apparatus Self-Ignition (in volume) Temperature apparatus Goldberg-Greenwald apparatus 	<ul style="list-style-type: none"> Rapid characterisation (not NMR) Easy sample preparation (not NMR) Qualitative results (not NMR) Possible to use for assessment of compliance with REACH regulations Useful for characterisation for pyrolysis *** [17,18,138]: <ul style="list-style-type: none"> Kinetics Oil yield
Ash (oxide) analysis	<ul style="list-style-type: none"> Atomic Absorption Spectroscopy (AAS) Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) Flame Emission Spectrometry (FES) 	
Thermogravimetry (TGA,DTA)	<ul style="list-style-type: none"> TGA/DTA 	
Functional groups	<ul style="list-style-type: none"> Fourier Transform Infra-Red spectroscopy (FTIR) Near Infra-Red spectroscopy (NIR) Nuclear Magnetic Resonance (NMR) 	

Table 3 (continued)

Characteristics/analysis	Analytical techniques/methods of determination	Advantages, disadvantages and possible use of information
		<ul style="list-style-type: none"> Oil composition Useful for characterisation for combustion *** [23,24,212]: <ul style="list-style-type: none"> Kinetics Emissions Useful for characterisation for densification (pelletizing, briquetting, etc.) *** [16,213]

* - not all analysers allow determination of S content.

** - requires information on fuel N/S conversion to NO_x/SO_x.

*** - indirectly, as certain functional groups might be used as an indicator of changes in the content of particular polymers between feedstock and biocoal.

NIR spectra could positively influence the reliability of QC.

Last, but not the least cost of the equipment should be taken into the account, along with the cost of its maintenance, as this would be the key cost of the laboratory, thus influencing the feasibility of the QC overall. Qualitative assessment of the potential suitability of various analytical techniques for QC of Biocoal is given in Table 4.

Table 4 shows both some advantages and disadvantages of the novel analytical techniques. Indeed, the fact that FTIR and NIR can only give qualitative results is a disadvantage as additional research needs to be initially performed in order to set the boundaries for specific peaks, which could subsequently serve as an indicator of the quality of the product. Any quality control only gives "binary" results – i.e., tested material can either conform with the set standard or not, therefore boundaries defined for selected peaks could most certainly serve this purpose, thus being suitable as a quality control tool. However, it is possible that separate boundaries would need to be set for biocoal, produced from different feedstocks. Here NMR has a clear advantage. However, it has some serious disadvantages as well, as sample preparation is time-consuming, and current prices would make such a quality control lab very costly. It seems better to use NMR as an auxiliary technique that could help to set the aforementioned boundaries for fast and cheap techniques, such as FTIR and NIR.

Ability to give the result quickly, quick and straightforward sample preparation and relatively low cost of the analytical equipment could definitely be considered as the advantages of FTIR and NIR. This makes those two techniques particularly useful for in-house QC for biocoal production plants when the result is needed fast to minimize the losses due to protracted production of the fuel not conforming to standards.

Overall it can be concluded that:

- Techniques giving qualitative results seem overall sufficient for the purpose of quality control of the solid fuels
- Rapid testing techniques, such as FTIR ATR or NIR might prove feasible for quality control of solid biofuels, such as Biocoal, especially for in-house QC
- There is a need for more research to establish sufficient data covering all aspects for its safe utilization and in order to establish a relationship that would allow to quantitatively determine the values that could be related to results obtained with qualitative methods. Traditional fibre analysis seems to be suitable as well as some novel techniques, such as NMR.

Further research is needed, in order to establish a novel, qualitative, rapid testing analytical techniques, such as FTIR ATR or NIR, as QC techniques for Biocoal, most of the work being the identification of particular wavenumbers/bandwidths relevant for the properties of the solid fuel. It would be even better if correlations between such characteristic wavenumbers/bandwidths and performance of the solid fuels in

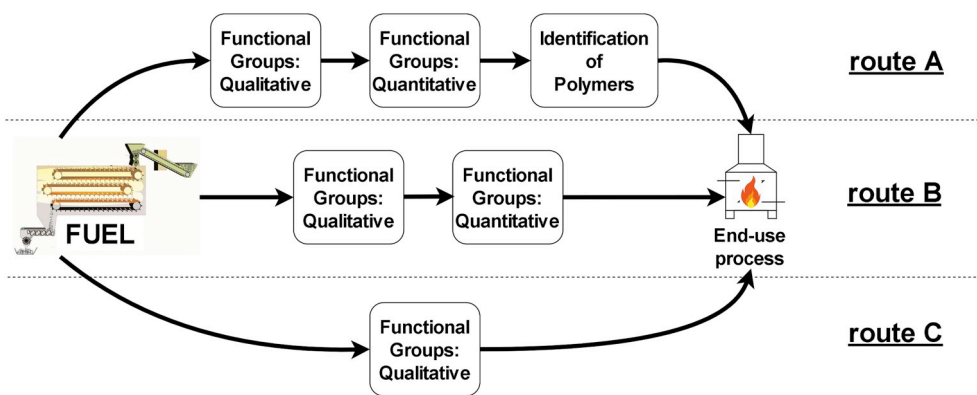


Fig. 1. Correlations that could be used for biocoal QC purposes.

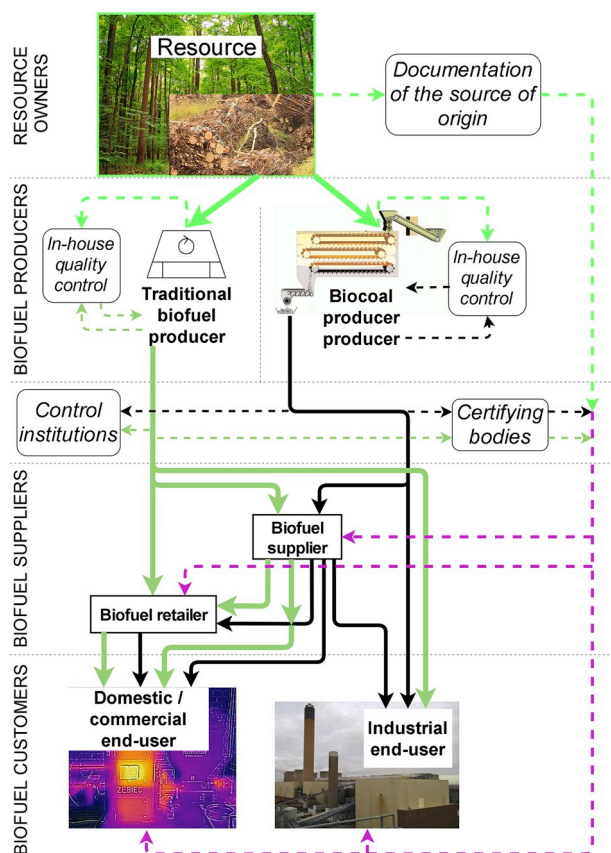


Fig. 2. The QC/QA and compliance to regulations in a supply chain – comparison of “traditional” solid biofuels (e.g., wood pellets) and biocoal. Flows of stock (solid lines), sample and information (dashed lines). Extended version, based on EN 15234 [214] (light green – feedstock; dark green – “traditional” solid biofuel; black – biocoal; purple – public information). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

subsequent energy conversion processes are established. Moreover, it seems sensible to note that the dissemination of knowledge is critical. Widely renowned databases for solid biofuels, such as Phyllis [215], should be expanded in order to include the aforementioned spectral characteristics.

Funding

Support of the subsidy no. 8201003902 of Wroclaw University of

Table 4

Qualitative assessment of various novel Quality Control analytical methods, potentially suitable for Biocoal, in comparison to standard methods for solid biofuels (qualitative rating visualised by the number of asterisks *).

	Standard methods	FTIR	NIR	NMR
Quantification	QNT	QLT	QLT	QNT
Equipment cost	*	***	***	*****
Sample preparation (labour intensiveness)	***	**	*	*****
Analysis time	*****	*	*	***
Abundance of literature data	*****	***	**	**

QNT – quantitative method (standalone); QLT – qualitative method (standalone).

Science and Technology is gratefully acknowledged. Support provided by Shaheed Bhagat Singh State Technical Campus is gratefully acknowledged.

References

- [1] World Carbon dioxide emissions from consumption of energy - energy (n.d.), http://www.indexmundi.com/world/carbon_dioxide_emissions_from_consumption_of_energy.html. accessed June 4, 2016.
- [2] European Parliament, Directive 2009/28/EC of the European parliament and of the Council of 23 April 2009, Off. J. Eur. Union 140 (2009) 16–62, <https://doi.org/10.3000/17252555.L.2009.140.eng>.
- [3] European Commission, Renewable energy progress report, Rep. Comm. Eur. Parliam. Counc. Eur. Econ. Soc. Comm. Reg. 293 (2015) 16, <https://doi.org/10.1017/CBO9781107415324.004>.
- [4] R. Sims, The Brilliance of Bioenergy: in Business and Practice, Earthscan Publications Ltd., 2002.
- [5] D.L. Klass, Biomass for Renewable Energy, Fuels, and Chemicals, Academic Press, 1998.
- [6] J. Richardson, R. Björheden, P. Hakkila, A.T. Lowe, C.T. Smith, Bioenergy from Sustainable Forestry, Springer, 2002.
- [7] G.-J. Nabuurs, M. Lindner, P.J. Verkerk, K. Gunia, P. Deda, R. Michalak, G. Grassi, First signs of carbon sink saturation in European forest biomass, Nat. Clim. Change 3 (2013) 792–796, <https://doi.org/10.1038/nclimate1853>.
- [8] Alan Simson, European forests absorbing less CO2 - time for a rethink?, Ecologist. http://www.theecologist.org/blogs_and_comments/commentators/othe_r_comments/2147297/european_forests_absorbing_less_co2_time_for_a_rethink.html, 2013 accessed September 30, 2019.
- [9] R.W. Gray, F. Seijo, Forest Sustainability: Bioenergy Breaks and Barriers, Biomass Mag., 2013. <http://biomassmagazine.com/articles/8949/forest-sustainability-bioenergy-breaks-and-barriers>. accessed September 30, 2019.
- [10] J.A. Gonzalez-Perez, F.J. Gonzalez-Vila, G. Almendros, H. Knicker, The effect of fire on soil organic matter - a review, Environ. Int. 30 (2004) 855–870, <https://doi.org/10.1016/j.envint.2004.02.003>.
- [11] J.M. Dinwoodie, Timber; its Nature and Behaviour, second ed., Routledge, 2000.
- [12] A. Anca-Couce, Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis, Prog. Energy Combust. Sci. 53 (2016) 41–79, <https://doi.org/10.1016/j.pecs.2015.10.002>.
- [13] A. Bruce, J. Palfreyman, Forest Products Biotechnology, CRC Press, 1997. <https://www.crcpress.com/Forest-Products-Biotechnology/Bruce-Palfreyman/9780748404155>.

- [14] S. Wang, G. Dai, H. Yang, Z. Luo, Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review, *Prog. Energy Combust. Sci.* 62 (2017) 33–86, <https://doi.org/10.1016/j.peccs.2017.05.004>.
- [15] S. Frodeson, G. Henriksson, J. Berghel, Pelletizing pure biomass substances to investigate the mechanical properties and bonding mechanisms, *BioResources* 13 (2018) 1202–1222, <https://doi.org/10.15376/biores.13.1.1202-1222>.
- [16] A.I. Anukam, J. Berghel, E.B. Famewo, S. Frodeson, Improving the understanding of the bonding mechanism of primary components of biomass pellets through the use of advanced analytical instruments, *J. Wood Chem. Technol.* (2019) 1–18, <https://doi.org/10.1080/02773813.2019.1652324>, 0.
- [17] A. Gani, I. Naruse, Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass, *Renew. Energy* 32 (2007) 649–661, <https://doi.org/10.1016/j.renene.2006.02.017>.
- [18] K.B. Ansari, J.S. Arora, J.W. Chew, P.J. Dauenhauer, S.H. Mushrif, Fast pyrolysis of cellulose, hemicellulose, and lignin: effect of operating temperature on bio-oil yield and composition and insights into the intrinsic pyrolysis chemistry, *Ind. Eng. Chem. Res.* 58 (2019) 15838–15852, <https://doi.org/10.1021/acs.iecr.9b00920>.
- [19] G. Xue, M. Kwapińska, W. Kwapiński, K.M. Czajka, J. Kennedy, J.J. Leahy, Impact of torrefaction on properties of *Miscanthus × giganteus* relevant to gasification, *Fuel* 121 (2014) 189–197, <https://doi.org/10.1016/j.fuel.2013.12.022>.
- [20] D. Lv, M. Xu, X. Liu, Z. Zhan, Z. Li, H. Yao, Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification, *Fuel Process. Technol.* 91 (2010) 903–909, <https://doi.org/10.1016/j.fuproc.2009.09.014>.
- [21] C. Moliner, B. Bosio, E. Arato, A. Ribes, Thermal and thermo-oxidative characterisation of rice straw for its use in energy valorisation processes, *Fuel* 180 (2016) 71–79, <https://doi.org/10.1016/j.fuel.2016.04.021>.
- [22] W. Cao, J. Li, T. Martí-Rosselló, X. Zhang, Experimental study on the ignition characteristics of cellulose, hemicellulose, lignin and their mixtures, *J. Energy Inst.* 92 (2019) 1303–1312, <https://doi.org/10.1016/j.joei.2018.10.004>.
- [23] A. Trubetskaya, A. Brown, G.A. Tompsett, M.T. Timko, J. Kling, M. Broström, M. L. Andersen, K. Umeki, Characterization and reactivity of soot from fast pyrolysis of lignocellulosic compounds and monolignols, *Appl. Energy* 212 (2018) 1489–1500, <https://doi.org/10.1016/j.apenergy.2017.12.068>.
- [24] Q. Ren, C. Zhao, NO_x and N₂O precursors from biomass pyrolysis: role of cellulose, hemicellulose and lignin, *Environ. Sci. Technol.* 47 (2013) 8955–8961, <https://doi.org/10.1021/es4017574>.
- [25] K.J. Mosciicki, L. Niedzwiecki, P. Owczarek, M. Wnukowski, Commoditization of biomass: dry torrefaction and pelletization—a review, *J. Power Technol.* 94 (2014) 233–249, <http://papers.itc.pw.edu.pl/index.php/JPT/article/view/562/610>.
- [26] D. Nhuchhen, P. Basu, B. Acharya, A comprehensive review on biomass torrefaction, *Int. J. Renew. Energy Biofuels.* 2014 (2014) 1–56, <https://doi.org/10.5171/2014.506376>.
- [27] J.S. Tumuluru, S. Sokhansanj, J.R. Hess, C.T. Wright, R.D. Boardman, A review on biomass torrefaction process and product properties for energy applications, *Ind. Biotechnol.* 7 (2011) 384–401, <https://doi.org/10.1089/ind.2011.0014>.
- [28] L.J.R. Nunes, J.C.O. Matias, J.P.S. Catalao, A review on torrefied biomass pellets as a sustainable alternative to coal in power generation, *Renew. Sustain. Energy Rev.* 40 (2014) 153–160, <https://doi.org/10.1016/j.rser.2014.07.181>.
- [29] M.J.C. van der Stelt, H. Gerhauser, J.H.A. Kiel, K.J. Ptasiński, Biomass upgrading by torrefaction for the production of biofuels: a review, *Biomass Bioenergy* 35 (2011) 3748–3762, <https://doi.org/10.1016/j.biombioe.2011.06.023>.
- [30] J. Koppejan, S. Sokhansanj, S. Melin, S. Madrali, Status Overview of Torrefaction Technologies, 2012.
- [31] J. Koppejan, S. Sokhansanj, S. Melin, S. Madrali, Status Overview of Torrefaction Technologies, International Energy Agency, 2015.
- [32] B. Acharya, A. Dutta, J. Minaret, Review on comparative study of dry and wet torrefaction, *Sustain. Energy Technol. Assess.* 12 (2015) 26–37, <https://doi.org/10.1016/j.seta.2015.08.003>.
- [33] M.A. Saeed, G.E. Andrews, H.N. Phylaktou, B.M. Gibbs, Raw and steam exploded pine wood: possible enhanced reactivity with gasification hydrogen, *Int. J. Hydrogen Energy* 41 (2016) 16566–16576, <https://doi.org/10.1016/j.ijhydene.2016.05.121>.
- [34] M.A. Saeed, N.F. Anez, G.E. Andrews, H.N. Phylaktou, B.M. Gibbs, Steam exploded pine wood burning properties with particle size dependence, *Fuel* 194 (2017) 527–532, <https://doi.org/10.1016/j.fuel.2017.01.028>.
- [35] M.T. Reza, J. Andert, B. Wirth, D. Busch, J. Pielert, J.G. Lynam, J. Mumme, Hydrothermal carbonization of biomass for energy and crop production, *Appl. Bioenergy* 1 (2014) 11–29, <https://doi.org/10.2478/apbi-2014-0001>.
- [36] H.A. Ruiz, R.M. Rodríguez-Jasso, B.D. Fernandes, A.A. Vicente, J.A. Teixeira, Hydrothermal processing, as an alternative for upgrading agriculture residues and marine biomass according to the biorefinery concept: a review, *Renew. Sustain. Energy Rev.* 21 (2013) 35–51, <https://doi.org/10.1016/j.rser.2012.11.069>.
- [37] A. Funke, F. Ziegler, Hydrothermal carbonisation of biomass: a summary and discussion of chemical mechanisms for process engineering, *Biofuels Bioprod. Biorefin.* 4 (2010) 160–177, <https://doi.org/10.1002/bbb.198>.
- [38] M.-M. Titirici, M. Antonietti, Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization, *Chem. Soc. Rev.* 39 (2010) 103–116, <https://doi.org/10.1039/b819318p>.
- [39] M.-M. Titirici, A. Thomas, M. Antonietti, Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the CO₂ problem? *New J. Chem.* 31 (2007) 787, <https://doi.org/10.1039/b616045j>.
- [40] M.H. Uddin, M.T. Reza, J.G. Lynam, C.J. Coronella, Effects of water recycling in hydrothermal carbonization of loblolly pine, *Environ. Prog. Sustain. Energy* 33 (2014) 1309–1315, <https://doi.org/10.1002/ep.11899>.
- [41] A. Kruse, A. Funke, M.M. Titirici, Hydrothermal conversion of biomass to fuels and energetic materials, *Curr. Opin. Chem. Biol.* 17 (2013) 515–521, <https://doi.org/10.1016/j.cbpa.2013.05.004>.
- [42] K.J. Mosciicki, L. Niedzwiecki, P. Owczarek, M. Wnukowski, Commoditization of wet and high ash biomass: wet torrefaction — a review, *J. Power Technol.* 97 (2017) 354–369.
- [43] M.T. Reza, J.G. Lynam, M.H. Uddin, C.J. Coronella, Hydrothermal carbonization: fate of inorganics, *Biomass Bioenergy* 49 (2013) 86–94, <https://doi.org/10.1016/j.biombioe.2012.12.004>.
- [44] M.T. Reza, W. Yan, M.H. Uddin, J.G. Lynam, S.K. Hoekman, C.J. Coronella, V. R. Vásquez, Reaction kinetics of hydrothermal carbonization of loblolly pine, *Bioresour. Technol.* 139 (2013) 161–169, <https://doi.org/10.1016/j.biortech.2013.04.028>.
- [45] W. Nan, A.R. Shende, J. Shannon, R.V. Shende, Insight into catalytic hydrothermal liquefaction of cardboard for biofuels production, *Energy Fuels* 30 (2016) 4933–4944, <https://doi.org/10.1021/acs.energyfuels.6b00479>.
- [46] A. Shende, W. Nan, E. Kodzomoyo, J. Shannon, J. Nicpon, R. Shende, Evaluation of aqueous product from hydrothermal liquefaction of cardboard as bacterial growth Medium: Co-liquefaction of cardboard and bacteria for higher bio-oil production, *J. Sustain. Bioenergy Syst.* 7 (2017) 51–64, <https://doi.org/10.4236/jsbs.2017.72005>.
- [47] R. Tungal, R.V. Shende, Hydrothermal liquefaction of pinewood (*Pinus ponderosa*) for H₂, biocrude and bio-oil generation, *Appl. Energy* 134 (2014) 401–412, <https://doi.org/10.1016/j.apenergy.2014.07.060>.
- [48] A. Funke, F. Ziegler, Heat of reaction measurements for hydrothermal carbonization of biomass, *Bioresour. Technol.* 102 (2011) 7595–7598, <https://doi.org/10.1016/j.biortech.2011.05.016>.
- [49] M. Wilk, A. Magdziarz, Hydrothermal carbonization, torrefaction and slow pyrolysis of *Miscanthus giganteus*, *Energy* 140 (2017) 1292–1304, <https://doi.org/10.1016/j.energy.2017.03.031>.
- [50] M. Wnukowski, P. Owczarek, L. Niedzwiecki, Wet torrefaction of miscanthus – characterization of hydrochars in view of handling, storage and combustion properties, *J. Ecol. Eng.* 16 (2015) 161–167, <https://doi.org/10.12911/22998993/2950>.
- [51] L. Gao, M. Volpe, M. Lucian, L. Fiori, J.L. Goldfarb, Does hydrothermal carbonization as a biomass pretreatment reduce fuel segregation of coal-biomass blends during oxidation? *Energy Convers. Manag.* (2018) 93–104, <https://doi.org/10.1016/j.enconman.2018.12.009>.
- [52] L. Wang, L. Zhang, A. Li, Hydrothermal treatment coupled with mechanical expression at increased temperature for excess sludge dewatering: influence of operating conditions and the process energetics, *Water Res.* 65 (2014) 85–97, <https://doi.org/10.1016/j.watres.2014.07.020>.
- [53] L. Wang, A. Li, Y. Chang, Hydrothermal treatment coupled with mechanical expression at increased temperature for excess sludge dewatering: heavy metals, volatile organic compounds and combustion characteristics of hydrochar, *Chem. Eng. J.* 297 (2016) 1–10, <https://doi.org/10.1016/j.cej.2016.03.131>.
- [54] N. Gao, Z. Li, C. Quan, N. Miskolczi, A. Egedy, A new method combining hydrothermal carbonization and mechanical compression in-situ for sewage sludge dewatering: bench-scale verification, *J. Anal. Appl. Pyrolysis* 139 (2019) 187–195, <https://doi.org/10.1016/j.jaap.2019.02.003>.
- [55] K. Svensson, O. Kjørtaug, M.J. Higgins, R. Linjordet, S.J. Horn, Post-anaerobic digestion thermal hydrolysis of sewage sludge and food waste: effect on methane yields, dewaterability and solids reduction, *Water Res.* 132 (2018) 158–166, <https://doi.org/10.1016/j.watres.2018.01.008>.
- [56] M.A. De la Rubia, J.A. Villamil, J.J. Rodríguez, A.F. Moledano, Effect of inoculum source and initial concentration on the anaerobic digestion of the liquid fraction from hydrothermal carbonisation of sewage sludge, *Renew. Energy* 127 (2018) 697–704, <https://doi.org/10.1016/j.renene.2018.05.002>.
- [57] J.A. Villamil, A.F. Moledano, J.J. Rodríguez, R. Borja, M.A. De la Rubia, Anaerobic Co-digestion of the organic fraction of municipal solid waste and the liquid fraction from the hydrothermal carbonization of industrial sewage sludge under thermophilic conditions, *Front. Sustain. Food Syst.* 2 (2018) 1–7, <https://doi.org/10.3389/fsufs.2018.00017>.
- [58] K.R. Parmar, A.B. Ross, Integration of hydrothermal carbonisation with anaerobic digestion; Opportunities for valorisation of digestate, *Energies* 12 (2019), <https://doi.org/10.3390/en12091586>.
- [59] M. Usman, H. Chen, K. Chen, S. Ren, J.H. Clark, J. Fan, G. Luo, S. Zhang, Characterization and utilization of aqueous products from hydrothermal conversion of biomass for bio-oil and hydro-char production: a review, *Green Chem.* 21 (2019) 1553–1572, <https://doi.org/10.1039/C8GC03957G>.
- [60] C. Aragón-Briceno, A.B. Ross, M.A. Camargo-Valero, Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment, *Appl. Energy* 208 (2017) 1357–1369, <https://doi.org/10.1016/j.apenergy.2017.09.019>.
- [61] B. Wirth, J. Mumme, Anaerobic digestion of waste water from hydrothermal carbonization of corn silage, *Appl. Bioenergy* 1 (2014) 1–10, <https://doi.org/10.2478/apbi-2013-0001>.
- [62] E. Erdogan, B. Atila, J. Mumme, M.T. Reza, A. Toptas, M. Elibol, J. Yanik, Characterization of products from hydrothermal carbonization of orange pomace including anaerobic digestibility of process liquor, *Bioresour. Technol.* 196 (2015) 35–42, <https://doi.org/10.1016/j.biortech.2015.06.115>.
- [63] F.C. Luz, S. Cordiner, A. Manni, V. Mulone, V. Rocco, Anaerobic digestion of coffee grounds soluble fraction at laboratory scale: evaluation of the biomethane

- potential, *Appl. Energy* 207 (2017) 166–175, <https://doi.org/10.1016/j.apenergy.2017.06.042>.
- [64] O. Das, A.K. Sarmah, The love-hate relationship of pyrolysis biochar and water: a perspective, *Sci. Total Environ.* 512–513 (2015) 682–685, <https://doi.org/10.1016/j.scitotenv.2015.01.061>.
- [65] M. Gray, M.G. Johnson, M.I. Dragila, M. Kleber, Water uptake in biochars: the roles of porosity and hydrophobicity, *Biomass Bioenergy* 61 (2014) 196–205, <https://doi.org/10.1016/j.biombioe.2013.12.010>.
- [66] S.E. Hale, J. Lehmann, D. Rutherford, A.R. Zimmerman, R.T. Bachmann, V. Shitumbanuma, A. O'Toole, K.L. Sundqvist, H.P.H. Arp, G. Cornelissen, Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars, *Environ. Sci. Technol.* 46 (2012) 2830–2838, <https://doi.org/10.1021/es203984k>.
- [67] E. Baltreñaitė, P. Baltreñas, A. Bhatnagar, T. Vilppo, M. Selenius, A. Koistinen, M. Dahl, O.P. Penttinen, A multicompound approach to using waste-derived biochar in biofiltration: a case study based on dissimilar types of waste, *Int. Biodeterior. Biodegrad.* 119 (2017) 565–576, <https://doi.org/10.1016/j.ibiod.2016.10.056>.
- [68] D.C. Cruz Ceballos, K. Hawboldt, R. Helleur, Effect of production conditions on self-heating propensity of torrefied sawmill residues, *Fuel* 160 (2015) 227–237, <https://doi.org/10.1016/j.fuel.2015.07.097>.
- [69] Q. Gao, M. Edo, S.H. Larsson, E. Collina, M. Rudolfsson, M. Gallina, I. Oluwoye, M. Altarawneh, B.Z. Dlugogorski, S. Jansson, Formation of PCDDs and PCDFs in the torrefaction of biomass with different chemical composition, *J. Anal. Appl. Pyrolysis* 123 (2017), <https://doi.org/10.1016/j.jaap.2016.12.015>.
- [70] M. Edo, N. Skoglund, Q. Gao, P.E. Persson, S. Jansson, Fate of metals and emissions of organic pollutants from torrefaction of waste wood, MSW, and RDF, *Waste Manag.* 68 (2017) 646–652, <https://doi.org/10.1016/j.wasman.2017.06.017>.
- [71] K. Jagodzińska, M. Czerep, E. Kudlek, M. Wnukowski, W. Yang, Torrefaction of wheat-barley straw: composition and toxicity of torrefaction condensates, *Biomass Bioenergy* 129 (2019) 105335, <https://doi.org/10.1016/j.biombioe.2019.105335>.
- [72] T. Keipi, H. Tolvanen, L. Kokko, R. Raiko, The effect of torrefaction on the chlorine content and heating value of eight woody biomass samples, *Biomass Bioenergy* 66 (2014) 232–239, <https://doi.org/10.1016/j.biombioe.2014.02.015>.
- [73] S.B. Saleh, J.P. Flensburg, T.K. Shoulaifar, Z. Sárossy, B.B. Hansen, H. Egsgaard, N. Demartini, P.A. Jensen, P. Glarborg, K. Dam-Johansen, Release of chlorine and sulfur during biomass torrefaction and pyrolysis, *Energy Fuels* 28 (2014) 3738–3746, <https://doi.org/10.1021/ef4021262>.
- [74] D. Thrän, J. Witt, K. Schaubach, J. Kiel, M. Carbo, J. Maier, C. Ndibe, J. Koppejan, E. Alakangas, S. Majer, F. Schipfer, Moving Torrefaction towards Market Introduction – Technical Improvements and Economic-Environmental Assessment along the Overall Torrefaction Supply Chain through the SECTOR Project, *Biomass and Bioenergy*, 2016, <https://doi.org/10.1016/j.biombioe.2016.03.004>.
- [75] CEN (European Committee for Standardisation), EN 303-5 Heating Boilers - Part 5: Heating Boilers for Solid Fuels, Manually and Automatically Stoked, Nominal Heat Output of up to 500 kW - Terminology, Requirements, Testing and Marking, 2012.
- [76] European Commission, Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), amending Directive 1999/4, establishing a European Chemicals Agency, 2000, 2004R0726 - v.7 of 05.06.2013.
- [77] European Chemical Agency, ECHA - website, n.d. <http://echa.europa.eu/about-us>, accessed April 29, 2016
- [78] Milieu Ltd, Report on Penalties Applicable for Infringement of the Provisions of the REACH Regulation in the Member States, 2010. https://ec.europa.eu/environment/chemicals/reach/pdf/report_reach_penalties.pdf.
- [79] CEN (European Committee for Standardisation), Appliances, Solid Fuels and Firelighters for Barbecuing Part 2: Barbecue Charcoal and Barbeques Charcoal Briquettes — Requirements and Test Methods, 2005.
- [80] CEN (European Committee for Standardisation), EN 15148:2009 Solid Biofuels - Determination of the Content of Volatile Matter, 2009.
- [81] International Biochar Initiative, Standardized product definition and product testing guidelines for biochar that is used in soil, 1.1, <http://www.biochar-international.org/characterizationstandard>, 22, 2013.
- [82] R.B. Armeçin, F.M. Gabon, Biomass, organic carbon and mineral matter contents of abaca (*Musa textilis* Nee) at different stages of growth, *Ind. Crop. Prod.* 28 (2008) 340–345, <https://doi.org/10.1016/j.indcrop.2008.03.014>.
- [83] ECHA PPORD - ECHA, <https://echa.europa.eu/support/dossier-submission-tools/reach-it/ppord> accessed August 3, 2016.
- [84] European Chemical Agency, Guidance for monomers and polymers. http://echa.europa.eu/documents/10162/13632/polymers_en.pdf, 2012.
- [85] C. Huéscar Medina, H. Sattar, H.N. Phylaktou, G.E. Andrews, B.M. Gibbs, Explosion reactivity characterisation of pulverised torrefied spruce wood, *J. Loss Prev. Process. Ind.* 36 (2014) 287–295, <https://doi.org/10.1016/j.jlp.2014.12.009>.
- [86] C. Huéscar Medina, B. Maccioitir, H. Sattar, D.J.F. Slatter, H.N. Phylaktou, G. E. Andrews, B.M. Gibbs, Comparison of the explosion characteristics and flame speeds of pulverised coals and biomass in the ISO standard 1 m³ dust explosion equipment, *Fuel* 151 (2015) 91–101, <https://doi.org/10.1016/j.fuel.2015.01.009>.
- [87] PTI/17 Solid biofuels committee, Draft BS EN ISO 17225-8 Solid Biofuels - Fuel Specifications and Classes; Part 8: Graded Thermally Treated and Densified Biomass Fuels, 2016.
- [88] CEN (European Committee for Standardisation), EN17225-1:2014 Fuel Specifications and Classes Part 1: General Requirements, 2014.
- [89] CEN (European Committee for Standardisation), EN ISO 17225-2:2014 Fuel Specifications and Classes Part 2: Graded Wood Pellets, 2014.
- [90] CEN (European Committee for Standardisation), EN17225-3:2014 Fuel Specifications and Classes Part 3: Graded Wood Briquettes, 2014.
- [91] CEN (European Committee for Standardisation), EN17225-4:2014 Fuel Specifications and Classes Part 4: Wood Chips for Non-Industrial Use, 2014.
- [92] CEN (European Committee for Standardisation), EN17225-5:2014 Fuel Specifications and Classes Part 5: Graded Firewood, 2014.
- [93] CEN (European Committee for Standardisation), EN17225-6:2014 Fuel Specifications and Classes Part 6: Graded Non-woody Pellets, 2014.
- [94] CEN (European Committee for Standardisation), EN17225-7:2014 Fuel Specifications and Classes Part 7: Graded Non-woody Briquettes, 2014.
- [95] ENplus, EN Plus for Wood Pellets EN Plus Handbook Part 3, Pellet Quality Requirements, 2015, <https://doi.org/10.1017/CB09781107415324.004>.
- [96] ISO, ISO 5074:1994 Determination of Hardgrove Grindability Index of Hard Coal, 1994.
- [97] T.G. Bridgeman, J.M. Jones, A. Williams, D.J. Waldron, An investigation of the grindability of two torrefied energy crops, *Fuel* 89 (2010) 3911–3918, <https://doi.org/10.1016/j.fuel.2010.06.043>.
- [98] D.T. Van Essendelft, X. Zhou, B.S.J. Kang, Grindability determination of torrefied biomass materials using the Hybrid Work Index, *Fuel* 105 (2013) 103–111, <https://doi.org/10.1016/j.fuel.2012.06.008>.
- [99] B. Arias, C. Pevida, J. Feroso, M.G. Plaza, F. Rubiera, J.J. Pis, Influence of torrefaction on the grindability and reactivity of woody biomass, *Fuel Process. Technol.* 89 (2008) 169–175, <https://doi.org/10.1016/j.fuproc.2007.09.002>.
- [100] A. Ohliger, M. Forster, R. Kneer, Torrefaction of beechwood: a parametric study including heat of reaction and grindability, *Fuel* 104 (2013) 607–613, <https://doi.org/10.1016/j.fuel.2012.06.112>.
- [101] M. Phanphanich, S. Mani, Impact of torrefaction on the grindability and fuel characteristics of forest biomass, *Bioresour. Technol.* 102 (2011) 1246–1253, <https://doi.org/10.1016/j.biortech.2010.08.028>.
- [102] C. Gobl, K. Jorg, U. Wolfesberger-Schwabl, SECTOR D. 8.4 Round Robin Report 2 - Validation of New Test Methods, 2015.
- [103] M. Hoelt, L. Pommer, J. Lemus, Requirements for a MSDS for Torrefied Material, 2013.
- [104] A. Janssen, MSDS according to EU regulations number 453/2010 of 20, 10, http://torrefactie.nl/wp-content/uploads/DTA_MSDS_according_to_EU_regulation_s_2010.pdf, 2010.
- [105] CEN (European Committee for Standardisation), EN ISO 18134-2:2015 Solid Biofuels — Determination of Moisture Content — Oven Dry Method Part 2 : Total Moisture — Simplified Method, 2015.
- [106] CEN (European Committee for Standardisation), EN ISO 18122:2015 Solid Biofuels — Determination of Ash Content, 2015.
- [107] Sweden Linnæus University (project leader), Estonia Tallinn University of Technology, Greece CERGY, Italy IVALLSA - Ireland Tipperary energy agency, the bioenergy system planners handbook - BISYPLAN, n.d. <http://bisyplan.bioenarea.eu/html-files-en/>, accessed July 24, 2016
- [108] H.S. Kambo, A. Dutta, Comparative evaluation of torrefaction and hydrothermal carbonization of lignocellulosic biomass for the production of solid biofuel, *Energy Convers. Manag.* 105 (2015) 746–755, <https://doi.org/10.1016/j.enconman.2015.08.031>.
- [109] T. Khazraie Shoulaifar, N. Demartini, M. Zevenhoven, F. Verhoeff, J. Kiel, M. Hupa, Ash-forming matter in torrefied birch wood: changes in chemical association, *Energy Fuels* 27 (2013) 5684–5690, <https://doi.org/10.1021/ef4005175>.
- [110] W. Yan, T.C. Acharjee, C.J. Coronella, V.R. Vasquez, Thermal pretreatment of lignocellulosic biomass, *Environ. Prog. Sustain. Energy* 28 (2009) 435–440, <https://doi.org/10.1002/ep>.
- [111] T. Kan, V. Strezov, T.J. Evans, Lignocellulosic biomass pyrolysis: a review of product properties and effects of pyrolysis parameters, *Renew. Sustain. Energy Rev.* 57 (2016), <https://doi.org/10.1016/j.rser.2015.12.185>, 126–1140.
- [112] Feng Xu, Jianming Yu, Tesfaye Tesso, Floyd Dowell, Donghai Wang, Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques : a mini-review, *Appl. Energy* 104 (2013) 801–809, <https://doi.org/10.1016/j.apenergy.2012.12.019>.
- [113] Thermo Scientific, Nicolet iS5 Spectrometer Fast Facts, 2010.
- [114] Thermo Scientific, iD5 ATR Sampling Accessory User Guide, 2010, pp. 1–19.
- [115] N.Q. Bui, P. Fongarland, F. Rataboul, C. Dartiguelongue, N. Charon, C. Vallée, N. Essayem, FTIR as a simple tool to quantify unconverted lignin from chars in biomass liquefaction process: application to SC ethanol liquefaction of pine wood, *Fuel Process. Technol.* 134 (2015) 378–386, <https://doi.org/10.1016/j.fuproc.2015.02.020>.
- [116] C.E. Brewer, K. Schmidt-Rohr, J.A. Satrio, R.C. Brown, Characterization of biochar from fast pyrolysis and gasification systems, *Environ. Prog. Sustain. Energy* 28 (2009) 386–396, <https://doi.org/10.1002/ep>.
- [117] J.S. Fabyi, B.M. Ogunleye, Mid-infrared spectroscopy and dynamic mechanical analysis of heat-treated obeche (*Triplochiton scleroxylon*) wood, *Maderas Cienc. Tecnol.* 17 (2015) 5–16, <https://doi.org/10.4067/S0718-221X2015005000001>.
- [118] M. Poletto, A.J. Zattera, Materials produced from plant biomass: part III: degradation kinetics and hydrogen bonding in lignin, *Mater. Res.* 16 (2013) 1065–1070, <https://doi.org/10.1590/S1516-14392013005000112>.

- [119] M. Wilk, A. Magdziarz, I. Kalemba, Characterisation of renewable fuels' torrefaction process with different instrumental techniques, *Energy* 87 (2015) 259–269, <https://doi.org/10.1016/j.energy.2015.04.073>.
- [120] R.L. McCreery, *Raman Spectroscopy for Chemical Analysis*, Wiley-Interscience, 2000, <https://doi.org/10.1002/0471721646>.
- [121] E. Smith, G. Dent, *Modern Raman Spectroscopy - A Practical Approach*, John Wiley & Sons, Ltd, 2005.
- [122] M. Kacurakova, N. Wellner, A. Ebringerova, Z. Hroma, R.H. Wilson, M. Kac, P. S. Belton, Characterisation of xylan-type polysaccharides and associated cell wall components by FT-IR and FT-Raman spectroscopies, *Food Hydrocolloids* 13 (1999) 35–41, [https://doi.org/10.1016/S0268-005X\(98\)00067-8](https://doi.org/10.1016/S0268-005X(98)00067-8).
- [123] W. Hoareau, W. Trindade, B. Siegmund, A. Castellan, E. Frollini, Sugar cane bagasse and curaua lignins oxidized by chlorine dioxide and reacted with furfuryl alcohol: characterization and stability, *Tissue Cell* 86 (2004) 567–576, <https://doi.org/10.1016/j.polymdegradstab.2004.07.005>.
- [124] J.C. del Río, A. Gutiérrez, I.M. Rodríguez, D. Ibarra, Á.T. Martínez, Composition of non-woody plant lignins and cinnamic acids by Py-GC/MS, Py/TMAH and FT-IR, *J. Anal. Appl. Pyrolysis* 79 (2007) 39–46, <https://doi.org/10.1016/j.jaap.2006.09.003>.
- [125] C. Li, B. Knierim, C. Manisseri, R. Arora, H.V. Scheller, M. Auer, K.P. Vogel, B. A. Simmons, S. Singh, Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification, *Bioresour. Technol.* 101 (2010) 4900–4906, <https://doi.org/10.1016/j.biortech.2009.10.066>.
- [126] A. Casas, M. Oliet, M.V. Alonso, F. Rodríguez, Dissolution of *Pinus radiata* and *Eucalyptus globulus* woods in ionic liquids under microwave radiation: lignin regeneration and characterization, *Separ. Purif. Technol.* 97 (2012) 115–122, <https://doi.org/10.1016/j.seppur.2011.12.032>.
- [127] J.S. Lupoi, S. Singh, B.A. Simmons, R.J. Henry, Assessment of lignocellulosic biomass using analytical spectroscopy: an evolution to high-throughput techniques, *Bioenergy Res.* 7 (2014) 1–23, <https://doi.org/10.1007/s12155-013-9352-1>.
- [128] M.H. Nuopponen, H.I. Wikberg, G.M. Birch, A.S. Jääskeläinen, S.L. Maunu, T. Vuorinen, D. Stewart, Characterization of 25 tropical hardwoods with fourier transform infrared, ultraviolet resonance Raman, and ¹³C-NMR cross-polarization/magic-angle spinning spectroscopy, *J. Appl. Polym. Sci.* 102 (2006) 810–819, <https://doi.org/10.1002/app.24143>.
- [129] S. Park, J.O. Baker, M.E. Himmel, P.A. Parilla, D.K. Johnson, Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance, *Biotechnol. Biofuels* 3 (2010) 1–10, <https://doi.org/10.1186/1754-6834-3-10>.
- [130] R. Sun, J. Tomkinson, S. Wang, W. Zhu, Characterization of lignins from wheat straw by alkaline peroxide treatment, *Polym. Degrad. Stabil.* 67 (2000) 101–109, [https://doi.org/10.1016/S0141-3910\(99\)00099-3](https://doi.org/10.1016/S0141-3910(99)00099-3).
- [131] X.F. Sun, F. Xu, R.C. Sun, Y.X. Wang, P. Fowler, M.S. Baird, Characteristics of degraded lignins obtained from steam exploded wheat straw, *Polym. Degrad. Stabil.* 86 (2004) 245–256, <https://doi.org/10.1016/j.polymdegradstab.2004.05.003>.
- [132] D. Djikanović, A. Kalauzi, K. Radotić, C. Lapierre, M. Jeremić, Deconvolution of lignin fluorescence spectra: a contribution to the comparative structural studies of lignins, *Russ. J. Phys. Chem.* 81 (2007) 1425–1428, <https://doi.org/10.1134/S0036024407090142>.
- [133] M.A. Garrido, R. Font, J.A. Conesa, Thermochemical study of the briquetting process of mattress foams, *Fuel Process. Technol.* 159 (2017) 88–95, <https://doi.org/10.1016/j.fuproc.2017.01.03>.
- [134] M.J. Blesa, J.L. Miranda, R. Moliner, Micro-FTIR study of the blend of humates with calcium hydroxide used to prepare smokeless fuel briquettes, *Vib. Spectrosc.* 33 (2003) 31–35, [https://doi.org/10.1016/S0924-2031\(03\)00089-4](https://doi.org/10.1016/S0924-2031(03)00089-4).
- [135] M.J. Blesa, J.L. Miranda, M.T. Izquierdo, R. Moliner, Curing temperature effect on mechanical strength of smokeless fuel briquettes prepared with molasses, *Fuel* 82 (2003) 943–947, [https://doi.org/10.1016/S0016-2361\(02\)00416-7](https://doi.org/10.1016/S0016-2361(02)00416-7).
- [136] D.L. Sills, J.M. Gossett, Using FTIR to predict saccharification from enzymatic hydrolysis of alkali-pretreated biomasses, *Biotechnol. Bioeng.* 109 (2012) 353–362, <https://doi.org/10.1002/bit.23314>.
- [137] M. Le Troedec, D. Sedan, C. Peyratout, J.P. Bonnet, A. Smith, R. Guinebriere, V. Gloaguen, P. Krausz, Influence of various chemical treatments on the composition and structure of hemp fibres, *Compos. Part A Appl. Sci. Manuf.* 39 (2008) 514–522, <https://doi.org/10.1016/j.compositesa.2007.12.001>.
- [138] Z. Zhang, M. Zhu, P. Hobson, W. Doherty, D. Zhang, Contrasting the pyrolysis behavior of selected biomass and the effect of lignin, *J. Energy Resour. Technol.* 140 (2018), <https://doi.org/10.1115/1.4039321>.
- [139] M.C. Silva, O.R. Lopes, J.L. Colodette, A.O. Porto, J. Rieumont, D. Chaussy, M. N. Belgacem, G.G. Silva, Characterization of three non-product materials from a bleached eucalyptus kraft pulp mill, in view of valorising them as a source of cellulose fibres, *Ind. Crop. Prod.* 27 (2008) 288–295, <https://doi.org/10.1016/j.indcrop.2007.11.005>.
- [140] M. Schwanninger, J.C. Rodrigues, H. Pereira, B. Hinterstoisner, Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose, *Vib. Spectrosc.* 36 (2004) 23–40, <https://doi.org/10.1016/j.vibspec.2004.02.003>.
- [141] S. Kubo, J.F. Kadla, Hydrogen bonding in lignin: a fourier transform infrared model compound study, *Biomacromolecules* 6 (2005) 2815–2821, <https://doi.org/10.1021/bm050288q>.
- [142] C.I. Lacayo, A.J. Malkin, H.Y.N. Holman, L. Chen, S.Y. Ding, M.S. Hwang, M. P. Thelen, Imaging cell wall architecture in single *Zinnia elegans* tracheary elements, *Plant Physiol.* 154 (2010) 121–133, <https://doi.org/10.1104/pp.110.155242>.
- [143] L. Fiorentino-Madiedo, E. Díaz-Faes, R. García, C. Barriocanal, Influence of binder type on greenhouse gases and PAHs from the pyrolysis of biomass briquettes, *Fuel Process. Technol.* 171 (2018) 330–338, <https://doi.org/10.1016/j.fuproc.2017.11.029>.
- [144] A.K. Varma, P. Mondal, Physicochemical characterization and pyrolysis kinetic study of sugarcane bagasse using thermogravimetric analysis, *J. Energy Resour. Technol.* 138 (2016) 1–11, <https://doi.org/10.1115/1.4032729>.
- [145] W. Liu, A.K. Mohanty, L.T. Drzal, P. Askel, M. Misra, Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites, *J. Mater. Sci.* 39 (2004) 1051–1054, <https://doi.org/10.1023/B:JMSE.0000012942.83614.75>.
- [146] J. Skvaril, K.G. Kyprianidis, E. Dahlquist, Applications of near-infrared spectroscopy (NIRS) in biomass energy conversion processes: a review, *Appl. Spectrosc. Rev.* 52 (2017) 675–728, <https://doi.org/10.1080/05704928.2017.1289471>.
- [147] C. Pasquini, Near infrared spectroscopy: fundamentals, practical aspects and analytical applications, *J. Braz. Chem. Soc.* 14 (2003) 198–219, <https://doi.org/10.1590/S0103-50532003000200006>.
- [148] D.A. Burns, E.W. Ciurczak, *Handbook of Near-Infrared Analysis*, CRC Press, 2008. <https://www.crcpress.com/Handbook-of-Near-Infrared-Analysis/Burns-Ciurczak/p/book/9780849373930>. accessed December 27, 2018.
- [149] M. Blanco, I. Villarroya, NIR spectroscopy: a rapid-response analytical tool, *TrAC Trends Anal. Chem. (Reference Ed.)* 21 (2002) 240–250, [https://doi.org/10.1016/S0165-9936\(02\)00404-1](https://doi.org/10.1016/S0165-9936(02)00404-1).
- [150] B. Hames, S.R. Thomas, A.D. Sluiter, C.J. Roth, D.W. Templeton, Rapid biomass analysis: new tools for compositional analysis of corn stover feedstocks and process intermediates from ethanol production, *Appl. Biochem. Biotechnol.* (2003) 105–108. <https://link.springer.com/content/pdf/10.1385/ABAB:105-1-3:5.pdf>.
- [151] O.E. Adedipe, S.D. Johannsmeier, V. Den Truong, G.C. Yencho, Development and validation of a near-infrared spectroscopy method for the prediction of acrylamide content in French-fried potato, *J. Agric. Food Chem.* 64 (2016) 1850–1860, <https://doi.org/10.1021/acs.jafc.5b04733>.
- [152] T.a. Lestander, M. Rudolfsson, L. Pommer, A. Nordin, NIR provides excellent predictions of properties of biocoal from torrefaction and pyrolysis of biomass, *Green Chem.* 16 (2014) 4906–4913, <https://doi.org/10.1039/C3GC42479K>.
- [153] P. Rousset, C. Aguiar, N. Labbé, J.M. Commandré, Enhancing the combustible properties of bamboo by torrefaction, *Bioresour. Technol.* 102 (2011) 8225–8231, <https://doi.org/10.1016/j.biortech.2011.05.093>.
- [154] T.A. Lestander, R. Samuelsson, Prediction of resin and fatty acid content of bioenergy feedstock by on-line near-infrared (NIR) spectroscopy, *Energy Fuels* 24 (2010) 5148–5152, <https://doi.org/10.1021/ef1004682>.
- [155] S.S. Kelley, T.G. Rials, R. Snell, L.H. Groom, A. Sluiter, Use of near infrared spectroscopy to measure the chemical and mechanical properties of solid wood, *Wood Sci. Technol.* 38 (2004) 257–276, <https://doi.org/10.1007/s00226-003-0213-5>.
- [156] W. He, H. Hu, Prediction of hot-water-soluble extractive, pentosan and cellulose content of various wood species using FT-NIR spectroscopy, *Bioresour. Technol.* 140 (2013) 299–305, <https://doi.org/10.1016/j.biortech.2013.04.115>.
- [157] A. Huang, G. Li, F. Fu, B. Fei, Use of visible and near infrared spectroscopy to predict Klason Lignin content of bamboo, Chinese Fir, Paulownia, and Poplar, *J. Wood Chem. Technol.* 28 (2008) 194–206, <https://doi.org/10.1080/02773810802347008>.
- [158] G. Li, A. Huang, G. Wang, D. Qin, Z. Jiang, Rapid determination of Klason lignin content in bamboo by NIR, *Guang Pu Xue Yu Guang Pu Fen Xi* 27 (2007), 1977–1980.
- [159] M.K.D. Rambo, A.R. Alves, W.T. Garcia, M.M.C. Ferreira, Multivariate analysis of coconut residues by near infrared spectroscopy, *Talanta* 138 (2015) 263–272, <https://doi.org/10.1016/j.talanta.2015.03.014>.
- [160] A. Watanabe, S. Morita, Y. Ozaki, A study on water adsorption onto microcrystalline cellulose by near-infrared spectroscopy with two-dimensional correlation spectroscopy and principal component analysis, *Appl. Spectrosc.* 60 (2006) 1054–1061, <https://doi.org/10.1366/000370206778397452>.
- [161] C. Krongtaew, K. Messner, T. Ters, K. Fackler, Characterization of key parameters for biotechnological lignocellulose conversion assessed by FT-NIR spectroscopy. Part I: qualitative analysis of pretreated straw, *BioResources* 5 (2010) 2063–2080, <https://doi.org/10.15376/biores.5.4.2063-2080>.
- [162] M.K.D. Rambo, M.M.C. Ferreira, E.P. Amorim, Multi-product calibration models using NIR spectroscopy, *Chemometr. Intell. Lab. Syst.* 151 (2016) 108–114, <https://doi.org/10.1016/j.chemolab.2015.12.013>.
- [163] Y. Xie, F.Y. Li, X.J. Fan, S.J. Hu, X. Xiao, J.F. Wang, Components analysis of biochar based on near infrared spectroscopy technology, *Chin. J. Anal. Chem.* 46 (2018) 609–615, [https://doi.org/10.1016/S1872-2040\(17\)61081-8](https://doi.org/10.1016/S1872-2040(17)61081-8).
- [164] B.K. Via, S. Adhikari, S. Taylor, Modeling for proximate analysis and heating value of torrefied biomass with vibration spectroscopy, *Bioresour. Technol.* 133 (2013) 1–8, <https://doi.org/10.1016/j.biortech.2013.01.108>.
- [165] M. Pojić, J. Mastilović, D. Palić, M. Pestorić, The development of near-infrared spectroscopy (NIRS) calibration for prediction of ash content in legumes on the basis of two different reference methods, *Food Chem.* 123 (2010) 800–805, <https://doi.org/10.1016/j.foodchem.2010.05.013>.
- [166] T.M. McLellan, J.D. Aber, M.E. Martin, J.M. Melillo, K.J. Nadelhoffer, Determination of nitrogen, lignin, and cellulose content of decomposing leaf material by near infrared reflectance spectroscopy, *Can. J. For. Res.* 21 (1991) 1684–1688, <https://doi.org/10.1139/x91-232>.

- [167] K. Ono, M. Hiraide, M. Amari, Determination of lignin, holocellulose, and organic solvent extractives in fresh leaf, litterfall, and organic material on forest floor using near-infrared reflectance spectroscopy, *J. For. Res.* 8 (2003) 191–198, <https://doi.org/10.1007/s10310-003-0026-2>.
- [168] S. Hou, L. Li, Rapid characterization of woody biomass digestibility and chemical composition using near-infrared spectroscopy, *J. Integr. Plant Biol.* 53 (2011) 166–175, <https://doi.org/10.1111/j.1744-7909.2010.01003.x>.
- [169] J.L. Wen, S.L. Sun, B.L. Xue, R.C. Sun, Recent advances in characterization of lignin polymer by solution-state nuclear magnetic resonance (NMR) methodology, *Materials* 6 (2013) 359–391, <https://doi.org/10.3390/ma6010359>.
- [170] C. Falco, F. Perez Caballero, F. Babonneau, C. Gervais, G. Laurent, M.M. Titirici, N. Baccile, Hydrothermal carbon from biomass: structural differences between hydrothermal and pyrolyzed carbons via ¹³C solid state NMR, *Langmuir* 27 (2011) 14460–14471, <https://doi.org/10.1021/la202361p>.
- [171] J. Mao, W. Hu, G. Ding, K. Schmidt-Rohr, G. Davies, E. Ghabbour, B. Xing, Suitability of different ¹³C solid-state NMR techniques in the characterization of humic acids, *Int. J. Environ. Anal. Chem.* 82 (2002) 183–196, <https://doi.org/10.1080/0306731029000953>.
- [172] F. Shafizadeh, Y. Sekiguchi, Development of aromaticity in cellulosic chars, *Carbon* N. Y. 21 (1983) 511–516, [https://doi.org/10.1016/0008-6223\(83\)90144-6](https://doi.org/10.1016/0008-6223(83)90144-6).
- [173] J.C.C. Freitas, T.J. Bonagamba, F.G. Emmerich, Investigation of biomass- and polymer-based carbon materials using ¹³C high-resolution solid-state NMR, *Carbon* N. Y. 39 (2001) 535–545, [https://doi.org/10.1016/S0008-6223\(00\)00169-X](https://doi.org/10.1016/S0008-6223(00)00169-X).
- [174] R.L. Johnson, J.M. Anderson, B.H. Shanks, X. Fang, M. Hong, K. Schmidt-Rohr, Spectrally edited 2D ¹³C-¹³C NMR spectra without diagonal ridge for characterizing ¹³C-enriched low-temperature carbon materials, *J. Magn. Reson.* 234 (2013) 112–124, <https://doi.org/10.1016/j.jmr.2013.06.006>.
- [175] M. Foston, Advances in solid-state NMR of cellulose, *Curr. Opin. Biotechnol.* 27 (2014) 176–184, <https://doi.org/10.1016/j.copbio.2014.02.002>.
- [176] R.K. Sharma, J.B. Wooten, V.L. Baliga, X. Lin, W.G. Chan, M.R. Hajjaligol, Characterization of chars from pyrolysis of lignin, *Fuel* 83 (2004) 1469–1482, <https://doi.org/10.1016/j.fuel.2003.11.015>.
- [177] J.J. Boon, I. Pastorova, R.E. Botto, P.W. Arisz, Structural studies on cellulose pyrolysis and cellulose chars by PYMS, PYGCMS, FTIR, NMR and by wet chemical techniques, *Biomass Bioenergy* 7 (1994) 25–32, [https://doi.org/10.1016/0961-9534\(94\)00044-T](https://doi.org/10.1016/0961-9534(94)00044-T).
- [178] J. Park, J. Meng, K.H. Lim, O.J. Rojas, S. Park, Transformation of lignocellulosic biomass during torrefaction, *J. Anal. Appl. Pyrolysis* 100 (2013) 199–206, <https://doi.org/10.1016/j.jaap.2012.12.024>.
- [179] L. Fu, S.A. McCallum, J. Miao, C. Hart, G.J. Tudryn, F. Zhang, R.J. Linhardt, Rapid and accurate determination of the lignin content of lignocellulosic biomass by solid-state NMR, *Fuel* 141 (2015) 39–45, <https://doi.org/10.1016/j.fuel.2014.10.039>.
- [180] R. Samuel, Y. Pu, M. Foston, A.J. Ragauskas, Solid-state NMR characterization of switchgrass cellulose after dilute acid pretreatment, *Biofuels* 1 (2010) 85–90, <https://doi.org/10.4155/bfs.09.17>.
- [181] CEN (European Committee for Standardisation), BS EN 12953-11 Shell Boilers Part 11, Acceptance tests, 2003.
- [182] CEN (European Committee for Standardisation), BS EN 12952-15 Water-Tube Boilers and Auxiliary Installations - Part 15: Acceptance Tests, 2003.
- [183] E. Houshfar, Ø. Skreiberg, D. Todorović, A. Skreiberg, T. Lovås, A. Jovović, L. Sørum, NO_x emission reduction by staged combustion in grate combustion of biomass fuels and fuel mixtures, *Fuel* 98 (2012) 29–40, <https://doi.org/10.1016/j.fuel.2012.03.044>.
- [184] C. Ndibe, J. Maier, G. Scheffknecht, Combustion, cofiring and emissions characteristics of torrefied biomass in a drop tube reactor, *Biomass Bioenergy* 79 (2014) 105–115, <https://doi.org/10.1016/j.biombioe.2015.05.010>.
- [185] P. McNamee, L.I. Darvell, J.M. Jones, A. Williams, The combustion characteristics of high-heating-rate chars from untreated and torrefied biomass fuels, *Biomass Bioenergy* 82 (2015) 63–72, <https://doi.org/10.1016/j.biombioe.2015.05.016>.
- [186] J. Li, E. Biagini, W. Yang, L. Tognotti, W. Blasiak, Flame characteristics of pulverized torrefied-biomass combusted with high-temperature air, *Combust. Flame* 160 (2013) 2585–2594, <https://doi.org/10.1016/j.combustflame.2013.05.010>.
- [187] P.W. Li, C.S. Chyang, A comprehensive study on NO_x emission and fuel nitrogen conversion of solid biomass in bubbling fluidized beds under staged combustion, *J. Energy Inst.* 93 (2020) 324–334, <https://doi.org/10.1016/j.joei.2019.02.007>.
- [188] E. Rokni, Y. Liu, X. Ren, Y.A. Levendis, Nitrogen-bearing emissions from burning corn straw in a fixed-bed reactor: effects of fuel moisture, torrefaction, and air flowrate, *J. Energy Resour. Technol. Trans. ASME*. 141 (2019), <https://doi.org/10.1115/1.4042564>.
- [189] M. Ostrycharczyk, K. Krochmalny, M. Czerep, H. Pawlak-Kruczek, J. Zgóra, Marcin Baranowski (another author), Examinations of the sulfur emission from pulverized lignite fuel, under pyrolysis and oxy-fuel combustion condition, *Fuel* 241 (2019) 579–584, <https://doi.org/10.1016/j.fuel.2018.11.110>.
- [190] F. Kazanc, R. Khatami, P. Manoel Crnkovic, Y.A. Levendis, Emissions of NO_x and SO₂ from coals of various ranks, bagasse, and coal-bagasse blends burning in O₂/N₂ and O₂/CO₂ environments, *Energy Fuels* 25 (2011) 2850–2861, <https://doi.org/10.1021/ef200413u>.
- [191] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenergy* 38 (2012) 68–94, <https://doi.org/10.1016/j.biombioe.2011.01.048>.
- [192] M.I. Jahiril, M.G. Rasul, A.A. Chowdhury, N. Ashwath, Biofuels production through biomass pyrolysis- A technological review, *Energies* 5 (2012) 4952–5001, <https://doi.org/10.3390/en5124952>.
- [193] K. Weber, S. Heuer, P. Quicker, T. Li, T. Lovås, V. Scherer, An alternative approach for the estimation of biochar yields, *Energy Fuels* (2018), <https://doi.org/10.1021/acs.energyfuels.8b01825> <https://doi.org/10.1021/acs.energyfuels.8b01825>.
- [194] CEN (European Committee for Standardisation), EN 1127-1 Explosive Atmospheres - Explosion Prevention and Protection - Part 1 : Basic Concepts and Methodology, 2011.
- [195] N. Fernandez-Anez, D.J.F. Slatter, M.A. Saeed, H.N. Phylaktou, G.E. Andrews, J. Garcia-Torrent, Ignition sensitivity of solid fuel mixtures, *Fuel* 223 (2018) 451–461, <https://doi.org/10.1016/j.fuel.2018.02.106>.
- [196] M.A. Saeed, G.E. Andrews, H.N. Phylaktou, B.M. Gibbs, Flame speed and Kst reactivity data for pulverised corn cobs and peanut shells, *J. Loss Prev. Process. Ind.* 49 (2017) 880–887, <https://doi.org/10.1016/j.jlp.2017.03.027>.
- [197] C. Huéscar Medina, H. Sattar, H.N. Phylaktou, G.E. Andrews, B.M. Gibbs, Explosion reactivity characterisation of pulverised torrefied spruce wood, *J. Loss Prev. Process. Ind.* 36 (2015) 287–295, <https://doi.org/10.1016/j.jlp.2014.12.009>.
- [198] M.A. Saeed, G.E. Andrews, H.N. Phylaktou, B.M. Gibbs, L. Niedzwiecki, R. Walton, Explosion and flame propagation properties of coarse Wood : raw and torrefied, in: J. Chao, A.N. Liu, V. Molkov, P. Sunderland, F. Tamanini, J. Torero (Eds.), Proc. Eighth Int. Semin. Fire Explos. Hazards, USTC Press, Hefei, China, 2016, pp. 579–588, <https://doi.org/10.20285/c.skifs.8thISFEH.057>.
- [199] M. Prodan, L.A. Lupu, E. Ghiciei, I. Nalbog, A. Szollosi-Mota, Pyrophoric sulfides influence over the minimum ignition temperature of dust cloud, *AIP Conf. Proc.* 1918 (2017), <https://doi.org/10.1063/1.5018496>.
- [200] M. Pronobis, Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations, *Biomass Bioenergy* 28 (2005) 375–383, <https://doi.org/10.1016/j.biombioe.2004.11.003>.
- [201] A. Mlonka-Mędrala, A. Magdziarz, M. Gajek, K. Nowińska, W. Nowak, Alkali metals association in biomass and their impact on ash melting behaviour, *Fuel* 261 (2020) 116421, <https://doi.org/10.1016/j.fuel.2019.116421>.
- [202] A. Magdziarz, M. Gajek, D. Nowak-Woźny, M. Wilk, Mineral phase transformation of biomass ashes – experimental and thermochemical calculations, *Renew. Energy* 128 (2018) 446–459, <https://doi.org/10.1016/j.renene.2017.05.057>.
- [203] K. Glód, J. Lasek, K. Słowik, J. Zuwała, D. Nabagło, K. Jura, M. Żyrkowski, Investigation of ash-related issues during combustion of maize straw and wood biomass blends in lab-scale bubbling fluidized bed reactor, *J. Energy Resour. Technol.* 142 (2020), <https://doi.org/10.1115/1.4044221>.
- [204] T. Sasi, M. Mighani, E. Örs, R. Tawani, M. Gräbner, Prediction of ash fusion behavior from coal ash composition for entrained-flow gasification, *Fuel Process. Technol.* 176 (2018) 64–75, <https://doi.org/10.1016/j.fuproc.2018.03.018>.
- [205] Y. Yin, J. Yin, W. Zhang, H. Tian, Z. Hu, M. Ruan, Z. Song, L. Liu, Effect of char structure evolution during pyrolysis on combustion characteristics and kinetics of waste biomass, *J. Energy Resour. Technol.* 140 (2018), <https://doi.org/10.1115/1.4039445>, 072203.
- [206] A. Mlonka-Mędrala, K. Gołombek, P. Buk, E. Cieślak, W. Nowak, The influence of KCl on biomass ash melting behaviour and high-temperature corrosion of low-alloy steel, *Energy* 188 (2019) 116062, <https://doi.org/10.1016/j.energy.2019.116062>.
- [207] A. Mlonka-Mędrala, A. Magdziarz, I. Kalemba-Rec, W. Nowak, The influence of potassium-rich biomass ashes on steel corrosion above 550 °C, *Energy Convers. Manag.* 187 (2019) 15–28, <https://doi.org/10.1016/j.enconman.2019.02.074>.
- [208] J. Li, M.C. Paul, K.M. Czajka, Studies of ignition behavior of biomass particles in a down-fire reactor for improving Co-firing performance, *Energy Fuels* 30 (2016) 5870–5877, <https://doi.org/10.1021/acs.energyfuels.6b01065>.
- [209] E.M. Gucho, K. Shahzad, E.A. Bramer, N.A. Akhtar, G. Brem, Experimental study on dry torrefaction of beech wood and miscanthus, *Energies* 8 (2015) 3903–3923, <https://doi.org/10.3390/en8053903>.
- [210] A. Magdziarz, S. Werle, Analysis of the combustion and pyrolysis of dried sewage sludge by TGA and MS, *Waste Manag.* 34 (2014) 174–179, <https://doi.org/10.1016/j.wasman.2013.10.033>.
- [211] T.T. Trinh, S. Werle, K.-Q. Tran, A. Magdziarz, S. Sobek, M. Pogrzeba, Energy crops for sustainable phytoremediation – thermal decomposition kinetics, *Energy Procedia* 158 (2019) 873–878, <https://doi.org/10.1016/J.EGYPRO.2019.01.224>.
- [212] G. Dorez, L. Ferry, R. Sonnier, A. Taguet, J.M. Lopez-Cuesta, Effect of cellulose, hemicellulose and lignin contents on pyrolysis and combustion of natural fibers, *J. Anal. Appl. Pyrolysis* 107 (2014) 323–331, <https://doi.org/10.1016/j.jaap.2014.03.017>.
- [213] S. Prodeson, G. Henriksson, J. Berghel, Effects of moisture content during densification of biomass pellets, focusing on polysaccharide substances, *Biomass Bioenergy* 122 (2019) 322–330, <https://doi.org/10.1016/j.biombioe.2019.01.048>.
- [214] CEN (European Committee for Standardisation), BS EN 15234-1:2011 Solid Biofuels. Fuel quality assurance. General requirements., (n.d.).
- [215] ECN (Energy research Centre of the Netherlands), Phyllis 2, (n.d.). <https://phyllis.nl/Home/Help> (accessed December 24, 2018).