

Valorization of Residues from Energy Conversion of Biomass for Advanced and Sustainable Material Applications

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1. Introduction

The reduction in greenhouse gas (GHG) emissions by shifting towards renewable energy sources to control global warming is one of the main challenges of the 21st century [1]. Recent studies have shown that bioenergy and bio-economy can positively contribute to this emissions reduction [2–4]. Bioenergy can also address the volatility of wind and solar energy and play a role in circular economy as one of the important goals of the European Green Deal [5]. In general, biomass can be classified into six different material classes, which are wood and woody biomass, herbaceous agricultural biomass, aquatic biomass, animal and human biomass wastes, contaminated biomass and industrial biomass wastes (semi-biomass), and biomass mixtures [6].

In recent years, agricultural residues as sustainable energy sources have attracted a lot of research attention. This is due to their low material cost, lack of conflict as a food source, as well as their annual production capacity and distribution in both developed and developing countries [7,8].

These assorted residues are characterized by a relatively high ash content, which can reach up to 20 times the ash content in woody biomass, implying an overall increased slag formation tendency [9]. Ash-forming elements are generally Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe, and Mn in varying amounts [9,10]. Therefore, the ash obtained from thermochemical conversion of biogenic residues and wastes can be employed in different material applications. In particular, Si-rich biomass assortments such as rice husk and rice straw have been increasingly investigated in the last few years [11,12]. Schneider considered the potential of regional feedstocks in Germany in the production of high-quality biogenic silica at the laboratory scale [13]. Schliermann et al. [14] investigated the quality of biogenic silica produced from combustion of rice husk in bench-scale biomass boilers. Their study overcame several challenges in operation of boilers and handling of the generated ashes. Further considerations on Si-rich biomass fuels are also reflected in several publications of the current Special Issue [15–21].

However, the composition of biomass ashes is not homogeneous due to their different origin and depending on fuel processing as well as thermochemical conversion conditions [22], and as a result, defining a specific application for all the biomass ashes is challenging [23]. The potential utilization of biomass ashes is mainly influenced by contaminations such as heavy metals and their slag formation tendencies [24]. Furthermore, the thermochemical conversion process should also be controlled in order to modify the ash composition for specific applications [25]. Considering diverse biomass ash compositions, there are different applications for these materials including cement and concrete production, soil stabilization, filler in asphalt, synthetic aggregate, catalysis, semiconducting materials, energy storage, drug delivery, electrochemical applications and batteries, carbon capture, etc. [23,26,27]. In this respect, any modification of fuel composition using a



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pre-treatment processes as well as different thermochemical conversion technologies can influence the ash characteristics [23,28].

2. The Special Issue

The present Special Issue entitled “Valorization of Residues from Energy Conversion of Biomass for Advanced and Sustainable Material Applications” includes 12 publications from several authors from Germany, Korea, South Africa, France, China, India, and Sweden.

The publications cover a wide range of topics related to biomass conversion and ash-related aspects. In this respect, Chun and Lee [17] provided an overview on recent developments in the purification of silica components and the production of engineered biogenic silica in a bottom-up process employing liquid silicate extracted from rice husk. The products can be used in various applications including heterogeneous catalysts, CO₂ capture, adsorbents for aqueous pollutants, biomolecule delivery, and cosmetic ingredients. Maseko et al. [16] investigated the quality of biogenic silica produced from the thermochemical conversion of different South African agricultural residues such as sugarcane leaves, pith and fiber, and maize leaves. Their investigation proved that silica with high purity and specific surface area can be produced from chemically pre-treated biomass fuels, especially from sugarcane-based input materials. Park et al. [21] extracted biogenic silica from rice husk using a novel two-stage attrition ball milling and alkaline leaching processes. The purity of the produced silica was comparable with the products generated from common thermochemical conversion processes. However, the advantages of the introduced synthesized method were a low production cost and higher productivity. Yan et al. [20] investigated a smoldering process, which is a slow, low-temperature, and flameless burning process to synthesize high-quality biogenic silica from rice husk. Their results showed a maximum conversion temperature of only 560 °C in the naturally piled fuel bed, which is lower than regularly reported combustion temperatures in different biomass combustion technologies. Produced biogenic silica had porous and amorphous nature due to the low conversion temperature. This publication reported a higher ash porosity generated from the smoldering of untreated rice husk as compared to the ashes produced from combustion processes in the literature. Therefore, smoldering shows great potential for the industrial production of high-quality biogenic silica from untreated silica-rich biomass fuels, and further investigations are required in this field. Singh et al. studied photocatalytic degradation of cationic dye using silica nanoparticles (SiNPs) synthesized from the combustion of rice straw followed by a sol-gel route. In this investigation, the effects of combustion temperature and ash crystallinity on the quality of SiNPs were studied, and it was shown that a higher combustion temperature leads to SiNPs with larger particle size with a crystalline nature. However, under controlled combustion temperatures, amorphous SiNPs with an average particle size lower than 30 nm can be synthesized from rice straw ash, which showed promising photocatalytic properties. Jung et al. [15] produced high-quality nano-structured silica as well as cellulose nano-fibrils through an alkaline fractionation process of rice husk. Mugadza et al. [29] synthesized nitrogen-doped carbon nanotubes (N-CNTs) from biomass as carbon precursors for supercapacitors and electrochemical applications. They showed that the initial biomass fuel can influence physicochemical and electrochemical properties of N-CNTs. Nitrogen migration behaviors during the pyrolysis of untreated and chemically pre-treated maize straw were investigated by Li et al. [18]. They proved that an appropriate chemical pre-treatment and pyrolysis temperature would guarantee the fixation of N in the generated biochar, which prevents NO_x emission during the pyrolysis process. The produced N-enhanced biochar can be employed as N fertilizer in order to improve soil quality and production yield in agriculture [30]. Furthermore, soil amendment by biochar is one of the potential applications of biomass fuels to reduce the global carbon emission, improve soil quality, and increase soil carbon sequestration [31–34]. Frikha et al. [35] studied the effect of pyrolysis temperature on the yield and quality of biochar produced from grape marc. Grape marc, as a winery waste, is produced throughout the winemaking process, which has 10–30 wt.% of the grape fresh weight in wet basis.

Their investigation revealed that pyrolysis temperature influences pyrolysis yields, as well as thermal stability, specific surface area, mineral composition, and ash content of the biochar. Bachmaier et al. [36] conducted comprehensive research work on analyzing different nutrients and pollutant contents of different ash fractions obtained from various biomass heating plants in Bavaria, Germany in order to use the ashes as fertilizers. As prescribed by the German Fertilizer Ordinance, the study showed that the ashes from waste wood can contain an elevated content of heavy metals. In addition, fuel quality and combustion conditions modified the concentrations of heavy metals in the ashes to ensure an appropriate ash quality.

The recovery of some of the ash-forming elements such as P is important, as it is one of the critical and irreplaceable elements in human nutrition with a limited resource. However, the annual consumption of P in the agriculture sector is 20 million tons [37]. Therefore, recovery of this element besides the energetic utilization of biomass fuels is very beneficial. In this respect, an economic feasibility investigation of energy and P recovery from municipal sewage sludge was conducted by Bagheri et al. [38], considering 16 different technology scenarios of investments in new combustion plants. This study provides insights into economic performance and required financial support for energetic utilization and P recovery from municipal sewage sludge in Europe.

In order to decrease GHG emissions in a sustainable way in the transport sector, production of biomethane from manure, agricultural residues, and biowaste can have a profound impact [39]. This aspect of biomass application was considered in the publication by Oehmichen et al. [40] by assessing the market. The study showed that different advanced biofuel pathways have significantly different GHG mitigation costs. Furthermore, the magnitude of this mitigation is influenced by the type of substrate used in biomethane production processes, GHG emissions from the fossil energy carrier substituted by biomethane, and the calculation method. These aspects should be considered in future developments in this field.

3. Summary and Future Prospects

The focus of this Special Issue was on biomass ash valorization with respect to their potential for various material applications. Most of the publications in this Special Issue focused on the production of biogenic silica with different properties. Additionally, some of the publications considered application of biomass ashes and biochar as a fertilizer, for soil amendment and recovery of ash forming elements such as N and P as well as the application of biomass feedstocks in biofuel production.

Accordingly, ashes produced from the thermochemical conversion of agricultural residues have high potential to be utilized for different material applications. However, local availability as well as scaling up the process and life-cycle assessment should be considered prior to the utilization of these materials. Furthermore, densification as a mechanical pre-treatment can be crucial to improve the fuel properties, while purification of some of the ash forming elements such as calcium, potassium and phosphorus should also not be disregarded in future investigations.

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References

1. Dotzauer, M.; Oehmichen, K.; Thrän, D.; Weber, C. Empirical greenhouse gas assessment for flexible bioenergy in interaction with the German power sector. *Renew. Energy* **2022**, *181*, 1100–1109. [CrossRef]
2. Sulaiman, C.; Abdul-Rahim, A.S.; Ofozor, C.A. Does wood biomass energy use reduce CO₂ emissions in European Union member countries? Evidence from 27 members. *J. Clean. Prod.* **2020**, *253*, 119996. [CrossRef]
3. Jonsson, R.; Rinaldi, F.; Pilli, R.; Fiorese, G.; Hurmekoski, E.; Cazzaniga, N.; Robert, N.; Camia, A. Boosting the EU forest-based bioeconomy: Market, climate, and employment impacts. *Technol. Forecast. Soc. Chang.* **2021**, *163*, 120478. [CrossRef]
4. Saidur, R.; Abdelaziz, E.A.; Demirbas, A.; Hossain, M.S.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2262–2289. [CrossRef]
5. ForschungsVerbund Erneuerbare Energien. Bioenergie für Eine Konsistente Klimaschutz- und Energiepolitik—Empfehlungen des FVEE. Available online: https://www.dbfz.de/fileadmin/user_upload/Referenzen/Statements/2020_08_25_FVEE-Bioenergie.pdf (accessed on 19 April 2022).
6. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89*, 913–933. [CrossRef]
7. Kaltschmitt, M. Renewable Energy from Biomass renewable energy from Biomass, Introduction. In *Renewable Energy Systems*; Kaltschmitt, M., Themelis, N.J., Bronicki, L.Y., Söder, L., Vega, L.A., Eds.; Springer: New York, NY, USA, 2013; pp. 1393–1396, ISBN 978-1-4614-5819-7.
8. IEA. *World Energy Outlook*; IEA: Paris, France, 2021. Available online: <https://www.iea.org/reports/world-energy-outlook-2021> (accessed on 19 April 2022).
9. Boström, D.; Skoglund, N.; Grimm, A.; Boman, C.; Öhman, M.; Broström, M.; Backman, R. Ash transformation chemistry during combustion of biomass. *Energy Fuels* **2011**, *26*, 85–93. [CrossRef]
10. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. *Fuel* **2013**, *105*, 40–76. [CrossRef]
11. Beidaghy Dizaji, H.; Zeng, T.; Hölzig, H.; Bauer, J.; Klöß, G.; Enke, D. Ash transformation mechanism during combustion of rice husk and rice straw. *Fuel* **2022**, *307*, 121768. [CrossRef]
12. Beidaghy Dizaji, H.; Zeng, T.; Enke, D. New fuel indexes to predict ash behavior for biogenic silica production. *Fuel* **2022**, *310*, 122345. [CrossRef]
13. Schneider, D. Biogenic Silica from Regional Feedstocks—Sustainable Synthesis and Characterization. Ph.D. Thesis, Universität Leipzig, Leipzig, Germany, 2019.
14. Schliermann, T.; Hartmann, I.; Beidaghy Dizaji, H.; Zeng, T.; Schneider, D.; Wassersleben, S.; Enke, D.; Jobst, T.; Lange, A.; Roelofs, F.; et al. High quality biogenic silica from combined energetic and material utilization of agricultural residues. In Proceedings of the 7th International Symposium of Energy from Biomass and Waste, Venice, Italy, 15–18 October 2018.
15. Jung, H.; Kwak, H.; Chun, J.; Oh, K. Alkaline fractionation and subsequent production of nano-structured silica and cellulose nano-fibrils for the comprehensive utilization of rice husk. *Sustainability* **2021**, *13*, 1951. [CrossRef]
16. Maseko, N.N.; Schneider, D.; Wassersleben, S.; Enke, D.; Iwarere, S.A.; Pocock, J.; Stark, A. The production of biogenic silica from different south african agricultural residues through a thermo-chemical treatment method. *Sustainability* **2021**, *13*, 577. [CrossRef]
17. Chun, J.; Lee, J.H. Recent progress on the development of engineered silica particles derived from rice husk. *Sustainability* **2020**, *12*, 10683. [CrossRef]
18. Li, H.; Mou, H.; Zhao, N.; Yu, Y.; Hong, Q.; Philbert, M.; Zhou, Y.; Dizaji, H.B.; Dong, R. Nitrogen migration during pyrolysis of raw and acid leached maize straw. *Sustainability* **2021**, *13*, 3786. [CrossRef]
19. Singh, G.; Beidaghy Dizaji, H.; Puttuswamy, H.; Sharma, S. Biogenic nanosilica synthesis employing agro-waste rice straw and its application study in photocatalytic degradation of cationic dye. *Sustainability* **2022**, *14*, 539. [CrossRef]
20. Yan, S.; Yin, D.; He, F.; Cai, J.; Schliermann, T.; Behrendt, F. Characteristics of smoldering on moist rice husk for silica production. *Sustainability* **2022**, *14*, 317. [CrossRef]
21. Park, J.Y.; Gu, Y.M.; Park, S.Y.; Hwang, E.T.; Sang, B.-I.; Chun, J.; Lee, J.H. Two-stage continuous process for the extraction of silica from rice husk using attrition ball milling and alkaline leaching methods. *Sustainability* **2021**, *13*, 7350. [CrossRef]
22. Mlonka-Mędrała, A.; Magdziarz, A.; Gajek, M.; Nowińska, K.; Nowak, W. Alkali metals association in biomass and their impact on ash melting behaviour. *Fuel* **2020**, *261*, 116421. [CrossRef]
23. James, A.; Thring, R.; Helle, S.; Ghuman, H. Ash Management Review—Applications of Biomass Bottom Ash. *Energies* **2012**, *5*, 3856–3873. [CrossRef]

24. Khan, A.A.; de Jong, W.; Jansens, P.J.; Spliethoff, H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Process. Technol.* **2009**, *90*, 21–50. [[CrossRef](#)]
25. Beidaghy Dizaji, H.; Zeng, T.; Hartmann, I.; Enke, D.; Schliermann, T.; Lenz, V.; Bidabadi, M. Generation of high quality biogenic silica by combustion of rice husk and rice straw combined with pre- and post-treatment strategies—A review. *Appl. Sci.* **2019**, *9*, 1083. [[CrossRef](#)]
26. Shen, Y. Rice husk silica derived nanomaterials for sustainable applications. *Renew. Sustain. Energy Rev.* **2017**, *80*, 453–466. [[CrossRef](#)]
27. Pode, R. Potential applications of rice husk ash waste from rice husk biomass power plant. *Renew. Sustain. Energy Rev.* **2016**, *53*, 1468–1485. [[CrossRef](#)]
28. Zareihassangheshlaghi, A.; Beidaghy Dizaji, H.; Zeng, T.; Huth, P.; Ruf, T.; Denecke, R.; Enke, D. Behavior of Metal Impurities on Surface and Bulk of Biogenic Silica from Rice Husk Combustion and the Impact on Ash-Melting Tendency. *ACS Sustain. Chem. Eng.* **2020**, *8*, 10369–10379. [[CrossRef](#)]
29. Mugadza, K.; Stark, A.; Ndungu, P.G.; Nyamori, V.O. Effects of ionic liquid and biomass sources on carbon nanotube physical and electrochemical properties. *Sustainability* **2021**, *13*, 2977. [[CrossRef](#)]
30. Chan, K.Y.; van Zwieten, L.; Meszaros, I.; Downie, A.; Joseph, S. Using poultry litter biochars as soil amendments. *Soil Res.* **2008**, *46*, 437. [[CrossRef](#)]
31. Schmidt, H.-P.; Kammann, C.; Niggli, C.; Evangelou, M.W.H.; Mackie, K.A.; Abiven, S. Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant growth, nutrient uptake, plant health and grape quality. *Agric. Ecosyst. Environ.* **2014**, *191*, 117–123. [[CrossRef](#)]
32. Bachmann, H.J.; Bucheli, T.D.; Dieguez-Alonso, A.; Fabbri, D.; Knicker, H.; Schmidt, H.-P.; Ulbricht, A.; Becker, R.; Buscaroli, A.; Buerge, D.; et al. Toward the standardization of biochar analysis: The COST Action TD1107 Interlaboratory Comparison. *J. Agric. Food Chem.* **2016**, *64*, 513–527. [[CrossRef](#)]
33. Hagemann, N.; Joseph, S.; Schmidt, H.-P.; Kammann, C.I.; Harter, J.; Borch, T.; Young, R.B.; Varga, K.; Taherymoosavi, S.; Elliott, K.W.; et al. Organic coating on biochar explains its nutrient retention and stimulation of soil fertility. *Nat. Commun.* **2017**, *8*, 1089. [[CrossRef](#)]
34. Joseph, S.; Cowie, A.L.; van Zwieten, L.; Bolan, N.; Budai, A.; Buss, W.; Cayuela, M.L.; Graber, E.R.; Ippolito, J.A.; Kuzyakov, Y.; et al. How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. *GCB Bioenergy* **2021**, *13*, 1731–1764. [[CrossRef](#)]
35. Frikha, K.; Limousy, L.; Arif, M.B.; Thevenin, N.; Ruidavets, L.; Zbair, M.; Bennici, S. Exhausted grape marc derived biochars: Effect of pyrolysis temperature on the yield and quality of biochar for soil amendment. *Sustainability* **2021**, *13*, 11187. [[CrossRef](#)]
36. Bachmaier, H.; Kuptz, D.; Hartmann, H. Wood ashes from grate-fired heat and power plants: Evaluation of nutrient and heavy metal contents. *Sustainability* **2021**, *13*, 5482. [[CrossRef](#)]
37. Mayer, B.K.; Baker, L.A.; Boyer, T.H.; Drechsel, P.; Gifford, M.; Hanjra, M.A.; Parameswaran, P.; Stoltzfus, J.; Westerhoff, P.; Rittmann, B.E. Total value of phosphorus recovery. *Environ. Sci. Technol.* **2016**, *50*, 6606–6620. [[CrossRef](#)] [[PubMed](#)]
38. Bagheri, M.; Öhman, M.; Wetterlund, E. Techno-economic analysis of scenarios on energy and phosphorus recovery from mono- and co-combustion of municipal sewage sludge. *Sustainability* **2022**, *14*, 2603. [[CrossRef](#)]
39. Oehmichen, K.; Thrän, D. Fostering renewable energy provision from manure in Germany—Where to implement GHG emission reduction incentives. *Energy Policy* **2017**, *110*, 471–477. [[CrossRef](#)]
40. Oehmichen, K.; Majer, S.; Thrän, D. Biomethane from manure, agricultural residues and biowaste—GHG mitigation potential from residue-based biomethane in the European transport sector. *Sustainability* **2021**, *13*, 14007. [[CrossRef](#)]