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CALL

Doktorandenprogramm des BMEL mit der Islamischen Republik Iran

Irasil: Ash-related aspects during the thermo-chemical conversion of leached silicon rich biomass assortments for the production of heat and power and the combined transformation into valuable inorganic multipurpose chemical compounds

country/countries	Germany, Iran
funding agency	Federal Ministry of Food and Agriculture – BMEL
project management	Federal Office for Agriculture and Food – BLE
project coordinator	DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH
project partner(s)	University of Leipzig, Institute of Chemical Technology, Faculty of Chemistry and Mineralogy, Professorship Chemical Reaction Engineering Iran University of Science and Technology (IUST), School of Mechanical Engineering

project budget	136.282,47 €
project duration	01.01.2018 – 30.06.2021
key words	Rice straw, rice husks, combustion, biogenic silica, ash
background	Despite Iran's current role as one of the leading oil exporting countries, the present trend of rising energy consumption and the depletion of fossil resources is expected to stimulate an increase of renewable energy consumption from currently 2% to 38% in 2030. Beside solar, hydrothermal and wind energy generation, bioenergy production, in particular the exploitation and valorization of agricultural side products and biogenic residues will play an important role to enable this sustainable development which, consequently, will accompany and contribute to the modernization of the Iranian agricultural sector. The core of the project is an innovative added value approach to improve the efficiency of the biomass use along the whole supply chain and to establish both sustainable agricultural processes (e.g. use of fertilizer), provide climate-neutral energy especially in (remote) rural regions and convert agricultural residues into basic materials (e.g. amorphous silica) for multiple advanced applications, e.g. as catalyst support. Thus, scientific prognoses about conversion parameters and control settings are needed to guarantee the desired and challenging quality of the silica rich bottom ash products for material use.
objective	In order to investigate ash-related aspects during combustion of silica-rich biomass fuels (i.e. rice husk (RH) and rice straw (RS) in particular), the following specific aims will be addressed: • Clarification of the effect of fuel pre-treatment and combustion parameters on the quality of biogenic silica and the bottom ash slag formation by a comprehensive literature review and a systematic experimental investigation. • Clarification of the bottom ash transformation mechanism with respect to macroscopic and microscopic aspects and the role of different ash forming elements on the ash transformation reactions. • Prediction of slag formation and biogenic silica quality using thermodynamic equilibrium calculations, relevant fuel indexes defined from chemical composition of the fuel ashes, and the ash viscosity calculations.
results	The results of the project have been published in several peer-reviewed papers: • H. Beidaghy Dizaji, T. Zeng, I. Hartmann, D. Enke, T. Schliermann, V. Lenz, M. Bidabadi, Generation of high-quality biogenic silica by com-

bustion of rice husk and rice straw combined with pre- and post-treatment strategies – A review, Applied Sciences 9 (2019) 1083. https://doi.org/10.3390/app9061083.

- A. Zareihassangheshlaghi, H. Beidaghy Dizaji, T. Zeng, P. Huth, T. Ruf, R. Denecke, D. Enke, Behavior of Metal Impurities on Surface and Bulk of Biogenic Silica from Rice Husk Combustion and the Impact on Ash-Melting Tendency. ACS Sustainable Chemistry & Engineering 8 (2020) 10369–10379. https://doi.org/10.1021/acssuschemeng.0c01484.
- H. Beidaghy Dizaji, T. Zeng, H. Hölzig, J. Bauer, G. Klöß, D. Enke, Ash transformation mechanism during combustion of rice husk and rice straw, Fuel 307 (2022) 121768. https://doi.org/10.1016/j.fuel.2021.121768.
- H. Beidaghy Dizaji, T. Zeng, D. Enke, New fuel indexes to predict ash behavior for biogenic silica production, Fuel, 122345, In Press. https://doi.org/10.1016/j.fuel.2021.122345.

The main scientific and technical results of the project and the main experience gained can be summarized as follows:

- Compared to chemical fuel pre-treatment, the application of fuel blends is limited to mitigate slag formation in the ash and the production of biogenic silica with high quality. However, depending on the biomass fuel, different fuel pre-treatments have to be applied. For rice straw, leaching with citric acid is more effective, while for rice husks, pretreatment with water is sufficient to improve silica quality and avoid ash slagging. It was also found that deionized water should be used instead of tap water to avoid the risk of Ca impurities in the ash matrix.
- The purity and specific surface area and of the biogenic silica from the combustion of the leached rice husks allows the application for medical applications, such as drug delivery.
- Below a crystalline content in the ash of about 10 wt.%, the conversion temperature as well as the type of fuel pretreatment affect the quality of the biogenic silica. Therefore, to produce high quality biogenic silica, the crystalline fraction of the ash should be kept below this threshold.
- To ensure a high quality of the biogenic silica, two-stage combustion processes with dedicated control of the combustion temperature should be applied to avoid slagging in the ash and crystalline phases.
- Prediction of ash melting behavior based on characteristic ash melting temperatures is limited. Through thermodynamic equilibrium calculations and calculation of ash viscosity, detailed predictions of ash slagging and chemical composition can be made.
- Likewise, the newly defined fuel index (K+Na+Mg)/P [mol/mol] offers a high potential to classify the slagging behavior of the ashes and the purity of the biogenic silica.

recommendations	Future lab-scale investigations should consider the following aspects: • The use of further analytical techniques (e.g., RAMAN, XPS, or EDX) in conjunction with image processing methods and artificial intelligence may provide further insight into the properties of biogenic silica. • Modeling the ash behavior with molecular dynamic simulation models can be beneficial to identify the ash melting behavior of problematic phases. • The developed Python code provides a good starting point for further development of fuel indices. For this purpose, large data sets should be used that take into account other potential silica-rich biomass fuels such as oat and spelt husks. It is recommended that transferability to laboratory and industrial scale combustion systems will also be investigated. • Since the viscosity models do not take P2O5 into account, experimental investigations are required to establish a viscosity database including synthetic oxide systems with P2O5. Thus, the viscosity models can represent the ashes more realistically in the future. • An optimization of the chemical fuel pre-treatment with respect to temperature, time and acid concentration is necessary, since this has a considerable influence on the slag formation in the ash and the quality of the biogenic silica. The following aspects can be considered in future research for technical upscaling of the process: • Technical upscaling of the chemical fuel pre-treatment and densification of the fuel should be considered to enable application in small- and medium-sized combustion plants. • The whole supply chain should be analyzed using a life cycle analysis (LCA) to evaluate sustainability aspects. • From a practical point of view, fixed-bed combustion plants using untreated Si-rich biomass fuels should be redesigned as a two-stage combustion process to avoid carbon fixation in the ash matrix. Thus, the organic matter is decomposed before the ash is melted due to a high potassium content. Thus, carbon fixation is avoided and a high quality biogenic silica can be obtained. Fuel pre-treatment with water can be applied to dissolve the potassium from the fuels prior to combustion and to avoid carbon fixation due to ash melting caused by the K-silicates. • The combustion of Si-rich biomasses in large-scale plants should be investigated using CFD simulations to avoid a combustion temperature above 900 °C, which leads to crystallization in the ash.

photos

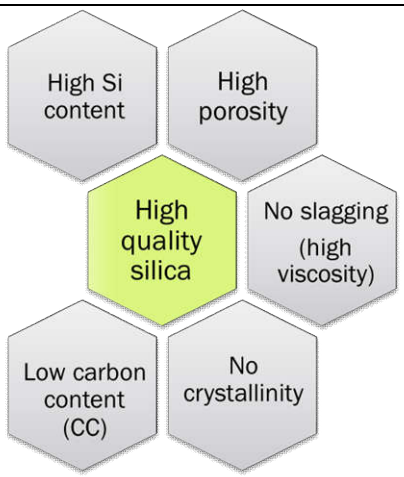

Figure 1. Parameters which are determining high quality biogenic silica.

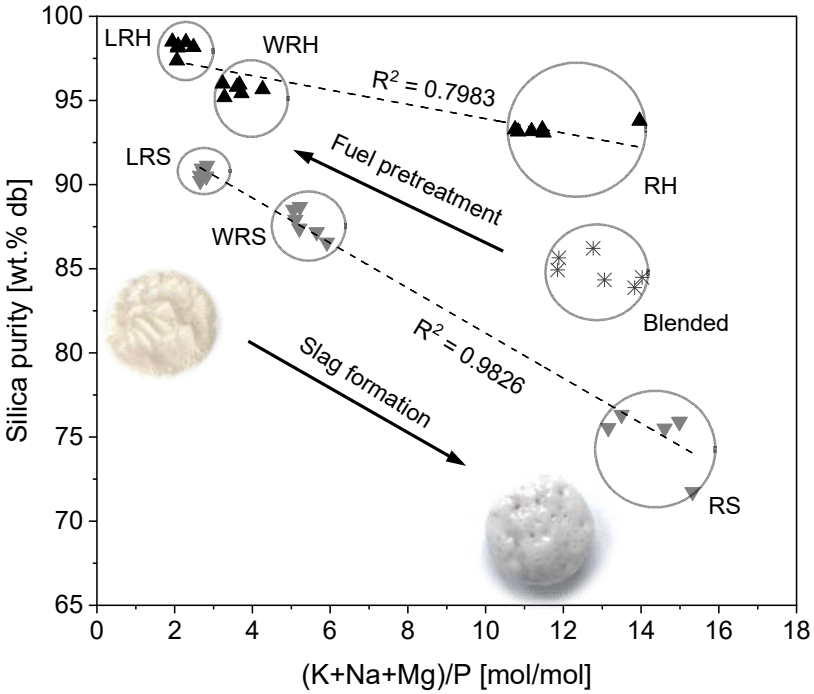

Figure 2. Silica purity as a function of selected new fuel index. Abbreviations: acid-leached rice husk (LRH), acid-leached rice straw (LRS), rice husk (RH), rice straw (RS), blended 50 wt.% db rice straw with 50 wt.% db rice husk (50RS-50RH), water-washed rice husk (WRH), water-washed rice straw (WRS).