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Combustion of Seaweed – a Fuel Design Strategy

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A B S T R A C T

The high ash content and varying ash composition in algal biomass is often mentioned as problematic if to be used for thermal energy conversion. This paper suggests an approach where detailed information on ash composition and predicted ash formation reactions are basis for successful remedies enabling the use of fuels considered to be difficult. The procedure is demonstrated on seaweed (*Saccharina latissima*) cultivated for biorefinery purposes. The ash composition of the seaweed was found suitable for co-combustion with *Miscanthus x giganteus*, an energy crop high in alkali and silicon. Fuel mixtures were combusted in a bubbling fluidized bed reactor and ash samples were analyzed by SEM-EDS and XRD. The results showed that Ca from the seaweed was very reactive and thus efficient in solving the silicate melting problems. The fuel design approach was proven successful and the potential for using otherwise difficult seaweed fuels in synergetic co-combustion was demonstrated.

1 Introduction

Seaweed based biorefineries are emerging worldwide aiming at producing renewable chemicals and energy carriers from macroalgae growing in the ocean. An important aspect to fully utilize the potential of the seaweed is to optimize the energy efficiency. From this perspective,

thermochemical energy conversion steps such as combustion or gasification are good candidates since they usually offer higher overall efficiencies compared to other processes. The organic composition of the fuel fed into these processes is generally not a limiting factor; it is rather the inorganic composition that may lead to problems in combustion or gasification due to formation of ashes with problematic properties. For this reason, seaweed has often been considered unsuitable for use in such processes due to its typically high ash content and high levels of NaCl compared to more traditional fuels. [1-3] For algal biomasses such as seaweeds there are currently few studies published that details ash composition [4, 5]. Existing literature reports heterogeneous and high concentrations of ash forming elements with higher molar ratios of Mg/Ca and Na/K, as well as higher Cl contents, than what is typically found in terrestrial biomass [4, 5]. These differences are explained by the living conditions of algae and their adaptation to it. Therefore, it is important to characterize and understand what properties of algal biomass that may be problematic or beneficial if such biomasses are to be introduced in the current energy system.

The traditional solid fuels are generally land-based and mostly comprised by biomass and coal which have been the subjects of research studies for decades in case of the former, and more than a century for the latter. The research conducted during this time has demonstrated the importance of analysing the ash forming elements and understanding their effect on how a fuel will perform when used in thermochemical energy conversion processes. This characterization has also revealed a large variation in composition of ash forming elements found in both coal and biomass. [6, 7] If these inherent variations are not considered, operational-related problems such as slagging, fouling, or deposit formation may occur upon their inclusion in a fuel feedstock, causing extra maintenance or in the worst case, unscheduled or emergency plant shutdowns.

Fuel design is a general approach to fuel characterization and blending primarily developed for biomass combustion that attempts to predict, reduce, and possibly avoid such expensive operational-related issues caused by unfavourable ash transformation reactions.[8, 9] The

starting point is to consider the total ash composition for a certain biomass by grouping elements forming positively charged metal ions acting as Lewis acids (K, Na, Ca, Mg, Fe, Al) and negatively charged molecular (Si, P, S) or atomic ions (Cl) acting as Lewis bases in reactions taking place during combustion. The relative concentrations of these main ash forming elements are considered in relation to fundamental knowledge about ash transformation reactions to predict what – if any – operational problems that may occur, and if necessary devise a strategy to change the total ash composition to promote more favourable ash transformation reactions. These changes will typically include choosing an additive, or more preferably by including another biomass as a co-combustion fuel that will remedy the issues presented by the evaluated fuel.[8] This fuel design approach has been applied to provide a reaction-based approach to ash chemistry, something that is lacking in conventional fuel indices[10] or in the use of thermodynamic equilibrium calculations[9]. The co-combustion approach can be used to promote the use of potentially problematic biomass fuels together with other biomass or suitable waste streams [11] to increase the renewable fuel feedstock available to replace fossil fuels. Once a strategy is developed to deal with improving ash quality or reduce potential ash-related problems from the fuel perspective, further optimization through process parameters are likely to be more cost-effective together with considerations such as pre-treatments or process integration of fuel blending.

The objective of this study was to demonstrate the use of seaweed biomass in thermochemical energy conversion processes using a fuel design strategy. This was achieved by thorough fuel characterization of seaweed based on ash composition, determining suitable additive or co-combustion fuel if necessary, and validating the suggested fuel blend in combustion experiments.

2 Materials and Methods

2.1 Seaweed preparation

The seaweed biomass was obtained from a cultivation of the brown macroalgae *Saccharina*

latissima. The algae were cultivated at 2 m depth on the west coast of Sweden (N 58°51.54, NE 11°04.06) from November 2014 and harvested in June 2015. The harvested biomass was stored and refrigerated for 7 days before further treatment. A washing procedure was employed where batches of approximately 50 kg of whole-plant seaweed was placed in a round 100 l vessel (radius 240 mm). Cold tap water was fed from below at 15 l/min aiming at a plug-flow type of washing. Channelling and stagnation zones were avoided by intermittent stirring approximately once every minute, causing some back-mixing and thus deviation from ideal plug flow. After 30 minutes, the effluent looked clean and the washing was stopped. The seaweed was analyzed with standard fuel analysis for lower heating value (LHV) and ash content (EN 15148:2009/15402:2011, EN 14918:2010/15400:2011), main elements C, H, N, O (EN 15104:2011/15407:2011), and detailed analysis of main ash forming elements (EN 187185, 187177, and ICP-AES analysis of elements dissolved in LiBO₂/HNO₃). The fuel compositions of un-treated and washed seaweed can be found with main elements in Table 1 and main ash forming elements in Figure 1 where the removal of water-soluble alkali chloride salts by washing is clearly noticeable. The washed seaweed was dried in a drying cabinet at 70 °C for four days prior to fuel preparation. A temperature of 105 °C is typically used for analytical drying of biomass, but in this case a lower temperature was selected to avoid degradation and volatilization of fuel components. The dry seaweed was prepared for pelletizing by milling with a cutting mill to 4 mm sieve size.

Table 1 Fuel composition of seaweed before and after washing.

	Seaweed, as received	Washed seaweed
LHV (MJ/kg, ds)	9.3	13.9
Ash (wt%,ds)	45.7	35.9
C (wt%,ds)	26.9	38.1
H (wt%,ds)	3.4	4.9
N (wt%,ds)	6.0	3.8
O (wt%,ds)	19.6	16.4

Figure 1 Fuel fingerprint of the main ash-forming elements in seaweed before and after washing.

2.2 Determining a fuel design strategy for seaweed

The balance between main ash forming elements in seaweed before and after washing was evaluated based on the relative abundance of elements shown in the “fuel fingerprint” (Figure 1). The high concentrations of K, Na, and Cl in unwashed seaweed makes it an unsuitable candidate for direct use in thermochemical energy conversion due to the high risk of alkali chloride-related operational problems [12]. The high Ca content in the washed seaweed could be considered non-problematic since Ca does not in general cause issues with regards to melt formation or problematic deposit formation in biomass combustion. On the contrary, this fuel characteristic could be useful in fuel design for using washed seaweed as a synergetic co-combustion fuel together with other biomass where adding Ca may prevent or remedy ash-related problems. Adding Ca is typically beneficial for improving ash properties of fuels that upon combustion form K-silicates with low melting points. For such fuels, addition of Ca through various sources increases the ash melting temperature primarily by changing what compounds are formed in the K_2O – CaO – SiO_2 system [13–15]. Further, the high ash content of washed seaweed (35.9 wt%, Table

1) suggests that adding seaweed to a fuel blend even at low blend ratios will have a large impact on the total ash composition.

However, evaluating the suitability of the washed seaweed as fuel based only on its Ca content is not enough; the entire inorganic composition needs to be considered. Replacing K with Ca in silicates to reduce issues with melt formation may at the same time contribute to volatilization of gaseous alkali compounds through tertiary ash transformation reactions [8], potentially causing an increased formation of volatilized alkali compounds. The washed seaweed had a relatively high S content in relation to alkali which could potentially counteract some of this chloride formation, provided that the gaseous SO_2/SO_3 reacts with KOH and/or NaOH to form less harmful alkali sulphates [16].

The characteristics of the washed seaweed suggested that it was a suitable fuel for co-combustion to improve combustion properties of biomass fuels that are expected to form the problematic K-silicates mentioned above. One such fuel is *Miscanthus* (*Miscanthus x giganteus*), a fast growing energy crop which is known for having a problematic ash composition [17]. In particular, its typically high content of Si, K, and Na readily leads to the formation of low temperature melting K/Na-silicates during combustion, directly affecting process efficiency.

2.3 Resulting fuel blends

Fuel blends with *Miscanthus* were prepared aiming to ensure a surplus of Ca compared to alkali, with total $\text{Ca}/(\text{K}+\text{Na})$ molar ratios of 1.5 and 3 (Figure 2). These values corresponded to fuel blends with 4 wt% and 14 wt% seaweed fractions, respectively, where the 14 wt% seaweed blend contained enough S to potentially reduce alkali chloride formation compared to pure *Miscanthus*. To further investigate the efficiency of Ca present in washed seaweed compared to conventional mineral-based Ca additives, *Miscanthus* was also blended with mineral CaCO_3 (<30 μm particles, Sigma-Aldrich) to reach equal levels of Ca additive as introduced by washed seaweed.

Figure 2 Fuel fingerprint of the main ash-forming elements for Miscanthus and the four fuel blends.

The total ash compositions are plotted in the ternary phase diagram of K_2O – CaO – SiO_2 (Figure 3) to illustrate how the addition of Ca at the selected levels may affect the melting point of silicates formed in the ash. This is a critical parameter for determining potential slagging issues. The position of Miscanthus fuel ash composition in the phase diagram is connected to a eutectic point at $\sim 740^\circ C$ through peritectic points. To avoid premature defluidization the process target temperature was set at a maximum of $720^\circ C$ for all experiments. At such low temperatures there is an elevated risk that Ca additives bond to S in sulphates instead of K and Na where higher process temperatures are more likely to either decompose $CaSO_4$ or possibly form $Ca_2K_2(SO_4)_3$, bonding some alkali in sulphates. However, it was required to allow longer periods of combustion for the Miscanthus reference fuel.

Figure 3 Fuel compositions for *Miscanthus* (triangle), with 4% seaweed (circle), 14% seaweed (square), low CaCO_3 addition (diamond) and high CaCO_3 addition (cross) shown in the K_2O – CaO – SiO_2 phase diagram, adapted from Figure 23 in *Silicate Melt Systems, Physics and Chemistry of the Earth* [18]. Total concentration of $\text{CaO}+\text{MgO}$ and $\text{K}_2\text{O}+\text{Na}_2\text{O}$ were plotted as CaO and K_2O , respectively.

2.4 Combustion experiments

The combustion tests were performed in an electrically heated bench-scale (5 kW) bubbling fluidized bed (Figure 4), a thorough description of the reactor is to be found elsewhere [19]. The fluidized bed combustion technique allows well-controlled bed temperatures which facilitate studies investigating changes in the potential for silicate melt formation. Olivine was selected as bed material since it is known to be less susceptible to reactions with gaseous alkali compounds than quartz [20, 21], the most commonly used bed material today. For all experiments, both the primary and secondary air flows were set to 40 l/min and 540 g of olivine bed particles with a sieving diameter size of 200–250 μm comprised the bed. All tests were performed with the electrically heated reactor temperature set to 700 °C, a temperature chosen to avoid total bed defluidization induced by alkali silicate melt formation according to Figure 3. The tests lasted for

6 h with a fuel feed of 500-600 g fuel/h with fuel gas levels of O₂ at 10±2 vol% and CO levels <20 ppm indicating stable combustion.

After this time period, a bed sample was extracted from the hot bed (sampling point A). An air-cooled (450 °C) deposition probe was introduced in the freeboard section of the reactor (sampling point C) to simulate a heat exchanger surface. The exposure time for the deposition probe was 4.5 hours under stable operation. Particulate matter, fly ash and entrained bed material larger than 10 µm was trapped in a cyclone situated directly after the freeboard sections (sampling point D). Particulate matter <10 µm was collected in a pre-heated 13-stage Dekati® low-pressure cascade impactor (DLPI, sampling point F) during 5-10 min depending on the prevailing combustion performance and fuel blend. The flue gas concentrations of CO, CO₂, SO₂, NO, NO₂, and HCl were continuously monitored using a Gasmeter DX-4000 Fourier transform infrared spectroscopy (FTIR, sampling point E) which also was used to monitor O₂. The reactor was allowed to cool to room temperature prior to sampling of cyclone ash (sampling point C). Combustion of Miscanthus and blends with CaCO₃ formed wall deposits that were collected from sampling point B after cooling, an ash fraction which is not normally present during biomass combustion.

Figure 4 Schematic overview of the reactor system with sampling points indicated: A) bed ash, B) wall deposits, C) deposition probe, D) cyclone ash, E) flue gas composition, F) particulate matter.

2.5 Analysis of ash fractions

The chemical composition of bed ash, deposits, cyclone ash, and submicron particulate matter (PM₁) from stage 2-5 on the impactor were analyzed using a Carl Zeiss Merlin field emission scanning electron microscope (SEM) combined with an energy-dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments X-MAX 80 mm²). The samples were mounted on carbon tape and average elemental concentrations of main ash forming elements were determined based on three area analyses for each ash fraction. A Bruker-AXS D8Advance X-ray diffractometer using Cu-K α radiation and a Văntec-1 detector with continuous rotating scans was used to collect diffractograms which were later evaluated with Diffraction EVA 4.2 with PDF-2 database for identification of crystalline phases in seaweed before and after washing, and ash fractions. Rietveld refinement was performed using Bruker TOPAS 4.2 software and reference crystal structures obtained from ICSD Web to provide semiquantitative analysis of compounds and estimate crystallite sizes in specific cases.

3 Results & Discussion

3.1 Seaweed fuel characterization

The seaweed blades used in this study were partly covered by fouling organisms, identified as the lace-like structures formed by colonies of Bryozoa (moss animals). The bryozoans were identified as *Electra pilosa* and *Membranipora membranacea* by the cell geometries of the exoskeleton tubes (Figure 5b), and these are normally settling and found during summer months [22]. The encrusting fouling layer is well known for causing damage to the kelp leaves, reducing growth and productivity for the seaweed [22] [23]. It consists of mineralized calcium, present as CaCO₃, comprising the walls enclosing each bryozoan individual within a colony [24, 25]. Together these walls form a clearly visible distinct pattern (Figure 5b), which was further characterized by SEM-EDS (Figure 5c-f). The presence of calcium in the walls was highlighted by elemental mapping (Figure 5d,f). The chemical speciation of crystalline calcium compounds was identified by X-ray

diffraction as being primarily dominated by magnesian calcite ($\text{Ca}_{0.9}\text{Mg}_{0.1}\text{CO}_3$ [26]) with only a minor share of biogenic aragonite (CaCO_3 [27]). No crystalline calcite grains similar to those in the mineral case (Figure 5a) could be observed by SEM analysis at the resolution reached here (Figure 5f). This observation, together with a calculated crystallite size of 40 nm (LVol-IB) as obtained from Rietveld refinement, indicated that calcite in seaweed with bryzoans has a higher surface area compared to that of CaCO_3 in the mineral based additive (Figure 5a). It is therefore likely that the Ca in seaweed will be more reactive than Ca from mineral additives in ash transformation reactions during combustion.

Figure 5 a) Scanning electron micrograph of crystalline CaCO_3 powder (BSE mode), b) Photography of bryozoan colonies on the seaweed, c) and e) Scanning electron micrograph of bryozoan colonies on the seaweed at different magnifications, d) and f) EDS elemental Ca mapping from c and e.

The washing process is a necessary step for improving the fuel properties of this seaweed enough for the material to be considered a candidate for the fuel design approach to thermochemical energy conversion applications. The unwashed seaweed was concluded unsuitable for combustion due to the risk of fouling and deposition caused by its high concentrations of K, Na, and Cl (Figure 1). The plug-flow type washing procedure applied efficiently reduced the total ash content from 45.7 wt% to 35.9 wt% and lead to an increase in LHV by 49 %, going from 9.3 MJ/kg_{ds} to 13.9 MJ/kg_{ds} (Table 1). The loss of K, Na, and Cl shown in Figure 1 was further studied by powder X-ray diffraction to determine crystalline compounds in seaweed. No crystalline chlorides were found in the seaweed after washing and the remaining K, Na, and Cl were probably intrinsic to the seaweed or Bryozoans. The apparent increase of the elements Ca and Si (Figure 1) is explained by their presence in structures of low water solubility, and after washing they comprised a larger share of the remaining fuel and ash forming elements.

3.2 *Combustion experiments*

Miscanthus combustion in the fluidized bed high-lighted some of the issues associated with this energy crop when used in energy conversion processes. Biomasses with total ash compositions located in this region of the ternary phase diagram (Figure 3) have been identified as having major slagging tendencies [10]. This is in part due to the secondary ash transformation reaction between gaseous KOH and SiO₂, which leads to initial melts with a K₂O–CaO–SiO₂ composition of 1:0:4 forming at a temperatures close to ~ 740 °C (Figure 3). Only small amounts of ash could be recovered as bed ash particles from the hot bed (sampling point A, Figure 4), which is highly unusual in combustion of biomass with a similar ash content. As can be seen in Figure 6a, the composition of these particles was dominated by K and Si supporting the conclusion that alkali-silicates were formed. These alkali-silicate melts contained embedded olivine bed grains but little to no reaction was observed between ash and bed material. Most of the ash forming elements were found in wall deposits (sampling point B, Figure 4). This implies that the low-density fuel particles of Miscanthus were largely entrained and burned out in the freeboard, forming ash

particles with alkali-silicate melts that subsequently stuck to the reactor wall rather than falling down into the bubbling bed material. The formation of such wall deposits led to very low amounts of ash forming elements being present at the cooled deposit probe (sampling point C, Figure 4), in coarse fly ash captured in cyclone ash (sampling point D, Figure 4) and PM₁ (sampling point F, Figure 4). Analysis with SEM-EDS showed that the composition of cyclone ash was similar to that of bed ash particles (Figure 6b), and that lee-ward deposits (Figure 6c) and PM₁ (Figure 6d) were dominated by alkali chlorides with more alkali sulphates in PM₁. Miscanthus combustion displayed the potential for severe operational issues, both due to alkali-silicate formation leading to problematic melts and alkali chloride formation which could lead to fouling and corrosion.

Figure 6. Elemental compositions of the different ash fractions. a) bed ash (sampling point A), b) cyclone ash (sampling point D), c) deposit probe leeward side (sampling point C), and d) PM₁ (sampling point F).

The mineral additive did not alleviate these deposition issues to any large extent; rather the additive was included in the wall deposits and identified as a separate compound both in deposits and cyclone ash with XRD. There was slightly more bed ash remaining in the bed for the high CaCO₃ additive case, suggesting some effect of the mineral additive on the entrainment of sticky

alkali-silicates particles. SEM-EDS analysis showed higher Ca content in bed ash particles and with some S present in the high CaCO_3 case (Figure 6a). The mineral additive was observed as unreacted CaCO_3 both on the deposition probe and in the cyclone ash which contributes to the elevated Ca concentrations for both additive levels (Figure 6b,c). This suggests that some of the additive was entrained rather than decomposing into CaO(s) and $\text{CO}_2(\text{g})$. The amount of alkali sulphates in PM_{10} as detected by XRD was reduced with low CaCO_3 addition and completely absent with high addition of CaCO_3 leaving the PM_{10} dominated by alkali chlorides, further supported by SEM-EDS (Figure 6d). This implies formation of $\text{CaSO}_4(\text{s})$ through reaction of CaO(s) from the additive with gaseous SO_2/SO_3 , which reduced the amount of S available to form alkali sulphates. The mineral additive alone did not change the ash distribution properties of *Miscanthus* enough to be considered a possible remedy to enable more extensive use of this energy crop in the experimental setup used here.

Co-combustion with seaweed improved the ash distribution to produce bed ash particles at levels normal for biomass combustion, even at the low seaweed admixing level of 4% (Figure 6a). The relative K concentration in bed ash particles was heavily reduced whereas the concentrations of Ca and to some extent Na increased. S was also identified in bed ash for the high algae case, possibly indicating formation of $\text{CaSO}_4(\text{s})$ or other Ca-containing sulphates. The abundance of bed ash particles correlated with a heavy reduction of wall deposits, especially for the high algae fuel blend despite the higher ash content in this fuel blend. The composition of cyclone ash (Figure 6b) resembles that of bed ash particles, but the higher concentration of Ca and lower Si concentration for the high algae fuel blend may indicate that some of the bryozoan exoskeletons have been entrained during combustion. The total alkali (K+Na) concentration were somewhat lower in lee-side deposits (Figure 6c) and PM_{10} (Figure 6d) with algae addition than for *Miscanthus*. The S content was reduced for the high algae case coupled with higher Cl in PM_{10} , which further suggests formation of $\text{CaSO}_4(\text{s})$ in coarser ash fractions. This would suggest that further measures may need to be implemented to avoid alkali chloride-dominated deposits,

where a co-combustion fuel allowing for higher process temperatures could be one important step. Higher temperatures may reduce the formation of $\text{CaSO}_4(\text{s})$ in bed ash which would leave gaseous SO_2/SO_3 to form alkali sulphates instead.

The fuel design strategy for co-combustion of seaweed with *Miscanthus* did remedy issues with problematic alkali-silicate melt formation observed for the *Miscanthus* case. Furthermore, the CaCO_3 present in biogenic calcite observed in the seaweed used in this design strategy proved more reactive than what was the case for the mineral-based CaCO_3 additive. This is likely related to the larger surface area of the calcite deposited by bryozoans on the seaweed used in this study as shown in (Figure 5). At the relatively low process temperature used in the present work, the SO_2/SO_3 capture by $\text{CaO}(\text{s})$ introduced both with seaweed and with mineral led to higher relative concentrations of alkali chlorides in the deposits and PM_{10} formed. This may be remedied by secondary measures such as sulphur additives, but it is important to be aware of this draw-back if washed seaweed with biofouling is employed as a Ca-rich fuel. The flue gas composition changed towards higher HCl and slightly elevated NO_x levels (see Supplementary S2) with co-combustion of seaweed which may require increased flue gas cleaning measures in an industrial setting.

The results obtained here suggest that even if harvests from seaweed farms are contaminated by biofouling, they may still be useful in thermal energy conversion processes provided that their inorganic content is carefully considered. This is an important application of contaminated seaweed since biofouling is mostly negative for biorefining processes to recover biomass components. For seaweed without biofouling, or residuals from biorefineries, the fuel design approach would have taken another route after fuel analysis. The washed seaweed had other interesting properties from a thermochemical energy conversion point of view, such as a suitable S to Cl molar ratio for potential reduction of chloride formation without excess Ca present. A washing procedure will be necessary to reduce the alkali chloride concentrations prior to including the seaweed in fuel blends suggested by a fuel design approach.

4 Conclusions

A washing procedure of seaweed was used to remove alkali chlorides which enabled their use in combustion. Using a fuel design approach, the composition of seaweed with Ca-containing bryozoans was combined with that of the difficult fuel *Miscanthus* to avoid issues related to alkali-silicate melt formation during combustion. In the combustion experiments, the Ca from the seaweed was found more efficient than a mineral-based CaCO_3 additive to prevent the ash melting problems. Besides the synergetic co-combustion with *Miscanthus* performed here, this approach opens for system integration advantages such as a thermochemical step in future algal based biorefineries.

5 Supplementary information

Supplementary information contains tabular data for fuel analysis (S1) and flue gas measurements (S2), and XRD diffractograms for unwashed and washed seaweed (S3 a-b).

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7 References

- [1] A.B. Ross, J.M. Jones, M.L. Kubacki, T. Bridgeman, Classification of macroalgae as fuel and its thermochemical behaviour, *Bioresource Technology*, 99 (2008) 6494-6504.
- [2] A. Bruhn, J. Dahl, H.B. Nielsen, L. Nikolaisen, M.B. Rasmussen, S. Markager, B. Olesen, C. Arias, P.D. Jensen, Bioenergy potential of *Ulva lactuca*: Biomass yield, methane production and combustion, *Bioresource Technology*, 102 (2011) 2595-2604.
- [3] T.N. Trinh, P.A. Jensen, K. Dam-Johansen, N.O. Knudsen, H.R. Sørensen, S. Hvilsted, Comparison of Lignin, Macroalgae, Wood, and Straw Fast Pyrolysis, *Energy & Fuels*, 27 (2013) 1399-1409.

- [4] S.V. Vassilev, C.G. Vassileva, Composition, properties and challenges of algae biomass for biofuel application: An overview, *Fuel*, 181 (2016) 1-33.
- [5] K. Werner, P. Piotrowska, F. Gentili, M. Holmlund, C. Boman, M. Broström, Characterization of Thermochemical Fuel Properties of Microalgae and Cyanobacteria, in: *Impacts of Fuel Quality on Power Production* October 26-31, 2014 Snowbird Resort & Conference Center Snowbird, Utah, 2014.
- [6] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, T.J. Morgan, An overview of the organic and inorganic phase composition of biomass, *Fuel*, 94 (2012) 1-33.
- [7] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the chemical composition of biomass, *Fuel*, 89 (2010) 913-933.
- [8] N. Skoglund, Ash chemistry and fuel design focusing on combustion of phosphorus-rich biomass, in: *Thermochemical Energy Conversion Laboratory, Department of Applied Physics and Electronics, Umeå university, Umeå, 2014*, pp. 50.
- [9] D. Boström, N. Skoglund, A. Grimm, C. Boman, M. Öhman, M. Broström, R. Backman, Ash Transformation Chemistry during Combustion of Biomass, *Energy & Fuels*, 26 (2012) 85-93.
- [10] I.L. Näzelius, J. Fagerström, C. Boman, D. Boström, M. Öhman, Slagging in Fixed-Bed Combustion of Phosphorus-Poor Biomass: Critical Ash-Forming Processes and Compositions, *Energy & Fuels*, 29 (2015) 894-908.
- [11] N. Skoglund, L. Bäfver, J. Fahlström, E. Holmén, C. Renström, Fuel design in co-combustion of demolition wood chips and municipal sewage sludge, *Fuel Processing Technology*, 141, Part 2 (2016) 196-201.
- [12] M. Broström, Aspects of alkali chloride chemistry on deposit formation and high temperature corrosion in biomass and waste fired boilers, in, *Umeå University, Umeå, Sweden, 2010*.
- [13] D. Boström, A. Grimm, C. Boman, E. Björnbom, M. Öhman, Influence of Kaolin and Calcite Additives on Ash Transformations in Small-Scale Combustion of Oat, *Energy & Fuels*, 23 (2009) 5184-5190.
- [14] S.J. Xiong, J. Burvall, H. Orberg, G. Kalen, M. Thyrel, M. Ohman, D. Bostrom, Slagging characteristics during combustion of corn stovers with and without kaolin and calcite, *ENERG FUEL*, 22 (2008) 3465-3470.
- [15] B.M. Steenari, O. Lindqvist, High-temperature reactions of straw ash and the anti-sintering additives kaolin and dolomite, *Biomass and Bioenergy*, 14 (1998) 67-76.
- [16] M. Broström, H. Kassman, A. Helgesson, M. Berg, C. Andersson, R. Backman, A. Nordin, Sulfation of corrosive alkali chlorides by ammonium sulfate in a biomass fired CFB boiler, *Fuel Processing Technology*, 88 (2007) 1171-1177.
- [17] J. Kaknics, F. Defoort, J. Poirier, Inorganic Phase Transformation in Miscanthus Ash, *Energy & Fuels*, 29 (2015) 6433-6442.
- [18] E. Roedder, Silicate melt systems, *Physics and Chemistry of the Earth*, 3 (1959) 224-297.
- [19] M. Öhman, A. Nordin, A new method for quantification of fluidized bed agglomeration tendencies: A sensitivity analysis, *Energy & Fuels*, 12 (1998) 90-94.
- [20] M. Kuba, H. He, F. Kirnbauer, N. Skoglund, D. Boström, M. Öhman, H. Hofbauer, Mechanism of Layer Formation on Olivine Bed Particles in Industrial-Scale Dual Fluid Bed Gasification of Wood, *Energy & Fuels*, 30 (2016) 7410-7418.

- [21] M. Kuba, H. He, F. Kirnbauer, N. Skoglund, D. Boström, M. Öhman, H. Hofbauer, Thermal Stability of Bed Particle Layers on Naturally Occurring Minerals from Dual Fluid Bed Gasification of Woody Biomass, *Energy & Fuels*, 30 (2016) 8277-8285.
- [22] H. Førde, S. Forbord, A. Handå, J. Fossberg, J. Arff, G. Johnsen, K.I. Reitan, Development of bryozoan fouling on cultivated kelp (*Saccharina latissima*) in Norway, *Journal of Applied Phycology*, 28 (2016) 1225-1234.
- [23] C. Peteiro, Ó. Freire, Epiphytism on blades of the edible kelps *Undaria pinnatifida* and *Saccharina latissima* farmed under different abiotic conditions, *Journal of the World Aquaculture Society*, 44 (2013) 706-715.
- [24] R. Seed, R.J. O'Connor, Community organization in marine algal epifaunas, *Annual Review of Ecology and Systematics*, 12 (1981) 49-74.
- [25] S.R. Hall, P.D. Taylor, S.A. Davis, S. Mann, Electron diffraction studies of the calcareous skeletons of bryozoans, *J Inorg Biochem*, 88 (2002) 410-419.
- [26] P.L. Althoff, Structural Refinements of Dolomite and a Magnesian Calcite and Implications for Dolomite Formation in Marine-Environment, *American Mineralogist*, 62 (1977) 772-783.
- [27] B. Pokroy, J.S. Fieramosca, R.B. Von Dreele, A.N. Fitch, E.N. Caspi, E. Zolotoyabko, Atomic structure of biogenic aragonite, *Chemistry of Materials*, 19 (2007) 3244-3251.

Table 1 Fuel composition of seaweed before and after washing.

Figure 1 Fuel fingerprint of the main ash-forming elements in seaweed before and after washing.

Figure 2 Fuel fingerprint of the main ash-forming elements for Miscanthus and the four fuel blends.

Figure 3 Fuel compositions for Miscanthus (triangle), with 4% seaweed (circle), 14% seaweed (square), low CaCO_3 addition (diamond) and high CaCO_3 addition (cross) shown in the K_2O – CaO – SiO_2 phase diagram, adapted from Figure 23 in Silicate Melt Systems, Physics and Chemistry of the Earth (Roedder, 1959). Total concentration of $\text{CaO}+\text{MgO}$ and $\text{K}_2\text{O}+\text{Na}_2\text{O}$ were plotted as CaO and K_2O , respectively.

Figure 4 Schematic overview of the reactor system with sampling points indicated: A) bed ash, B) wall deposits, C) deposition probe, D) cyclone ash, E) flue gas composition, F) particulate matter.

Figure 5 a) Scanning electron micrograph of crystalline CaCO_3 powder (BSE mode), b) Photography of bryozoan colonies on the seaweed, c) and e) Scanning electron micrograph of bryozoan colonies on the seaweed at different magnifications, d) and f) EDS elemental Ca mapping from c and e.

Figure 6. Elemental compositions of the different ash fractions. a) bed ash (sampling point A), b) cyclone ash (sampling point D), c) deposit probe leeward side (sampling point C), and d) PM_{10} (sampling point F).