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### Combustion of seaweed – A fuel design strategy

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### ABSTRACT

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. © 2017 Elsevier B.V. All rights reserved.

### 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.

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http://dx.doi.org/10.1016/j.fuproc.2017.04.017 0378-3820/© 2017 Elsevier B.V. All rights reserved. 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

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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 wholeplant 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 min, 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, 187,177, and ICP-AES analysis of elements dissolved in LiBO<sub>2</sub>/HNO<sub>3</sub>). The fuel compositions of un-treated and washed seaweed can be found with main elements in Table 1 and main ash forming elements in Fig. 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.

### 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

Table I			
	Fuel compositi	n of seaweed befor	e 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

ds - dry substance.

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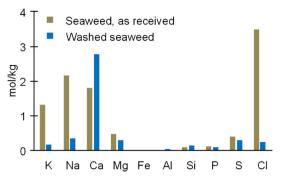


Fig. 1. Fuel fingerprint of the main ash-forming elements in seaweed before and after washing.

elements shown in the "fuel fingerprint" (Fig. 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 nonproblematic 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<sub>2</sub>O–CaO–SiO<sub>2</sub> 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<sub>2</sub>/SO<sub>3</sub> 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 Ca/(K + Na) molar ratios of 1.5 and 3 (Fig. 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<sub>3</sub> (<30  $\mu$ m particles, Sigma-Aldrich) to reach equal levels of Ca additive as introduced by washed seaweed.

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