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Preliminary understanding on the ash behavior of algae during co-gasification in an entrained flow reactor

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ABSTRACT

Algae are considered as a promising alternative fuel to produce energy due to its advantages such as high production yield, short growth cycle and flexible growing environment. Unfortunately, ash-related issues restrict its thermochemical utilization due to the high ash content and especially the high alkali metal concentration. In this paper, the gasification performance and ash behavior were experimentally analysed for three macro- and micro-algal species. Clear differences in the proximate and ultimate compositions were found between the cultivated algae used in this study and macroalgae (seaweed) harvested from the marine environments. Algal biomass generally contained higher Na and P contents than lignocellulosic biomass. Microalgae also had a relatively high mineral content due to the impurities in the harvesting process which included centrifugal pumping followed by sedimentation. Co-gasification of 20 wt% algae with softwood was investigated using an entrained flow reactor. The addition of both macroalgal species *Derbersia tenuissima* and *Oedogonium* to softwood had a limited influence on the gas yields and carbon conversion. On the other hand, the addition of the microalgal species *Scenedesmus* significantly decreased the main gas yields and carbon conversion. Moreover, the addition of algae clearly changed the residual ash composition of the base fuel. Finally, a preliminary understanding of the ash behavior of the tested algae blends was obtained through the analysis of the fuel ashes and the collected residual ashes. Fouling and corrosion were presumably occurred during the co-gasification of wood/macroalgae blends in view of the high alkali metal content. Microalga *Scenedesmus* had a high mineral content which could potentially capture the alkali metal in the ash and mitigate fouling when gasified with softwood. The growing environment and harvesting method were found to be significantly affecting the ash behavior implying the need for careful consideration regarding co-gasification process.

1. Introduction

Biomass is a carbon neutral renewable energy source which has the potential to replace fossil fuels in all areas of energy utilization, e.g. heat and electricity production, chemicals and liquid fuels synthesis [1]. Algae, including both microalgae and macroalgae, are considered as a promising alternative biomass to traditional terrestrial feedstocks to produce energy due to their high production yield, short growth cycle and flexible growing environment [2].

The harvested algae generally have a high moisture content as a result of cultivation conditions. Consequently, research of algae-to-energy has focused on anaerobic digestion [3,4], fermentation [5], hydrothermal liquefaction [6,7], and hydrothermal gasification [8] as these processes can successfully utilize feedstocks with a high moisture content. However, anaerobic digestion and fermentation usually need a long reaction time with a comparatively low conversion rate compared to thermochemical conversion methods [9]. Additionally, hydrothermal liquefaction/gasification technologies are currently immature,

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and considerable technical difficulties need to be overcome prior to broad industrial-scale application. On the other hand, the development of drying technologies and the proposition of integrated drying, gasification, and combined cycle electricity generation substantially decreases the need for external energy in the drying of algae [9,10]. This makes conventional gasification (hereafter referred to as gasification) a promising method considering its maturity, and reliability, in addition to the advantages of a high conversion efficiency and low reaction time.

Current gasification technologies mainly include fixed bed, fluidized bed and entrained-flow gasification [11]. Among them, entrained-flow technology has advantages of larger throughput, faster reaction rate and higher conversion efficiency compared to fixed bed and fluidized bed processes. During the conversion process, the inorganic species in the fuels tend to form molten substances and release to the gas phase under high temperature [12,13]. These gas phase inorganics subsequently condense on the colder parts of the system and cause operating problems such as fouling. Several studies [14–18] have been conducted to investigate the ash transformation and behaviors of inorganics during the entrained-flow biomass combustion and gasification with the aim of the alleviation of ash-related operating difficulties. These works generally focus on the woody biomass [16,18] and agricultural residues such as straw [15,17] and corn stover [15,18]. Entrained-flow gasification of straw [14] indicated that approximately 40% of K and 70% of Na in the fuel ash transformed into the gas phase at the operating temperature of 1200 °C. Simon Leiser et al. [15] found that most of K, Cl, and S are released into the gas phase and formed sub-micrometer particles < 0.5 μm during entrained flow gasification of straw and corn stover. In the case of corn stover, large fraction of K was retained in the ash/slag due to the abundance of aluminosilicates and lower Cl content in the fuel ash [15].

Algal biomass generally has a high ash and also alkali metal (both K and Na) content due to the specific cultivation environment and harvesting method [19]. Therefore, the ash content and composition of algae differs significantly from that of woody biomass and agricultural residues [20]. Different inorganic transformations and ash formation behaviors have been observed during the thermochemical conversion process. The release of K, Na, P, Cl, S of one macroalga (*Oedogonium* sp.) and two microalgal species (a polyculture species TPC and *Tetraselmis* sp.) during the thermochemical process were studied in a fixed bed reactor [21]. Lane et al. [21] found that approximately 20% of the K, 30–40% of the Na and almost all Cl and S and were released at 1000 °C for *Oedogonium* and *TPC*. For *Tetraselmis*, the release of alkali metal was 60–100% at 1000 °C due to the existence of high amount of Cl in the fuel. The high release ratio of alkali metals, Cl and S in combination with the high ash content may cause operating difficulties during the gasification process, e.g. agglomeration, fouling and deposition. Pure algae gasification in fluidized bed reactor was unsuccessful due to the rapid bed sintering and ash agglomeration [22]. Therefore, co-gasification of algae with coal/biomass has been proposed [19,23] to mitigate the ash related problems during pure algae gasification. Zhu et al. [19] found that bed agglomeration was significantly improved during co-gasification of algae with Victorian brown coal. The gasification tests lasted for 4 h without defluidization for co-gasification of *Derbersia* and *Oedogonium* with brown coal. Meanwhile, research [24] indicated that synergetic effects exist during the co-utilization of algae with other fuels. The algal char had a catalytic effect on the degradation of the textile dyeing sludge and increased the burnout rate [24]. Moreover, as a relatively new biofuel, algae-related infrastructure is currently still underdeveloped. Co-utilization of small amount algae could also facilitate the development of algae-related infrastructure and lay a foundation for the algae only system. Therefore, research on the co-gasification of algae has received increasing attentions in the past decade [19,22,23,25–27].

Although works related to co-gasification of algae with other fuel has been published previously, they were generally conducted in fixed bed/thermogravimetric analyzer [26,27] and fluidized bed [19,22,23,25]. Given the differences of temperature, gas velocity and fuel particle size in the reaction zone, the ash formation in entrained-flow reactor differs markedly from those in fixed bed and fluidized bed [18]. Previous research [28,29] indicated that the release of K, Na and S for wood chips increased as the bed temperature increased. Frandsen et al. [16] concluded that the total inorganics released from pulverized fuel-fired furnace were markedly higher than that from the fixed bed. It was also observed [17,18] that fly ash from straw suspension firing contained mainly Si, K and Ca, while fly ash straw grate firing was mainly composed of volatile elements K, and Cl. Similar compositional difference of deposits was also seen for these two gasification technologies [18]. So obviously the experience from fixed bed, fluidized bed and pulverized fuel-fired furnaces cannot be directly extrapolated for the entrained flow reactor. However, to the best of the authors' knowledge, research on ash behavior in entrained flow gasification of algae is scarce and thus corresponding research is needed.

Entrained flow gasification tolerates 40 wt% ash at the maximum for the dry feed gasifer whereas the gasification efficiency decreases notably with the increase of ash content [30]. Therefore, co-gasification of small amount of algae (20 wt%) with softwood (ash content 0.3 wt%) in an entrained flow reactor was conducted in this study considering the high ash content of algae especially microalgal species. This research has several aims. These are: 1) identify the difference of the fuel properties between the algae and lignocellulosic biomass fuels; 2) investigate the effects of the addition of algae to lignocellulosic biomass on gas yields and carbon conversion; and 3) investigate the effects of the addition of algae on the ash behavior to understand ash transformation in the algae co-gasification process.

2. Experimental

2.1. Fuels

The fuels employed in this study include: softwood pellets and three species of algae. The wood pellets (hereafter referred to as WD), which is a commercial softwood pellet of pine and spruce, is mainly used for small-medium scale heating applications as well as a large-scale combined heat and power system in Sweden [23].

The two species of macroalgae, *Derbersia tenuissima* (hereafter referred to as Deb) and *Oedogonium intermedium.*, were cultivated in tanks at the Marine & Aquaculture Research Facilities (James Cook University, Townsville, Queensland, Australia). *Oedogonium* was cultured in both high (~12 $mg \cdot L^{-1}$) and low (< 0.1 $mg \cdot L^{-1}$) nitrogen conditions and the corresponding harvested algae are referred to as *Oedogonium* N+ (hereafter referred to as ODN+) and *Oedogonium* N- (hereafter referred to as ODN-). The species were chosen as they are targets for the treatment of waste-water. *Derbesia* is a marine species and has application in the bioremediation of waste-water from land-based marine aquaculture, for example shrimp and marine fish. *Oedogonium* is a freshwater species and has broad application in the treatment of waste-water from municipal water treatment and intensive agriculture [31]. More importantly, both *Derbesia* and *Oedogonium* have a high productivity [31,32] and have been identified as a feedstock for energy production [33,34]. The microalga *Scenedesmus* sp. (hereafter referred to as SA), which was cultivated in the algae pilot plant at Swedish University of Agricultural Sciences (Umeå, Sweden), has been tested for municipal and industrial wastewater treatment in the Umeå – ÖrnskÖldsvik region. Detailed information about the growing conditions and harvesting method of the employed algae is presented elsewhere [19,35,36]. The proximate analysis, ultimate analysis, heating value, and ash elemental analysis of the algal samples and softwood are shown in Tables 1 and 2, respectively. The as received samples were milled using a knife mill and sieved to 100–250 μm for the following experiments. The blends of wood/algae were prepared by homogenously mixing 20 wt% algae and 80 wt% of wood. Table 1 presents the proximate analysis, ultimate analysis, and heating value of