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Research paper

Impact of inorganic contaminants on microalgal biofuel production through multiple conversion pathways

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ABSTRACT

Commercial scale production of microalgal based biofuels will likely require co-location with a carbon dioxide point source such as coal-fired power plants. Inorganic contaminants innate in coal will ultimately be introduced to the culture system with the potential to impact growth, conversion, and adversely impact the quality of biofuel and other microalgal derived products. Microalgae biomass (*Nannochloropsis salina*) cultivated in the presence of the inorganic contaminants As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V and Zn was processed into biofuel through one of two different in-situ transesterification methods, 1) acid-catalyzed or 2) supercritical methanol transesterification. The acid catalyzed transesterification resulted in a recovery efficiency increase from 80.5 ± 6.7% for the control biofuel (uncontaminated biomass conversion) to 88.9 ± 6.9% for the biofuel containing inorganic contaminants. Supercritical methanol conversion displayed a similar trend corresponding to the recovery efficiency increasing from 98.5 ± 8.3% for the control biofuel to 100.3 ± 2.6% for the biofuel containing inorganic contaminants. Inorganic contaminant analysis was performed on all biofuel conversion products and co-products of both transesterification types. Results indicated minimal contamination was found in the biofuel resulting from acid catalyzed transesterification, while substantial contamination was found in the biofuel resulting from supercritical methanol transesterification. Significant amounts of contamination were found in the lipid extracted algae resulting from both types of transesterification. Results show coal flue gas integration with algal production could have negative impacts on yields from standard biofuel conversion processes and limit the end use of bio-based products.

1. Introduction

In response to concern over global climate change, petroleum resource availability, and increasing global energy consumption, society continues to search for more efficient, economic, and environmentally stable alternatives to fossil fuels. Revived interest in microalgal based biofuels has resulted from the economic volatility surrounding fossil fuels and inherent advantageous qualities of microalgae such as: high lipid production per ground area, year-round cultivation, not requiring agricultural land for cultivation, and integration with various waste streams [1,2] A promising avenue for producing microalgae based biofuel and improving the sustainability of coal fired power plants is the integration of carbon dioxide in flue gas with microalgae cultivation systems.

To date, the effects of integration of industrial flue gas with microalgae cultivation on end products and co-products remains largely unknown [3]. Despite this fact, the large majority of microalgae to biofuel sustainability assessments including: economic [4,5], lifecycle [6,7] and scalability [8,9] assessments make a simplifying assumption of seamless integration of industrial flue gas with cultivation. Flue gas has been shown to contain a variety of inorganic contaminants including: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V and Zn [10,11]. The coupling of flue gas with cultivation facilities will ultimately introduce contaminants into the growth system with the potential to be assimilated into the biomass and impact downstream processing.

Previous research has shown microalgae to be an effective inorganic contaminant bioaccumulator [12]. Studies using simulated and actual flue gas integrated with cultivation have been conducted, with the majority failing to evaluate the end fate of inorganic contaminants [13,14]. Napan et al. [15] evaluate the impacts of inorganic contaminants on freshwater algae and in a follow up study evaluate limitations on the end use of contaminated biomass cultivated in the presence of inorganic contaminants [3]. Results show the accumulation of inorganic contaminants in the biomass exceed standards for high value products such as human and fish consumption. Napan et al. [15] limit the work to contamination levels in biomass and fail to evaluate the end

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fate and impact of the conversion of the biomass to bio-products. Hess et al. [16] specifically investigate the impact of inorganic contaminants on biomass and lipid productivity in a saline species reported to be a promising biofuel feedstock, *Nannochloropsis salina*. Results showed a significant amount of the inorganic contaminants to be sorbed into the biomass with no work done to evaluate downstream processing impacts.

In this study the effects of inorganic contaminants on downstream conversion processes and the impact of contamination levels in the end products and co-products are directly assessed. Inorganic contaminant analysis was used to understand the end fate of the inorganic contaminants and used to evaluate possible limitations to the end use of products and co-products based on contamination levels. This study was conducted with the intent to provide vital information for the improvement of future life cycle, economic, and scalability assessments for better sustainability evaluations of the microalgae to biofuel process.

2. Materials and methods

2.1. Biomass generation summary

Microalgae was cultivated in a growth media intended to simulate the exposure of algae to inorg from the integration of coal based flue gas [16]. Metal salts were added to the growth media in concentrations that would be expected based the assumption that 99% of the fly ash is captured and the remaining 1% being introduced into the media during sparging of flue gas for the delivery of carbon dioxide. *Nannochloropsis salina* was cultivated for 7 days in the presence of 14 inorganic contaminants As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V and Zn, as outlined in Hess et al. [16]. The growth did not consider SOx or NOx contamination impacts as previous research has characterized these impacts [17–20]. Prior to conversion to biofuel, the contaminated biomass from multiple reactors was homogenized and analyzed to determine contamination levels in the media and biomass at the conclusion of the growth process. Results show significant levels of inorganic contaminants in the resulting biomass see Tables S1 and S2 of the supplementary information (SI).

2.2. Acid catalyzed transesterification

The conversion of microalgae to biofuel using acid catalyzed transesterification was performed based on the methods of Wahlen et al. [21]. Control and inorganic contaminant microalgae that had been previously freeze dried using a Labconco lyophilizer was used. Six transesterification runs were performed, 3 of which were performed using control microalgae and 3 using microalgae containing inorganic contaminants. Conversions were performed in a 2 necked spherical 500 mL glass reactor heated on all sides by a temperature controlled electric mantel (System illustration is presented in the SI). For all runs a 10:1 solvent to mass ratio was used in which 30 g of freeze dried microalgae was added to 300 mL of solvent consisting of 98% methanol and 2% sulfuric acid. The mixture was heated to 62 °C and stirred continually for 6 h. After the transesterification process was complete the lipid extracted algae (LEA) was separated from the biofuel, and water/methanol mixture using an Erlenmeyer filtering funnel utilizing both course and fine filters (Whatman 1541–125 and 1542–125). A 1:1 solvent to water ratio (300 mL) and a 3:1 solvent to chloroform ratio (100 mL) were added to induce a phase separation accruing over a 12 h period. Biofuel and chloroform were separated from the methanol/water mixture using a separation funnel. Biofuel and chloroform separation was achieved by heating the mixture to 62 °C at approximately 2°C-min^{-1} and then running the evaporated chloroform gas through a condenser. Samples were taken of each product and co-product excluding chloroform so that a mass balance could be performed and the end fate of the inorganic contaminants could be determined. Biofuel yield was determined using gas chromatography (GC, Agilent Technologies 7890A) as detailed in the biofuel yield section below.

The effects of inorganic contaminants on the production of biofuel was quantified by measuring the changes in the production and recovery efficiency. Recovery efficiency is defined as the total FAME recovered after transesterification divided by the total FAME available within the microalgae before conversion. Production efficiency is defined as the grams of biofuel produced per gram of microalgae used in the transesterification process. For high production efficiencies to be achieved stoichiometric molar ratios of methanol to oil (3:1) [22] must be met or surpassed. In practice the molar ratios utilized are often in the hundreds [23,24]. In addition, a sufficient reaction time must be provided which can be reduced as the molar ratio of methanol to oil increases. At higher molar ratios reaction times sufficient for high production efficiency was found to be at or above 2 h [25,26]. To ensure a high production efficiency, a methanol to oil molar ratio of 215:1 and a reaction time of 6 h was used in this study.

2.3. Supercritical methanol transesterification

Six supercritical methanol transesterification runs were performed, 3 of which were performed using control microalgae biomass and 3 using microalgae biomass containing inorganic contaminants. Conversions were performed in a Parr 4575 500 mL reactor (schematic presented in the SI). Control biomass and inorganic contaminant biomass was harvested and centrifuged to 22% solids for the inorganic contaminant microalgae and 26.7% solids for the control microalgae. For all runs a 10:1 solvent to biomass ratio was used in which 10 g of microalgae biomass corresponding to 45.1 g of wet inorganic contaminant biomass or 37.5 g of wet control biomass was added to 100 mL of the methanol solvent, corresponding to a methanol to oil Molar ratio of 220:1. The mixture was initially pressurized to 1724 kPa using N_2 gas and then heated at 5°C-min^{-1} up to a pressure of 8274 kPa and a temperature of 253 ± 2 °C while being stirred continually. This condition was maintained for 90 min. Excess pressure was carefully released to maintain desired pressure. After the transesterification process was complete the LEA was separated from the biofuel, and water/methanol mixture using filters (Whatman 1541–125 and 1542–125). Phase separation was induced through the addition of water (200 mL), chloroform (100 mL), and methanol (100 mL). Biofuel and chloroform were separated from the methanol/water mixture using a separation funnel. The chloroform and biofuel were separated by evaporating and recovering the chloroform by heating the mixture to 62 °C and then running the chloroform gas through a condenser. Biofuel yield was determined using gas chromatography as detailed in the biofuel yield section below.

2.4. Trace inorganic contaminant analysis

Trace inorganic contaminant analysis was performed based on the methods of Napan et al. [27]. Analysis was performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS Agilent 7700× Series) for all products and co-products of the acid catalyzed transesterification and supercritical methanol transesterification processes; including the biofuel, lipid extracted algae (LEA), water/methanol mixture, and filters. First, all LEA and filters of both conversion types were placed in a −80 °C freezer and freeze dried. Biofuel, LEA, water/methanol, and filter samples for both conversion types were digested at 105 °C over a period of 3 days or until the solution was visibly clear by adding analytical trace metal grade nitric acid (70%) to either 100 mg LEA sample, 100 mg of filter sample, 100 µL of biofuel or 5 mL of water/methanol mixture. Throughout the digestion process volumes of 0.1–0.5 mL of nitric acid was added incrementally due to evaporative losses during digestion so that the final volume of the digested sample was approximately 2 mL. Samples were regularly vortexed throughout the process. After digestion was complete all samples were transferred into