Environmental Impact and Scalability of Utilizing Coal Fired Power Plant Flue Gas in Microalgal Biofuel Production

D. Hess*, K. Napan*, B, McNeil* and J. Quinn*

*Utah State University, Logan, UT, USA, derekhess7@aggiemail.usu.edu

ABSTRACT

Large scale production of microalgal based biofuels will require the integration of point source CO_2 sources. Flue gas integration from coal fired power plants fulfills this requirement while providing an environmental service. Heavy metals inherent in coal will ultimately be introduced to the culture system. Introduction of heavy metals have the potential to impact growth and negatively impact the quality of biofuel and other products. Heavy metals As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V and Zn were added to microalgae (*Nannochloropsis salina*) growth medium at concentrations representative of 7-day growth periods using coal flue gas as the carbon source. Heavy metal introduction resulted in an average decrease of 52% in biomass yield and 19% in lipid content. Microalgae biomass was processed into biofuel through one of two different in-situ transesterification techniques. Total production of biofuel from the heavy metal contaminated system decreased by over 50% for both conversion types.

Keywords: biofuel, flue gas, microalgae, coal, heavy metals

1 INTRODUCTION

Microalgal cultivaiton systems require large amounts of CO_2 to support accelerated growth. Co-locating cultivation faclities with coal power systems fulfills this requirement while providing an environmental service through the utilization of waste carbon. Previous studies have shown that integration of industrial flue gas can cause undesirable contaminants such as heavy metals to be introduced into the growth media (Borkenstein et al., 2011). Few studies have assessed the effects of the integration of industrial flue gas with microalgae cultivation, yet the majority of the studies of the microalgae to biofuels process including: economic (Benemann & Oswald, 1996; Davis et al., June 2012; Lundquist et al., 2010), lifecycle (Frank et al., 2011; Sills et al., 2012; Vasudevan et al., 2012), and scalability (Pate et al., 2011; Quinn et al., 2012) assessments make a simplifying assumption of seamless integration with no negative effects caused by the introduction of heavy metals. Due to the toxicity of some heavy metals and seeing that microalgae is a known metal bioaccumulator (Davis et al., 2003; Kratochvil & Volesky, 1998), the introduction of heavy metals into the microalgae growth system will likely negatively effect the production and quality of biofuel and other products made from microalgae. This study directly assess the impact of heavy metals on biomass, lipid, and biofuel production and evaluates the end fate of heavy metals in the biomass to biofuel process.

2 APPROACH

Heavy metals As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V and Zn were added to microalgae growth medium at a base concentration estimated to be representative of concentrations expected from 7 day growth periods using coal flue gas (See Table 1).

Element	PBR (mg metal * L^{-1})
As	0.078
Cd	0.015
Co	0.016
Cr	0.130
Cu	0.131
Hg	0.010
Mn	0.149
Ni	0.250
Pb	0.054
Sb	0.041
Se	0.010
Sn	0.004
V	0.113
Zn	0.440

Table 1: Concentrations of heavy metals added to Photobioreactors (PBRs)

Experimentation was conducted with *Nannochloropsis salina* cultivated in photobioreactors (PBR) at a light intensity of 1000 µmol m^{-2} s^{-1}. Daily growth measurements were taken for both heavy metal contaminated PBRs and control PBRs to determine how heavy metals impact the growth and average productivity. The heavy metals analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) to determine the end fate of the heavy metals within the growth system. The lipid content in the biomass from the control PBRs and heavy metal contaminated biomass was determined using gas chromatography (GC). Control and heavy metal contaminated biomass were processed into biofuel through one of two different in-situ transesterification techniques, being either an acid-catalyzed or supercritical methanol conversion. The effects of the heavy metals on biofuel production and lipid content were quantified for both conversion types and (ICP-MS) analysis was used to determine the end fate of the heavy metals after conversion.

3 RESULTS AND DISCUSSION

The integration of heavy metals present in flue gas was found to impact the biofuel production process in a variety of ways including microalgae growth, lipid production, and two different types of biofuel conversion processes. Heavy metals negatively impacted the growth with the average productivity being 0.54 ± 0.28 g L^{-1} d^{-1}, corresponding to an average decrease of 52% in biomass yield compared to control growths (see Figure 1).

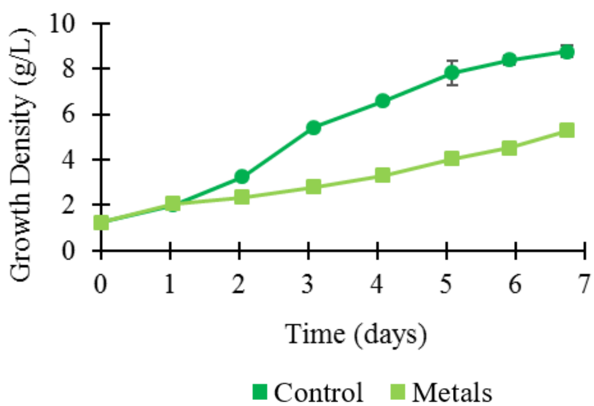

Figure 1: Effects of heavy metals on growth of microalgae

Lipid content analysis performed using gas chromatography (GC) on the control and heavy metal contaminated biomass showed a decrease in lipid content from 38.8 ± 0.62 to 31.58 ± 0.50 (percent dry biomass) respectively (See Figure 2).

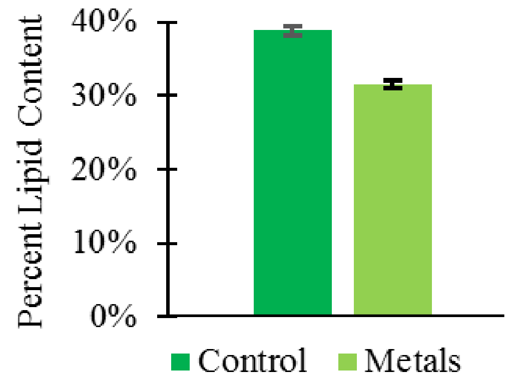

Figure 2: Effects of heavy metals on the lipid yield of microalgae

Heavy metals (ICP-MS) analysis was used to determine the end fate of each of the heavy metals added into the growth system. It was found that there was significant binding of the majority of the heavy metals to the biomass (See Figure 3). Due to the small concentration of heavy metals that were found to be contained in the media, media reuse to save production costs may be feasible.

Control and heavy metal contaminated biomass were processed into biodiesel through either an acid-catalyzed or supercritical methanol conversion. The effects of the heavy metals on biofuel production and lipid content were quantified for both conversion types. For the acid-catalyzed conversion, average crude biodiesel production decreased from 0.31 ± .03 grams biodiesel/gram microalgae for the control growths to 0.28 ± .02 grams biodiesel/gram microalgae from the heavy metals growths, representing a 9.7% reduction. For the supercritical methanol conversion, average crude biodiesel production decreased from 0.38 ± .03 grams biodiesel/gram microalgae for the control growths to 0.32 ± .01 grams biodiesel/gram microalgae from the heavy metals growths, representing a 15.8% reduction. Compared to the control the total production of biofuel from the contaminated system was decreased by 51% for the acid catalyzed conversion and 55% for the supercritical methanol conversion. Heavy metal analyses of the biofuel and particulates present in the crude were performed using the ICP-MS (See Figure 4). Results show a minimal transfer of heavy metals to the biofuel product. Metal contamination in the residual biomass could result in limited use as a co-prodcut.

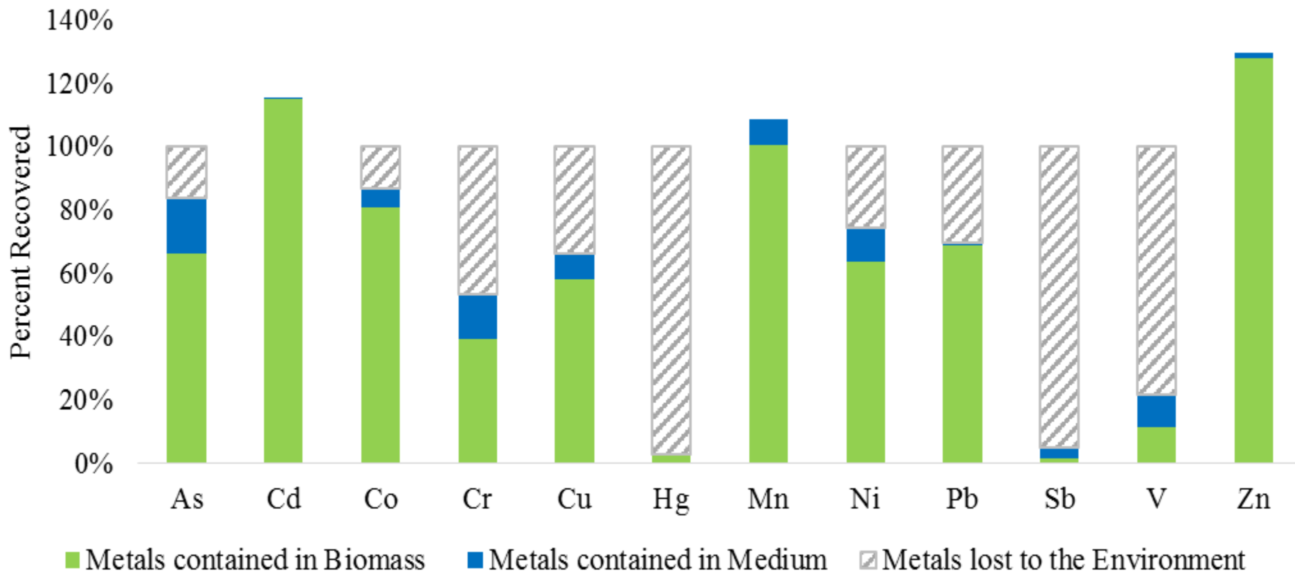

Figure 3: End fate of heavy metals after microalagal growth phse allocated between biomass, medium, and lost to the environment. Metals Se and Sn are not shown because they did not fall within quality control.

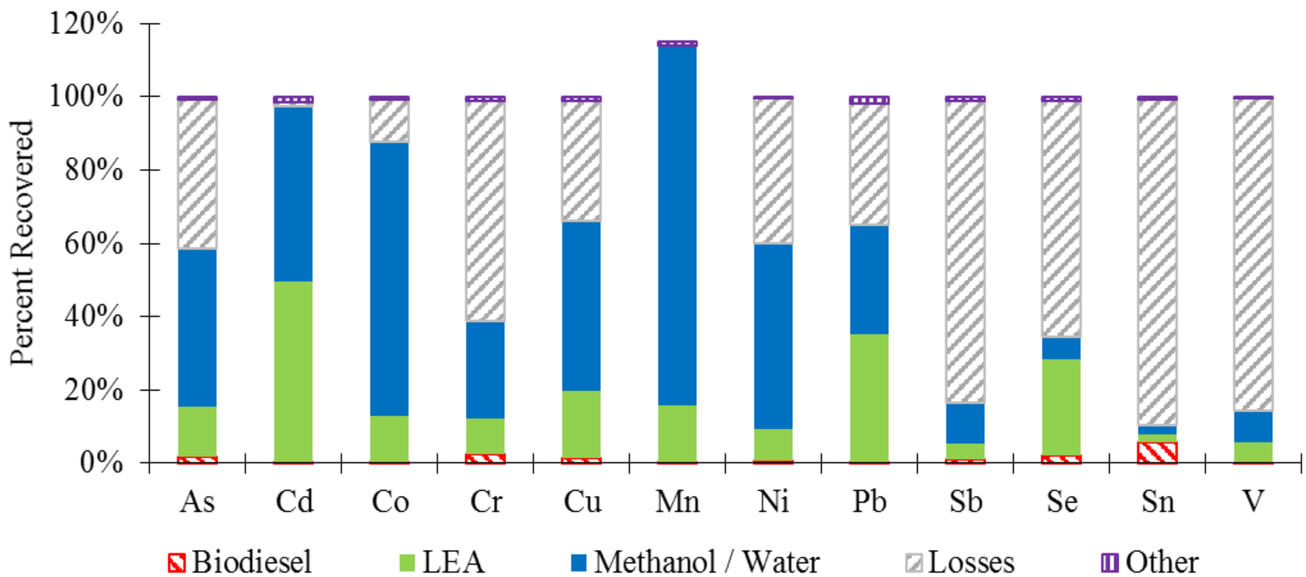

Figure 4: End fate of heavy metals after acid catalized in-situ transesterification allocated between biodiesel, lipid extracted algae, mehtanol/water byproduct, lost to the environment, and all other byproducts. Zn is not shown due high levels of contamination.

4 CONCLUSIONS

Economic large-scale production of microalgal based biofuels will require the integration of point source CO_2 sources. Flue gas integration from coal fired power plants fulfills this requirement while providing an environmental service by carbon sequestration. Heavy metals inherent in coal will ultimately be introduced to the culture system. Introduction of heavy metals have the potential to impact growth due to toxicity and negatively impact the quality of biofuel and other microalgal derived products. Heavy metals As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, V and Zn were added to microalgae (Nannochloropsis salina) growth medium at concentrations representative of 7-day growth periods using flue gas as the carbon source. Heavy metal introduction resulted in an average decrease of 52% in biomass yield and 19% in lipid content. Biomass from control and heavy metal contaminated bioreactors were processed into biodiesel through one of two different in-situ transesterification techniques, being either an acid-catalyzed or supercritical methanol conversion. For the acid catalyzed and supercritical methanol conversions, heavy metals were found to reduce biofuel productivity by 9.7% and 15.8%. Compared to the control, total production of biofuel from the heavy metal contaminated system was decreased by 51% and 55% for the acid catalyzed and supercritical methanol conversion types. Metal contamination in the residual biomass after conversion could result in limited use as a co-prodcut.

REFERENCES

[1] Borkenstein, C.G., Knoblechner, J., Fruhwirth, H., Schagerl, M., "Cultivation of Chlorella emersonii with flue gas derived from a cement plant," Journal of Applied Phycology, 23(1), 131-135, 2011.

[2] Benemann, J.R., Oswald, W.J., "Systems and economic analysis of microalgae ponds for conversion of CO2 to biomass," Final report. DOE/PC/93204--T5, 1996.

[3] Davis, R., Fishman, D., Frank, E.D., Wigmosta, M.S., Aden, A., Coleman, A.M., Pienkos, P.T., Skaggs, R.J., Venteris, E.R., Wang, M.Q., Renewable diesel from algal lipids: An integrated baseline for cost, emissions, and resource potential from a harmonized model," US Department of Energy Biomass Program, 2012.

[4] Lundquist, T.J., Woertz, I.C., Quinn, N.W.T., Benemann, J.R, "A realistic technology and engineering assessment of algae biofuel production," Energy Biosciences Institute, 2010.

[5] Frank, E.D., Han, J., Palou-Rivera, I., Elgowainy, A., Wang, M.Q., "Life-cycle analysis of algal lipid fuels with the GREET model," Center for Transportation Research, Energy Systems Division, Argonne National Laboratory, 2011.

[6] Sills, D.L., Paramita, V., Franke, M.J., Johnson, M.C., Akabas, T.M., Greene, C.H., Tester, J.W., "Quantitative uncertainty analysis of life cycle assessment for algal biofuel production," Environmental Science & Technology, DOI: 10.1021/es3029236, 2012.

[7] Vasudevan, V., Stratton, R.W., Pearlson, M.N., Jersey, G.R., Beyene, A.G., Weissman, J.C., Rubino, M., Hileman, J.I., "Environmental performance of algal biofuel technology options," Environmental Science & Technology, 46(4), 2451-2459, 2012.

[8] Pate, R., Klise, G., Wu, B, "Resource demand implications for US algae biofuels production scale-up," Applied Energy, 88(10), 3377-3388, 2011.

[9] Quinn, J.C., Catton, K.B., Johnson, S., Thomas, H.B., "Geographical assessment of microalgae biofuels potential incorporating resource availability," BioEnergy Research, DOI 10.1007/s12155-012-9277-0, 2012.

[10] Davis, T.A., Volesky, B., Mucci, A., "A review of the biochemistry of heavy metal biosorption by brown algae," Water Research, 37(18), 4311-4330, 2003.

[11] Kratochvil, D., Volesky, B., "Advances in the biosorption of heavy metals," Trends in Biotechnology, 16(7), 291-300, 1998.