Life Cycle Assessment of Drop-in Bio-jet Fuel and Acetic Acid from the Bioconversion of Poplar Biomass

Erik Budsberg

A dissertation

submitted in partial fulfillment of the

requirements for the degree of:

Doctor of Philosophy

University of Washington

2021

Reading Committee:

Rick Gustafson, Chair

Renata Bura

Joyce Cooper

Program Authorized to Offer Degree:

School of Environmental and Forest Sciences

University of Washington

Abstract

Life Cycle Assessment of Drop-in Bio-jet Fuel and Acetic Acid from the Bioconversion of Poplar Biomass

Erik Budsberg

Chair of the Supervisory Committee:

Rick Gustafson

School of Environmental and Forest Sciences

In this dissertation, research to evaluate the environmental impacts resulting from the commercial scale production of bio-jet fuel and bio-acetic acid produced from short rotation coppice harvest poplar tree feedstock is presented. The poplar feedstock is chipped during harvest and transported to a biorefinery where enzymatic hydrolysis and fermentation steps are used to convert the lignocellulosic biomass to acetic acid. The acetic-acid can be pulled out through a distillation recovery process and sold as a standalone commodity. Or, the acetic acid can go through additional chemical conversion steps, including hydrogenation, to produce a hydrocarbon jet fuel. In either case, the bio-jet fuel and bio-acetic acid are identical to the petroleum based versions of the products they are intended to replace. Life cycle assessment is used to analyze the potential environmental impacts of producing bio-jet fuel and bio-acetic acid at commercial scale. The research in this dissertation consists of three separate, but related studies. The first study is an LCA of bio-jet fuel production. It looks at the system as a whole, without defining a location for the poplar bioenergy farm or the

biorefinery, and focuses on the 'cradle to wake' global warming potential and fossil fuel use of bio-jet fuel production and use. The second study is a regional poplar feedstock 'cradle to farm gate' assessment that uses spatial analysis to locate lands in the western U.S. that could be used to grow poplar trees for regionally located biorefineries. The final study is a LCA 'cradle to biorefinery exit gate' analysis of bio-acetic acid production and assesses the global warming potential and fossil fuel use of two different acetic acid recovery methods. Below follows abstracts for the three studies:

Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment

Bio-jet fuels compatible with current aviation infrastructure are needed as an alternative to petroleum based jet fuel to lower greenhouse gas emissions and reduce dependence on fossil fuels. Cradle to grave life cycle analysis is used to investigate the global warming potential and fossil fuel use of converting poplar biomass to drop-in bio-jet fuel via a novel bioconversion platform. Unique to the biorefinery designs in this research is an acetogen fermentation step. Following dilute acid pretreatment and enzymatic hydrolysis, poplar biomass is fermented to acetic acid and then distilled, hydroprocessed, and oligomerized to jet fuel. Natural gas steam reforming and lignin gasification are proposed to meet hydrogen demands at the biorefineries. Separate well to wake simulations are performed using the hydrogen production processes to obtain life cycle data. Both biorefinery designs are assessed using natural gas and hog fuel to meet excess heat demands.

Global warming potential of the natural gas steam reforming and lignin gasification bio-jet fuel scenarios range from CO_2 equivalences of 60 g MJ^{-1} to 66 g MJ^{-1}

and 32 g MJ^{-1} to 73 g MJ^{-1}, respectively. Fossil fuel usage of the natural gas steam reforming and lignin gasification bio-jet fuel scenarios range from 0.78 MJ MJ^{-1} to 0.84 MJ MJ^{-1} and 0.71 MJ MJ^{-1} to 1.0 MJ MJ^{-1}, respectively. Lower values for each impact category result from using hog fuel to meet excess heat/steam demands. Higher values result from using natural gas to meet the excess heat demands.

Bio-jet fuels produced from the bioconversion of poplar biomass reduce the global warming potential and fossil fuel use compared to petroleum based jet fuel. Production of hydrogen is identified as a major source of greenhouse gas emissions and fossil fuel use in both the natural gas steam reforming and lignin gasification bio-jet simulations. Using hog fuel instead of natural gas to meet heat demands can help lower the global warming potential and fossil fuel use at the biorefineries.

Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment of site specific impacts

Hydrocarbon drop-in bio-jet fuels could help to reduce greenhouse gas emissions within the aviation sector. The commercial scale production of these bio-jet fuels will require investments into new bioconversion facilities to convert biomass to hydrocarbon drop-in jet fuel. These conversion facilities will need dependable year-round supply of biomass feedstock. Large tracts of land will be required to grow this feedstock and the change in management of these lands could have significant environmental impacts. This research investigates potential environmental impacts associated with converting land to grow poplar trees for conversion to drop-in bio-jet fuel. Spatial analysis and life cycle methodologies are used to evaluate changes to land use and management in 4 different regions within the western United States. The four regions are based around

biorefineries proposed to be located near Pilchuck WA, Hayden ID, Jefferson OR, and Clarksburg CA. Each of the four regions would annually supply 125 million tonnes of poplar biomass to a biorefinery producing 380 million liters of bio-jet fuel. The amount of land converted is based off of predicted poplar yields for each region. The type of land converted to growing poplar, as well as the impacts associated with land use change will depend on regionally specific factors.

The Clarksburg region is predicted to have the highest poplar yield and least amount of land converted. Of the land converted in the Clarksburg region, the majority of the land would come from croplands. Relative to the other regions, the conversion of intensively managed cropland to less intensively managed poplar production results in a decrease of fertilizer use and small increase in chemical inputs and fuel use. This translates to the lowest annual Global Warming Potential (GWP) for the Clarksburg region relative to the GWPs of Pilchuck, Jefferson, and Hayden. Conversely, the land in the Jefferson region would primarily come from unmanaged rangelands. Bringing this rangeland into managed production results in a regional increase of nitrogen fertilizer use, chemical inputs, and fuel use, as well as the largest increase in GWP, relative to the other regions. The type of land converted isn't the only predictor for changes in agricultural inputs and GWP; total land converted also plays a significant role as demonstrated by the Hayden region. Poplar yields are predicted to be lower in the Hayden region and more land must be converted to meet the biorefinery feedstock needs. The increased use of land leads to higher fuel use and greater greenhouse gas emissions in the Hayden region.

Combining life cycle assessment methodology with spatial analysis can help provide a more detailed view of the shifts in land use and resulting impacts. Feedstock growth and harvesting is a necessary and important process in the production for biofuels. The total contribution of feedstock production to the overall global warming potential likely will not be as significant as downstream conversion and processing of biomass into biofuel, but changes to land use and management could result in changes at the local level that could result in unintended negative environmental consequences. It is important that these impacts to land use, along with greenhouse gas emissions, are modelled and evaluated to better understand the regional and local implications of building a biofuels industry.

Production routes to bio-acetic acid: Life cycle assessment

Similar to biofuels, numerous chemicals produced from petroleum resources can also be made from biomass. In this research we investigate cradle to biorefinery exit gate life cycle impacts of producing acetic acid from poplar biomass using a bioconversion process. A key step in developing acetic acid for commercial markets is producing a product with 99.8 % purity. This process has been shown to be potentially energy intensive and in this work two distillation and liquid-liquid extraction methods are evaluated to produce glacial bio-acetic acid. Method one uses ethyl acetate for extraction. Method two uses alamine and diisobutyl ketone. Additionally two different options for meeting energy demands at the biorefinery are modeled. Option one involves burning lignin and natural gas onsite to meet heat/steam and electricity demands. Option two uses only natural gas onsite to meet heat/steam demands, purchases electricity from the grid to meet biorefinery needs, and sells lignin from the

poplar biomass as a co-product to a coal burning power plant to be co-fired with coal. System expansion is used to account for byproducts and co-products for the main life cycle assessment. Allocation assessments are also performed to compare the life cycle tradeoffs of using system expansion, mass allocation, or economic allocation for bio-acetic acid production. Finally, a sensitivity analysis is conducted to determine potential effects of a decrease in the fermentation of glucose to acetic acid.

Global warming potential (GWP) and fossil fuel use (FFU) for ethyl acetate extraction range from 1000 - 2500 kg CO_2eq. and 32 - 56 GJ per tonne of acetic acid, respectively. Alamine and diisobutyl ketone extraction method GWP and FFU ranges from -370 - 180 kg CO_2eq. and 15 - 25 GJ per tonne of acetic acid, respectively.

Overall the alamine/diisobutyl ketone extraction method results in lower GWP and FFU values compared to the ethyl acetate extraction method. Only the alamine/diisobutyl extraction method finds GWP and FFU values lower than those of petroleum based acetic acid. For both extraction methods, exporting lignin as a co-product produced larger GWPs and FFU values compared to burning the lignin at the biorefinery.

Table of Contents

Background

Climate change has the potential to drastically alter Earth and the life it supports. A driving factor in the strength of climate change is a significant increase in atmospheric greenhouse gas (GHG) emitted by humans, starting in the industrial revolution of the 1700s. Since the 1880s, when reliable temperature readings began, the Earth's mean surface temperature has increased by 0.85^{o} C and if we do not decrease emissions of GHGs, Earth could warm by as much as an additional 2.6^{o} C to 4.8^{o} C degrees by 2100 [1]. Warming the atmosphere by this much could be catastrophic, not only to plants and animals who cannot adapt quickly to changes in their habitats, but also to people living in regions where climate change will exacerbate difficult living conditions (i.e. draught, hurricanes, rising sea levels, etc.). Research has identified that to limit climate change to between 1.5^{o}C to 2^{o}C, a target that would limit the more severe effects of climate change, we must take action now to decrease GHG emissions [1].

Of all the GHGs, carbon dioxide is of primary concern. It is a naturally occurring chemical that cycles through the environments around the globe. Sources of CO_2 to the atmosphere include cellular respiration, volcanic eruptions, and combustion or decomposition of carbon rich material. CO_2 can be removed by photosynthesis, ocean uptake, and the chemical weathering of rocks. Sources and sinks work to balance atmospheric CO_2 concentrations as new states of equilibrium are achieved. However, over the last 250+ years CO_2 has been emitted to the atmosphere at rates faster than sinks can remove it and therefore its concentration in the atmosphere has been rapidly increasing. The rapid increase in CO_2 is directly related to the extraction, conversion, and use of petroleum based products such as transportation fuels and chemicals. If we

are to reduce atmospheric CO_2 emissions and mitigate the long term detrimental effects of climate change we must research and develop new technologies that significantly reduce, or all together eliminate, the use of petroleum based products [1].

Biofuels and biochemicals could provide an answer to transitioning societies away from the use of petroleum based fuels and chemicals towards a more sustainable bio-based economy. Biofuels and biochemicals, produced from bio-based feedstocks have the potential to reduce GHG emissions if produced using efficient and responsible methods. Research and development of biofuels has steadily increased over the last few decades. The first generation of these biofuels being ethanol produced from the bioconversion of corn grain [2], followed by second generation biofuels proposed to convert lignocellulosic biomass to ethanol (The National Renewable Energy Laboratory model being the more commonly proposed method [3-4]). Unfortunately, ethanol fuel use is limited by a lack of compatibility with much of the existing transportation infrastructure. This lack of compatibility extends to the aviation sector where the chemical and physical properties of ethanol prohibit its use as an alternative to petroleum based jet fuel. Safety concerns regarding fuel performance and large financial costs associated with a new fuel type dictate that alternative aviation fuels must be chemically identical to the fossil fuels they intend to replace [5]. If biofuels are to be used to reduce fossil fuel use within the aviation sector (or any transportation sector), then they must be designed to be used with minimal to no changes to existing infrastructure.

As technology for biofuel production has developed, so has the need to produce biochemicals, and the use of biofuel production technology is moving beyond fuels to

produce these biochemicals. When the research contained in this report was first started in 2011 petroleum was selling above $110 per barrel, 4 years later it was selling below $35 per barrel, and since then the price has fluctuated between a high of $57 and a low $16 [6]. The price instability of the petroleum market highlights the need for biorefineries to diversify their product portfolios to be able to adapt to changing market prices/demands [7]. Turning to biochemicals is a logical step to achieve this goal. Techno-economic assessment work by Morales-Vera et al. 2021 [8] indicted that bio-acetic acid could be produced at $756 - $877 / ton, and while global markets have been in state of flux over the last year, this selling price of bio-acetic acid could be competitive and profitable with petroleum based acetic acid. In addition to bio-acetic acid, other potential options of chemicals proposed to be produced from lignocellulosic biomass include: polylactic acid [9-12], polyethylene [9], polyethylene terephthalate [12], polyhydroxyalkanote [10-11], and starch based polymers [10-11]. Designing biorefineries to be able to produce both biofuels and biochemicals, depending market pricing/demands, could lay the foundation for an economically feasible bio-products industry.

A primary goal of these bioproducts is to decrease greenhouse gas emissions and other environmental impacts compared to petroleum based fuels and chemicals. However, the potential environmental impacts of a new bio-based fuels and chemicals industry must first be evaluated in order to ensure these new methods of production do not create more harm than good. The evaluation of potential environmental impacts can be conducted using Life cycle Assessment (LCA) methodology and to date there have been numerous LCAs conducted for different types of biofuel and biochemical

production and use. In addressing the potential environmental impacts of biofuels and biochemicals, many of the LCAs typically focus on global impacts (i.e. greenhouse gas emissions and fossil fuel use). These are important impacts to address as these products are intended to help mitigate climate change effects by replacing petroleum based fuels and chemicals. In general, these LCA studies have found that while there is variability amongst the biofuel and biochemical production methods related to feedstock type, conversion method, and end product, many of these bio-based products will have a lower global warming potential than the fossil fuel- based product they are intended to replace [11,13-20] The variability in these LCA studies highlights the need to develop LCAs specific to each bioproduct as raw material use and emissions are dependent on the feedstock type, biorefinery conversion methods, product use, and disposal.

Producing fuels and chemicals from biomass could lead to a large bio-based economy that may help mitigate the anthropogenic effect on climate change [7,9]. However, in addition to addressing global issues such as climate change, the switch to a bio-based economy could lead to regional and local environmental impacts associated with land use and changes to land management. Bio-based products are reliant on bio-based feedstocks, such as poplar trees, and acquiring the biomass at commercial industry scale would very likely lead to an increased demand for agricultural land. Biorefinery systems and bioproducts must therefore be thoroughly assessed and compared with each other to ensure efficient use of these lands [9]. Few of the biofuel and biochemical LCA studies report on the life cycle inventory contribution to regional impacts [13,16,21-22] and fewer still take into account the spatial variability of these

impacts [21,23]. Regional impacts can be difficult to accurately address when the location of a biorefinery and lands growing the lignocellulosic feedstock are unknown; but excluding this information has led to an incomplete view of the life cycle impacts of producing biofuels [23]. To evaluate the life cycles of biofuel and biochemical production as completely as possible, both global and regional environmental impacts should be considered.

The work presented in this dissertation focuses on using life cycle analysis to investigate environmental impacts of producing biofuels and biochemicals from poplar biomass. The dissertation is divided into three standalone, but interrelated, studies that address important issues in biofuel and biochemical life cycle assessment. Each study uses poplar biomass for the feedstock and a bioconversion biorefinery platform utilizing acetogenic bacteria in the fermentation stage. The studies differ in either the product produced at the biorefinery or the approach to evaluating life cycle impacts. The studies are presented in journal format as two of these articles have already been published, and the third study is in the process of being submitted for publication in a peer reviewed scientific journal.

In the first study, cradle to grave LCAs are conducted to investigate the life cycle impacts from the conversion of poplar tree chips into jet fuel via fermentation and subsequent hydrogenation. In addition to assessing the overall life cycle impacts of producing bio-jet fuel from poplar biomass via a bioconversion route, different methods for obtaining hydrogen and meeting heat and steam demands are investigated. Hydrogenation steps are a crucial part of upgrading acetic acid to a hydrocarbon biofuel. Two hydrogen production methods, natural gas steam reforming and lignin

gasification, are integrated into biorefinery system simulations to determine the life cycle effect of each process in producing hydrogen. Biorefinery heat and steam demands cannot be entirely met from combustion of lignin, as is commonplace in many second generation ethanol biorefineries (Borrion et al. 2012, Budsberg et al. 2015), and energy must be imported. Natural gas and hog fuel are tested as energy sources to meet these energy demands. The bio-jet fuel life cycle results are compared to each other, as well as to petro-jet.

The second study evaluates regional environmental impacts that have been overlooked in biofuel LCAs. The work builds on the LCA research presented in the first study and uses the same biorefinery model that is designed to produce bio-jet fuel from poplar biomass. In order to evaluate regional environmental impacts four potential biorefinery locations are identified within the western U.S. Cradle to biorefinery gate feedstock analyses are conducted for each site. Life cycle unit process data are tailored to represent environmental and technological flows that occur within the respective region each biorefinery is assumed to operate. Site suitability models are used to identify lands that could potentially be converted to poplar crop production for each biorefinery location. Poplar crop management and site specific emissions are based on data collected from current poplar test plots at each of the four locations. The LCI data is combined with spatial mapping software to identify potentially affected areas. The maps identify lands that could potentially be converted to poplar crops and the resulting changes to land management if a biorefinery producing bio-jet fuel was located in each area. When combined with research presented in the first study, these

results help complete the picture of potential life cycle environmental impacts resulting from a commercial scale biofuels industry in the western United States.

In the third study, the research switches from producing bio-jet fuel to bio-acetic acid. The work focuses on addressing the life cycle impacts of bio-acetic acid production. Scenarios are assessed that measure the life cycle environmental tradeoffs between two different solvent extraction methods and burning lignin onsite versus selling it to a coal power plant. System expansion and allocation (mass and economic) are used to evaluate the impact of selling a lignin co-product for bioenergy purposes. Cradle to biorefinery gate system boundaries are set for acetic acid production to include the growth and harvesting of poplar biomass, biorefinery operations, and manufacturing of all necessary inputs (i.e. process chemicals, energy). System boundaries also include combusting lignin onsite or at a coal power plant. Environmental impacts to be assessed include the global warming potential and fossil fuel use.

References

1. IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, 151 pp.
2. Wang, M. Q., Han, J., Haq, Z., Tyner, W.E., Wu, M., and A. Elgowainy. 2011. Energy and Greenhouse Gas Emissions Effects of Corn and Cellulosic Ethanol With Technology Improvements and Land Use Changes. Biomass and Bioenergy 35(5): 1885-1896.

3. Aden, A., M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, B. Wallace, L. Montague, A. Slayton, and J. Lukas. 2002. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. National Renewable Energy Laboratory.
4. Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., Schoen, P., Lukas, J., Olthof, B., Worley, M., Sexton, D., and D. Dudgeon. 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol; Dilute-acid Pretreatment and Enzymatic Hydroylsis of Corn Stover. National Renewable Energy Laboratory, Golden, Colorado.
5. Hileman JI, Stratton RW. Alternative jet fuel feasibility. Transport Policy 2014; 34:52-62.
6. U.S. Crude Oil First Purchase Price [internet]. Washington DC. U.S. Department of Energy; U.S. Energy Information Administration. C2021 Available from https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=pet&s=f000000__3&f=m
7. Cherubini F, Stromman AH. Production of biofuels and biochemical from lignocellulosic biomass: Estimation of maximum theoretical yields and efficiencies using matrix algebra. Energ Fuel 2010;24(3):2657-66.
8. Morales-Vera R, Crawford J, Dou C, Bura R, Gustafson R. Techno-Economic Analysis of Producing Glacial Acetic Acid from Poplar Biomass via Bioconversion. Molecules. 2020;25(18):4328. Published 2020 Sep 21. doi:10.3390/molecules25184328
9. Bos HL, Meesters KPH, Conijn SG, Corre WJ, Patel MK. Accounting for the constrained availability of land: a comparison of bio-based ethanol, polyethylene, and PLA with regard to non-renewable energy use and land use. Biofuels Bioproducts & Biorefining 2012;6(2):146-158.
10. Hottle TA, Bilec MM, Landis AE. Sustainability assessments of bio-based polymers. Polymer degradation and stability 2013;98:1898-1907.
11. Yates MR, Barlow CY. Life cycle assessments of biodegradable, commercial biopolymers – A critical review. Resources, Conservation and Recycling 2013;78:54-66
12. Papong S, Malakul P, Trungkavashirakun R, Wenunun P, Chom-in T, Nithitanakul M, Sarobol E. Comparative assessment of the environmental profile of PLA and PET drinking water bottles from a life cycle perspective. Journal of Cleaner Production 2014;65:539-550.
13. Borrion AL, McManus MC, Hammond GP. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. Renew Sustain Energ Rev 2012;16(7):4638-50.

14. Budsberg E, Crawford J, Gustafson R, Bura R, Puettmann M. Ethanologens vs. acetogens: Environmental impacts of two ethanol fermentation pathways. Biomass Bioenerg 2015;83(12):23-31.
15. Staples MD, Malina R, Olcay H, Pearlson MN, Hileman JI, Boies A, et al. Lifecycle greenhouse gas footprint and minimum selling price of renewable diesel and jet fuel from fermentation and advanced fermentation production technologies. Energy Environ. Sci. 2014;7:1545-1554.
16. Wiloso EI, Heijungs R, de Snoo GR. LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice. Renew Sustain Energ Rev 2012;16(7):5295-308.
17. Stratton RW, Wong HM, Hileman JI. Life cycle greenhouse gas emissions from alternative jet fuels. Cambridge (MA): Massachusetts Institute of Technology; 2010 June. PARTNER Project 28 Report PARTNER-COE-2010-001.
18. Agusdinata DB, Zhao F, Ilelji K, DeLaurentis D. Life cycle assessment of potential biojet fuel production in the United States. Environ Sci Technol 2011;45(21):9133-43.
19. Elgowainy A, Han J, Wang M, Carter N, Stratton R, Hileman J, et al. Life-cycle analysis of alternative aviation fuels in GREET. Lemont (IL): Argonne National Laboratory; 2012 June. 76 p. Technical Report ANL/ESD/12-8.
20. Han J, Elgowainy A, Cai H, Wang MQ. Life-cycle analysis of bio-based aviation fuels. Bioresource Tech. 2013;150:447-456.
21. Nordborg M, Cederberg C, Berndes G. Modeling Potential Freshwater Ecotoxicity Impacts Due to Pesticide Use in Biofuel Feedstock Production: The Cases of Maize, Rapeseed, Salix, Soybean, Sugar Cane, and Wheat. Environmental Science & Technology 2014 48 (19), 11379-11388 DOI: 10.1021/es502497p
22. Kim J, Yalaltdinova A, Sirina N, Baranovskaya N. Integration of life cycle assessment and regional emission information in agricultural systems. J Sci Food Agric. 2015;95(12):2544-2553. doi:10.1002/jsfa.7149
23. Mutel CL, Pfister S, Hellweg S. GIS-Based Regionalized Life Cycle Assessment: How Big Is Small Enough? Methodology and Case Study of Electricity Generation. Environmental Science & Technology 2012 46 (2), 1096-1103 DOI: 10.1021/es203117z

Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment

Erik Budsberg, Jordan T Crawford, Hannah Morgan, Chin Wei Shan, Renata Bura PhD, Rick Gustafson PhD

This article was published open access in Biotechnology for Biofuels in 2016. It can be found at:

Budsberg E, Crawford JT, Morgan H, Chin WS, Bura R, Gustafson R. Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment. Biotechnology for Biofuels 2016;9(170): DOI 10.1186/s13068-016-0582-2

A note to the reader - the below article follows the publication format as required by the journal Biotechnology for Biofuels. The order is as follows: Background, Results, Discussion, Conclusion, Methods. The below version has been slightly modified for inclusion in this dissertation.

Abstract

Background – Bio-jet fuels compatible with current aviation infrastructure are needed as an alternative to petroleum based jet fuel to lower greenhouse gas emissions and reduce dependence on fossil fuels. Cradle to grave life cycle analysis is used to investigate the global warming potential and fossil fuel use of converting poplar biomass to drop-in bio-jet fuel via a novel bioconversion platform. Unique to the biorefinery designs in this research is an acetogen fermentation step. Following dilute acid pretreatment and enzymatic hydrolysis, poplar biomass is fermented to acetic acid and then distilled, hydroprocessed, and oligomerized to jet fuel. Natural gas steam reforming and lignin gasification are proposed to meet hydrogen demands at the biorefineries. Separate well to wake simulations are performed using the hydrogen

production processes to obtain life cycle data. Both biorefinery designs are assessed using natural gas and hog fuel to meet excess heat demands.

Results – Global warming potential of the natural gas steam reforming and lignin gasification bio-jet fuel scenarios range from CO_2 equivalences of 60 g MJ^{-1} to 66 g MJ^{-1} and 32 g MJ^{-1} to 73 g MJ^{-1}, respectively. Fossil fuel usage of the natural gas steam reforming and lignin gasification bio-jet fuel scenarios range from 0.78 MJ MJ^{-1} to 0.84 MJ MJ^{-1} and 0.71 MJ MJ^{-1} to 1.0 MJ MJ^{-1}, respectively. Lower values for each impact category result from using hog fuel to meet excess heat/steam demands. Higher values result from using natural gas to meet the excess heat demands.

Conclusion – Bio-jet fuels produced from the bioconversion of poplar biomass reduce the global warming potential and fossil fuel use compared to petroleum based jet fuel. Production of hydrogen is identified as a major source of greenhouse gas emissions and fossil fuel use in both the natural gas steam reforming and lignin gasification bio-jet simulations. Using hog fuel instead of natural gas to meet heat demands can help lower the global warming potential and fossil fuel use at the biorefineries.

Background

Political instability in oil rich regions and the threat of climate change are driving a demand for sustainable biomass based transportation fuels. Until recently, a significant amount of research in biofuel production has focused on ethanol. A general consensus from this research indicates ethanol has the potential to reduce greenhouse gas

emissions compared to petroleum based fuels [1,2]. However, its use is limited by a lack of compatibility with much of the existing transportation infrastructure. This lack of compatibility extends to the aviation sector where the chemical and physical properties of ethanol prohibit its use as an alternative to petroleum based jet fuel. Attempting to restructure the world's airline fleet to operate on new type of fuel could cost close to a trillion U.S. dollars [3].

Safety concerns regarding fuel performance and large financial costs associated with a new fuel type dictate that alternative aviation fuels must be chemically identical to the fossil fuels they intend to replace. Hydrocarbon biofuels, also known as "drop-in" biofuels, meet these requirements. Currently, bio-jet fuel researchers propose to make these fuels from the hydroprocessing of oil seeds, pyrolysis, gasification/ Fischer-Tropsch, or advanced fermentation of biomass [4-8]. Like ethanol, these drop-in bio-jet fuels have the potential to significantly reduce GHG emissions. Global warming potential (GWP) for oil seed based jet fuels are 41 % to 70 % lower than petroleum based jet (petro-jet) fuel [4,6,7]. Bio-jet fuel from pyrolysis of corn stover has GWP reductions of 55 % to 68 % compared to petro-jet [6,7]. Fischer-Tropsch bio-jet fuel from biomass can reduce the GWP by as much as 81 % to 89 % compared to petro-jet if CO_2 is sequestered at the biorefinery using a carbon capture system [4,7]. Using economic factors Agusdinata et al. [5] projects a median GWP reduction of 74 %, compared to petro-jet, for hydroprocessed and Fischer-Tropsch bio-jet fuels in 2050. Staples et al. [8] predict GWP reduction ranges of 130 % to 0.2 % of petro-jet fuel for the advanced fermentation of biomass. This large range is a result of varied feedstock type and conversion methods [8].

The above results present large reductions in the GWP compared to the baseline petroleum jet fuel, however none of these theoretical GWP values of bio-jet fuel include land use change emissions. Land use change (both direct and indirect) emissions have been left out of many biofuel life cycle assessment (LCA) studies as there is still a great deal of uncertainty in land use change models, especially for oil seed feedstocks [7]. If land use change emissions for oil seeds are applied to the oil seed LCAs, the GWP of the bio-fuels increases significantly [7]. Stratton et al. [4] assessed different simulations, included land use change emissions in some of these, and found that when oil seed simulations include land use change the GWP is estimated to increase from 22 % to as much 2000 %. Adding direct land use change emissions to bio-jet fuels fermented from switchgrass could increase the GWP CO_2 eq. values by 2.9 g MJ^{-1} to 12.2 g MJ^{-1} [8].

To date limited research has been reported on drop-in biofuels that use the bioconversion platform that has been widely modeled to produce ethanol [8]. A benefit of this platform is the ability to use a wide range of feedstocks such as corn, sugarcane, switchgrass, corn stover, and short rotation woody crops (SRWC) [1,2,8]; many of which – such as switchgrass and SWRC - can be cultivated on marginal lands [9,10]. Cultivating marginal lands for growing biomass for biofuels can potentially help limit direct and indirect land use change emissions [2]. The advanced fermentation work of Staples et al. [8] considers using sugar cane, corn grain, and switchgrass along with pretreatment and bioconversion techniques appropriate for each feedstock. The survey research is theoretically based and calculates yields and emissions that identify life cycle GWP ranges from producing and using middle distillates (diesel and jet fuel). As noted above, the authors predict significant GWP reductions, but that the results vary

and are dependent on the feedstock and conversion methods used [8]. The large range in GWP values reported in Staples et al. [8], and other biofuel LCAs [1,4-7], indicate the sensitivity of the GWP to feedstock and conversion method; necessitating the need for a detailed LCA of any biofuel production method proposed for commercial scale application.

The work presented here is part of an investigation into the environmental and economic impacts of bio-jet fuel commercially produced via an advanced bioconversion pathway. The research focuses on the use of a novel fermentation method to convert poplar biomass to jet fuel. The work is part of a collaboration between industry, government, and academia to develop a sustainable bio-fuels and biochemicals industry. In this article LCA is used to determine potential environmental impacts. A second article, also published in this journal, investigates the techno-economics of the proposed bio-jet fuel pathway and includes detailed descriptions of bioconversion processes [11].

Poplar biomass, a SRWC, is selected as the feedstock as it presents an attractive option for diversifying and expanding biomass available for biofuel production. Used in the past for various products such as fuel wood, lumber, and paper, these well-established crops present good characteristics for biofuel use. In general they require little fertilizer input, have the ability to resprout after multiple harvests, and have a high biomass production [9]. The lignocellulosic material in the wood can also be fractionated without extensive pretreatment [12] and hardwoods don't exhibit the recalcitrance reported in softwoods [13]. Research has shown that these trees can be grown on marginal lands [9]. Using marginal/ fallow lands is unlikely to induce large

land use change emissions [2], potentially avoiding the land use concerns observed with oil seeds and food crops.

An acetogen fermentation pathway is used in the biorefinery to convert lignocellulosic material to liquid fuel. The acetogen pathway is chosen over an ethanologen pathway because of its ability to achieve a much higher fuel yield. During digestion of sugars, ethanologens produce 1 mol of CO_2 for every mol of ethanol produced. This limits the theoretical ethanol yield at 67 % [14]. Acetogens only produce acetic acid as they digest sugars and have a theoretical yield of 100 % [15]. Fermentation of sugars from biomass to acetic acid using *Moorella thermoacetica* is being investigated in our laboratories at the University of Washington [16]. Yields and titers depend on glucose to xylose ratios and the presence of compounds such as phenolics, furfural, and hydroxymethyfurfural. It has been found that conversion yields of over 70% and titers of 40 g L^{-1} are readily achievable. Higher yields and titers have been reported by Crawford et al. [11] based on data from our industry partners. The acetic acid is then converted to ethanol [17]. No carbon is lost as CO_2 and the ethanol yield is 80 % higher than if an ethanologen were used [18]. From here the ethanol is then upgraded to jet fuel via dehydration, oligomerization, and hydroprocessing [17].

Jet fuel is a complex mixture of a large number of different hydrocarbons. The focus of this research is on the life cycle assessment of producing biomass based molecules that could be readily incorporated into the jet fuel supply chain. n-Dodecane, $C_{12}H_{26}$, is a good first approximation for kerosene-type jet fuel, and has an appropriate carbon number of 12 [19]. The carbon number is important for calculating the degree of oligomerization required. Dodecane also has similar density, viscosity, thermal

conductivity, and heat capacity to kerosene based jet fuel [20]. It is therefore chosen as the end product (i.e. bio-jet fuel) to be modeled in this work.

It should be noted that the acetogen based biorefinery could also be used produce acetic acid, ethanol, ethylene, and ethyl acteate. All of these chemicals are intermediates produced – some at high purities - in route to bio-jet fuel production. Details of these other chemicals that can be produced in the modeled process are discussed in Crawford et al. [11].

Cradle to grave (well to wake) LCAs are conducted to investigate the life cycle impacts of four production scenarios for the conversion of poplar tree chips into jet fuel via fermentation and subsequent hydrogenation. The goal of producing bio-jet fuel from poplar biomass is to create an alternative to petroleum based jet fuel (petro-jet). In addition to assessing the overall life cycle impacts of producing bio-jet fuel from poplar biomass via a bioconversion route, different methods for obtaining hydrogen and meeting heat and steam demands are investigated. Hydrogenation steps are a crucial part of upgrading acetic acid to a hydrocarbon biofuel. Two hydrogen production methods, natural gas steam reforming (NGSR) and lignin gasification (LG), are integrated into biorefinery system simulations to determine the effect of each process in producing hydrogen. Biorefinery heat and steam demands cannot be entirely met from combustion of lignin, as is commonplace in many second generation ethanol biorefineries [1,18], and energy must be imported. Natural gas and hog fuel are tested as energy sources to meet these energy demands.

The hog fuel used in the simulations is assumed to be an unprocessed mix of woody biomass (chips, bark, residue, etc.) produced as a byproduct of lumber mill operations. Burning hog fuel allows for the use of a renewable energy source in place of fossil fuel. CO_2 released from burning the hog fuel is of biogenic origin and will not contribute to the net GWP of the jet fuel as compared to burning natural gas which releases non-biogenic CO_2 and increases the net global warming potential of the jet fuel. However, using hog fuel is not completely free of non-biogenic greenhouse gas emissions as GHGs are emitted during the production and transportation of hog fuel.

In total four biorefinery designs are assessed to make bio-jet fuel: NGSR used to produce hydrogen with natural gas and lignin burned for heat and steam (NGSR bio-jet), NGSR for hydrogen with hog fuel and lignin burned for heat and steam (NGSR-HF bio-jet), LG used for hydrogen production and natural gas for heat and steam (LG bio-jet), and LG for hydrogen and hog fuel for heat and steam (LG-HF bio-jet). One mega joule (MJ) of jet fuel combusted in a jet engine is used as the functional unit. The bio-jet fuel results are compared to each other, as well as petro-jet.

Results

The following categories are used to identify areas within the system boundaries that contribute to the environmental impacts.

- Carbon in biomass: CO_2 absorbed by photosynthesis in harvested chips, above ground and below ground stumps, and coarse roots modeled over 21 years. The

equivalent amount of CO_2 stored in the poplar wood is calculated using the stoichiometric relationship of CO_2 to carbon of 3.66 kg kg^{-1}.

- Poplar growth & harvesting: All technosphere processes associated with growing and harvesting poplar; includes direct land use change emissions.
- Ancillary chemicals: All chemical inputs to the biorefinery.
- Transportation: Includes transportation of poplar from farm to biorefinery gate, all chemical inputs to the biorefinery, and bio-jet fuel from the biorefinery to a distribution center.
- Biorefinery: All operations performed, raw materials used, and emissions from each biorefinery.
- Avoided production (NGSR based bio-jet fuels): Avoided production of electricity resulting from the production of excess electricity. It is assumed that marginal electricity, created by natural gas combustion, will be displaced.
- Purchased electricity (LG based bio-jet fuels): Electricity needed for biorefinery operations.
- Jet fuel use: Combustion of jet fuel in a jet engine.
- Petro-jet fuel production and use: Life cycle data for the production and use of petroleum based jet fuel are obtained from the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model v1.2.0.11425 (GREET).

Global Warming Potential

GWP values, as well as contributions from each area within the biorefinery life cycles, are shown in Figure 1 for the four bio-jet simulations and petro-jet. Net GWP for each simulation are listed in Table 1. For all simulations, the biorefinery category is the

largest source of greenhouse gases (GHGs) that contribute to the GWP and jet fuel use is the second largest. However, all of the CO_2 emissions from jet-fuel use and most of the CO_2 emissions from the biorefineries are from biogenic sources and are offset by the CO_2 that was removed from the atmosphere and stored as carbon in the biomass during growth. When biogenic CO_2 emissions are removed from the GWP calculation (by subtracting biogenic CO_2 in from biogenic CO_2 out), the biorefinery is the still the largest source of CO_2 for the NGSR, NGSR-HF, and LG bio-jet simulations, but the ancillary chemicals become the second largest contributor to the GWPs. In the LG-HF bio-jet process the ancillary chemicals group has the largest impact on the GWP when biogenic CO_2 emissions are removed. The largest contributions to the GWP of poplar growth and harvesting are direct land use change and nitrogen fertilizer. Direct land use change emissions contribute GWP CO_2 eq. of 12 g MJ^{-1} of bio-jet fuel to each simulation. Processes associated with manufacturing nitrogen fertilizer and N_2O emissions resulting from its use generate GWP CO_2 eq. of 5 g MJ^{-1} for each bio-jet fuel simulation. Transportation and purchased electricity (LG and LG-HF bio-jet) comprise only small percentages of the GWPs. Avoided production credit for NGSR and NGSR bio-jet has little effect in reducing the net GWP of the two bio-jet processes. Biorefinery and ancillary chemical GWP contributions are discussed in more detail below.

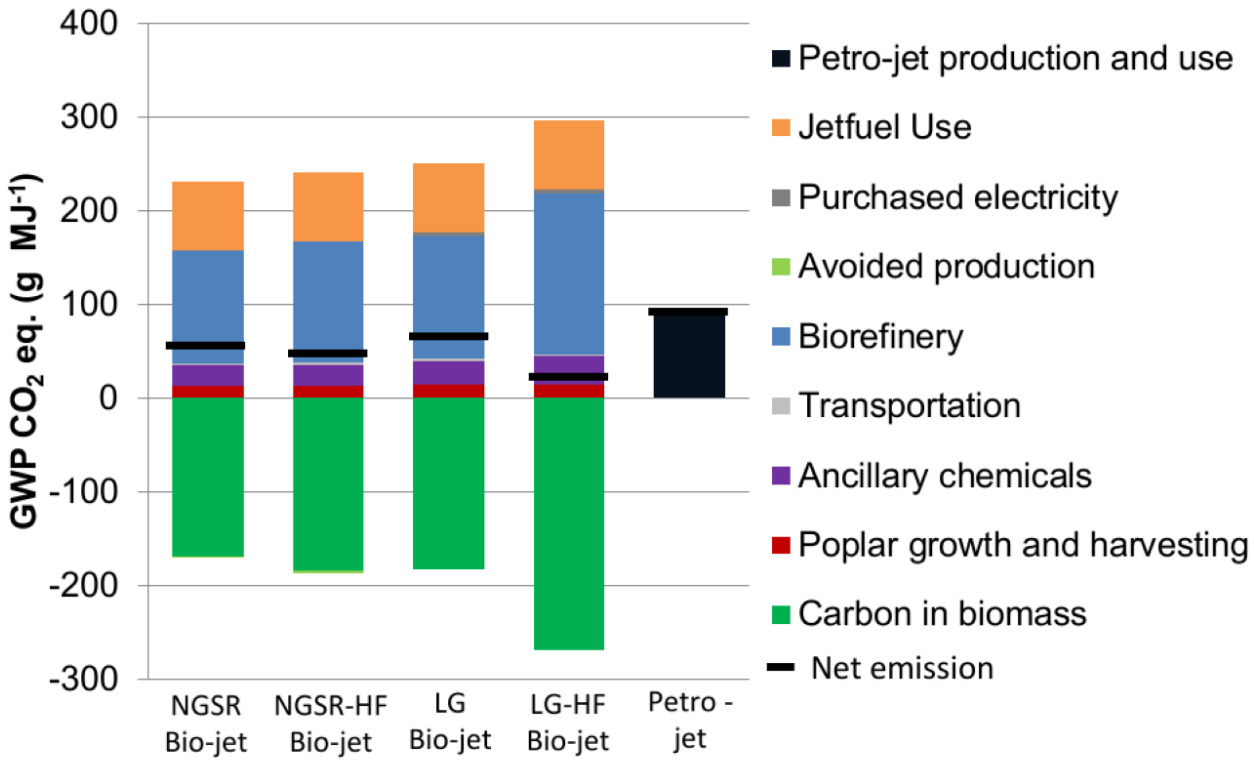

Figure 1: Cradle to grave global warming potentials of bio-jet fuel production simulations. Petro-jet shown for comparison.

Impact	NGSR bio-jet	NGSR-HF bio-jet	LG Bio-jet	LG-HF Bio-jet	Petro-jet
Net GWP CO_2 eq. (g MJ^{-1})	66	60	73	32	93
Net fossil fuel use (MJ MJ^{-1})	0.84	0.78	1.0	0.71	1.2

Table 1: Global warming potentials and fossil fuel use for four bio-jet production simulations

GHGs emitted from the biorefineries are almost entirely CO_2. Sources of the CO_2 emissions for each biorefinery are shown in Figure 2. CO_2 emissions in Figure 2 are identified as biogenic or non-biogenic. In all four simulations the largest source of biogenic CO_2 is the burning of biomass. In the NGSR bio-jet this biomass is the lignin in the burner/boiler. For NGSR-HF this is lignin and hog fuel in the burner/boiler. NGSR-HF bio-jet emits more CO_2 than NGSR bio-jet, but the increase is from a biogenic source and do not increase the net GWP. The result is a lower net GWP for NGSR-HF compared to NGSR bio-jet (Table 1).

In the LG bio-jet, the lignin gasification process emits CO_2 of biogenic source. Natural gas steam reforming to produce the supplemental hydrogen emits non-biogenic CO_2 (LG/NGSR – non-biogenic, Figure 2). To meet the heat and steam demand in the LG bio-jet simulation, significantly more natural gas for heat and steam must be used than in NGSR bio-jet. Combustion of this natural gas is the largest source of non-biogenic CO_2 emissions in LG bio-jet (Burner – non-biogenic, Figure 2). In the LG-HF biorefinery, burning hog fuel increases biogenic CO_2 emissions and decreases

non-biogenic CO_2 emissions, achieving a net reduction in the GWP compared to LG bio-jet (Table 1). Wastewater treatment and fugitive CO_2 emissions are minor and the same for all four simulations.

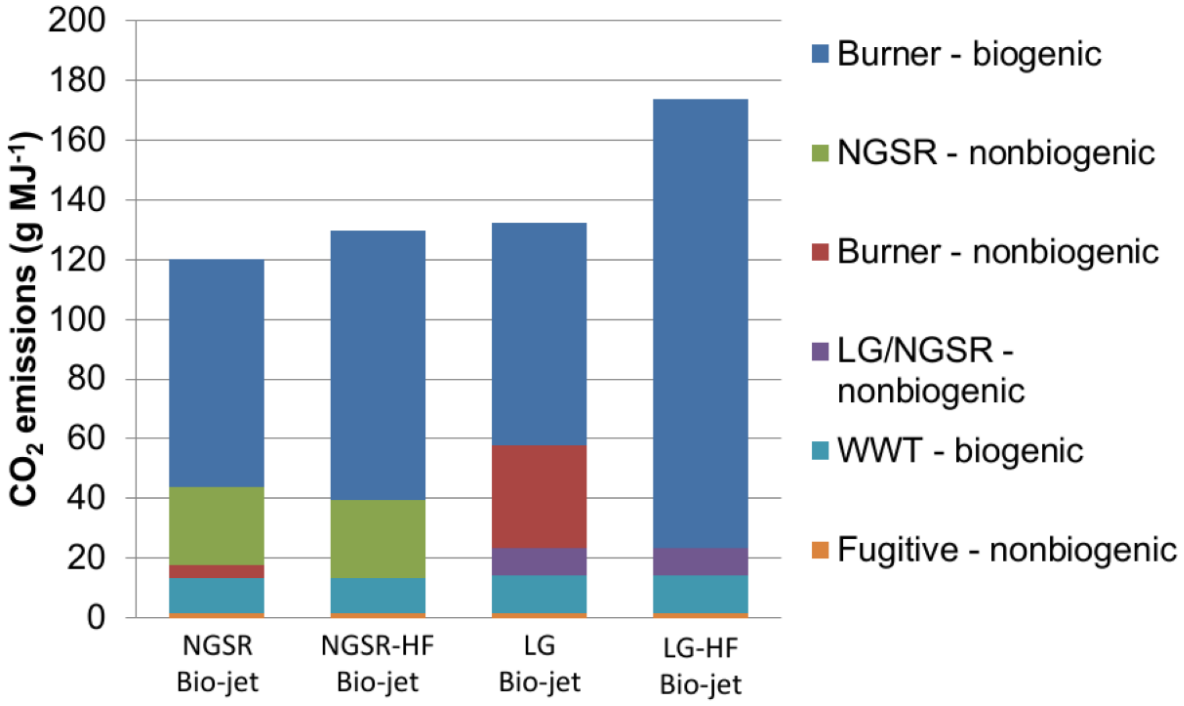

Figure 2: Biorefinery CO_2 emission sources for each biorefinery configuration. Emissions are identified as being from either a biogenic or non-biogenic source. NGSR refers to emissions from natural gas steam reforming. LG/NGSR refers to emissions from NGSR to produce supplemental hydrogen in the lignin gasification simulations. WWT refers to emissions from the onsite wastewater treatment facility.

In the ancillary chemicals category, the processes that contribute the most to the GWP depends on the bio-jet fuel production method (Figure 3). For NGSR and

NGSR-HF bio-jet these are the manufacturing of enzymes and the acquisition/ production of natural gas to be used in hydrogen production. These two processes produce GWP CO_2 eq. of 7.0 g MJ^{-1} and 5.1 g MJ^{-1} jet fuel, respectively. Acquisition/ production of natural gas for heating only contribute GWP CO_2 eq. of 1.2 g MJ^{-1} to the NGSR bio-jet GWP. Acquiring hog fuel to produce heat and steam in NGSR-HF bio-jet produces GWP CO_2 eq. of 2.1 g MJ^{-1}.

The largest contributors from the ancillary chemicals in the LG bio-jet GWP are the acquisition/ production of natural gas for heat and steam, and the production of enzymes. These two processes produce GWP CO_2 eq. of 6.7 g MJ^{-1} and 5.5 g MJ^{-1}, respectively. Natural gas for supplemental hydrogen production creates GWP CO_2 eq. of 2.4 g MJ^{-1}. In the LG-HF bio-jet process acquisition of hog fuel for heat and steam produces GWP CO_2 eq. of 11 g MJ^{-1}. Production of enzymes and acquisition/ production of natural gas for supplemental hydrogen production contribute GWP CO_2 eq. of 5.5 g MJ^{-1} and 2.4 g MJ^{-1}, respectively, to the LG-HF bio-jet GWP (Figure 3).

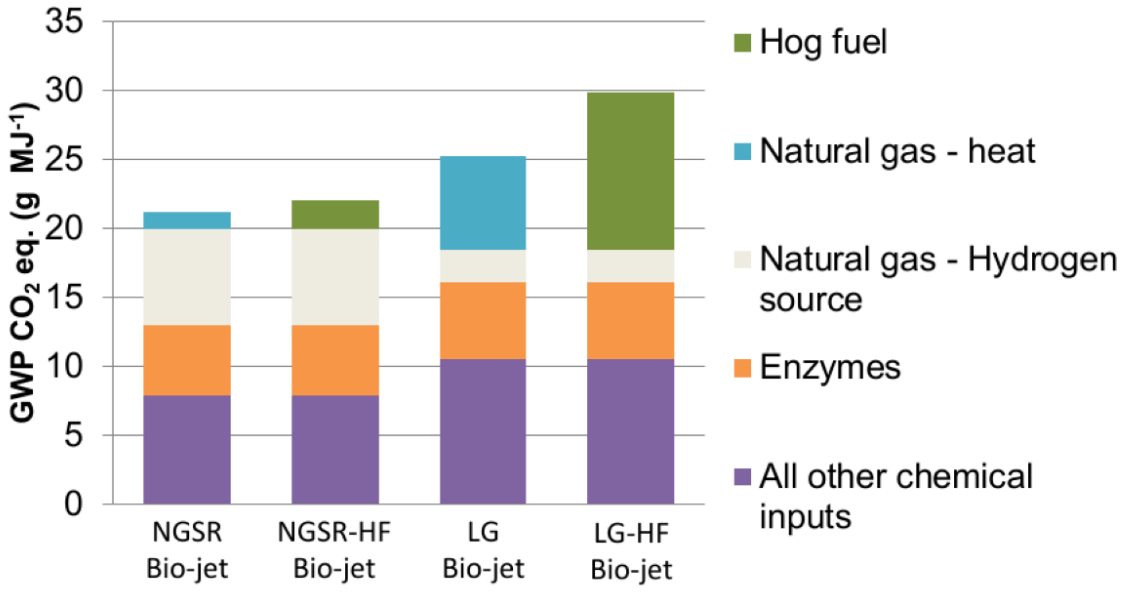

Figure 3: Global warming potential: ancillary chemicals. The top 4 global warming potential contributors are identified for each biorefinery simulation. All other chemical inputs are grouped together.

Fossil fuel use

FFU values of each biorefinery are presented in Figure 4. Net FFU values for each simulation are listed in Table 1. Acquisition/ manufacturing of products within the ancillary chemicals use 85 % to 97 % of the fossil fuels consumed in the making of the bio-jet fuels. FFU in transportation, poplar growth and harvesting, and purchased electricity (for LG and LG-HF bio-jet) are minor compared to the ancillary chemicals

group (Figure 4). Avoided production credit in NGSR and NGSR-HF bio-jet simulations reduce the net FFU by 0.029 MJ / MJ^{-1} of jet fuel.

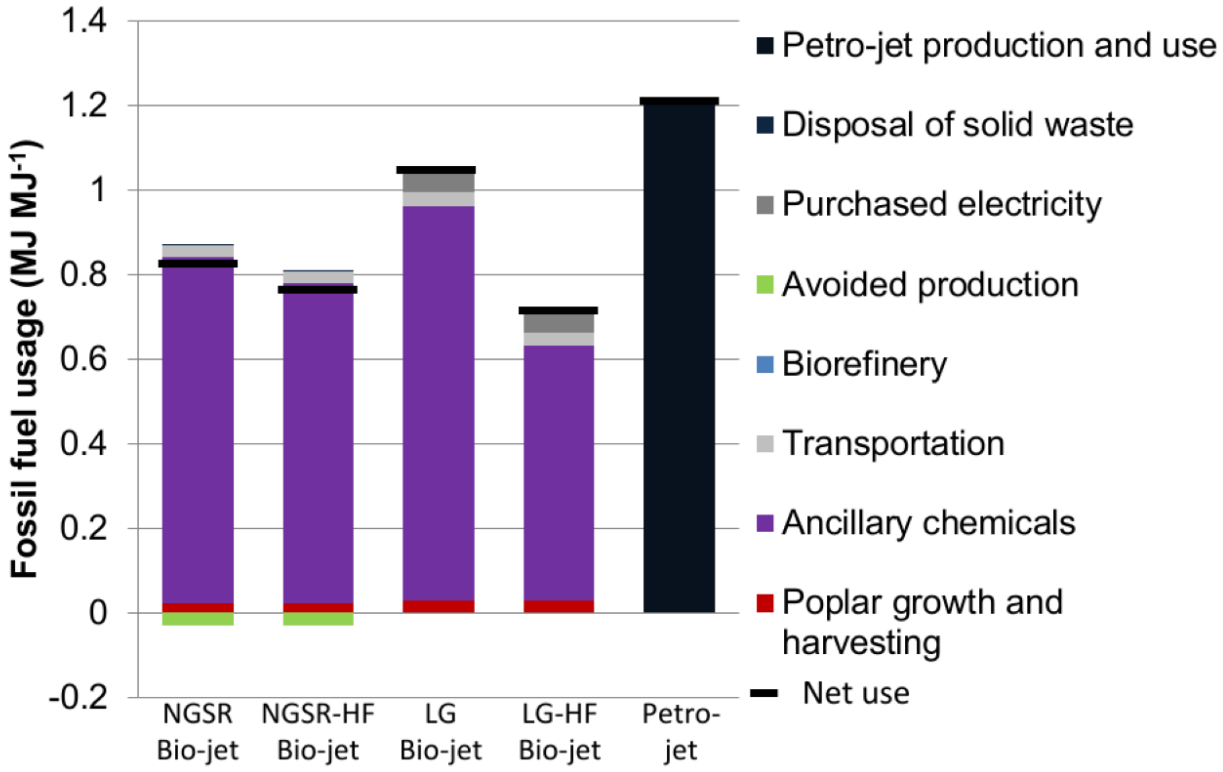

Figure 4: Fossil fuel use for each biorefinery process. Petro-jet shown for comparison.

The largest consumers of fossil fuels in the ancillary chemicals group depend on the bio-jet method (Figure 5). In the NGSR and NGSR-HF simulations enzyme production and natural gas use for hydrogen production are the largest users of fossil fuels. Acquisition/ production of natural gas for hydrogen production and enzyme production use 0.54 MJ MJ^{-1} and 0.077 MJ MJ^{-1}, respectively. Natural gas for heating

consumes 0.096 MJ MJ^{-1} and is the third largest consumer of fossil fuels in NGSR bio-jet. Acquiring hog fuel requires 0.035 MJ / MJ^{-1} in NGSR-HF bio-jet. All other ancillary chemicals in NGSR and NGSR-HF bio-jet combine to use 0.10 MJ MJ^{-1}.

In LG bio-jet natural gas for heat and steam is the largest consumer of fossil fuels (0.52 MJ fossil fuel / MJ). In LG-HF bio-jet hog fuel acquisition is the largest consumer of fossil fuels, requiring 0.19 MJ / MJ^{-1}. In both the LG and LG-HF bio-jet simulations natural gas for supplemental hydrogen production is the second largest user of fossil fuels, at 0.18 MJ / MJ^{-1}, followed by enzyme production which uses 0.084 MJ / MJ^{-1}. All other ancillary chemicals in the LG and LG-HF bio-jet pathways combine to use 0.15 MJ / MJ^{-1}.

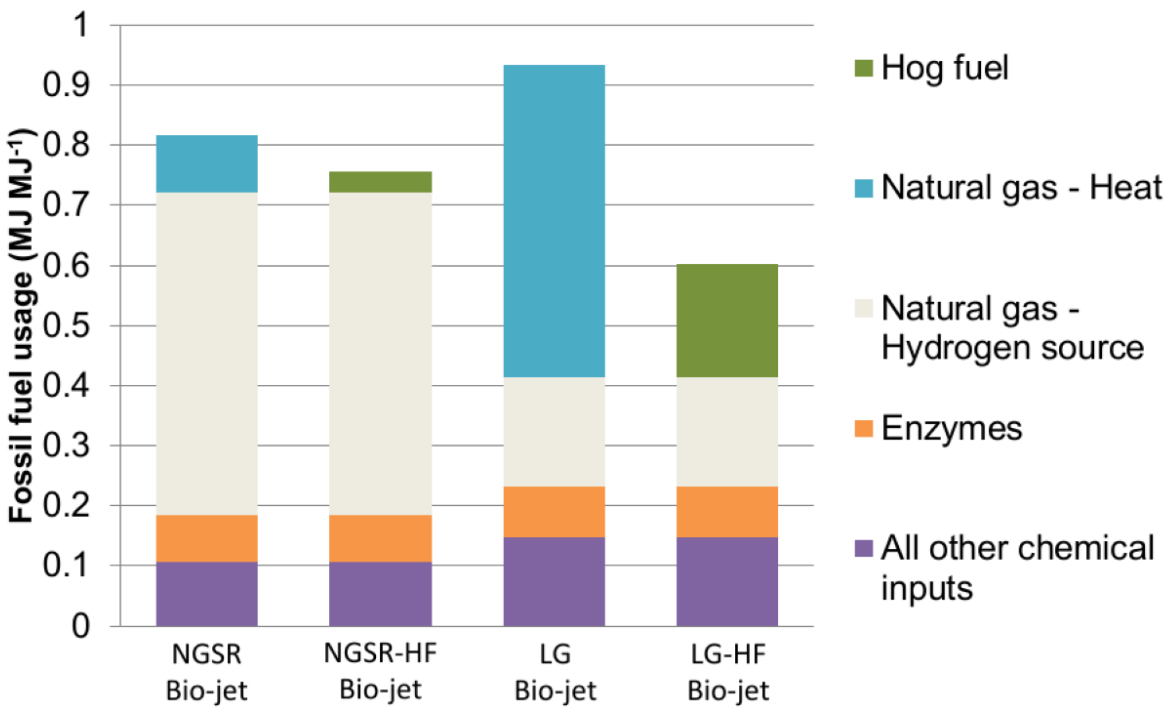

Figure 5: Fossil fuel use: ancillary chemicals. The top 4 fossil fuel consumers are identified for each biorefinery simulation. All other chemical inputs are grouped together.

Discussion

All four bio-jet pathways have lower GWP and FFU values compared to petroleum based jet fuel. The range of the GWP and FFU values for the bio-jet fuels are based on the method chosen to produce hydrogen and the energy source used to provide heat and steam at the biorefineries (Table 1). NGSR-HF bio-jet pathway has a net GWP that is 9 % lower than NGSR bio-jet. Net FFU is reduced by 8 % by using hog

fuel to replace natural gas for steam production. The similarity between the two NGSR based bio-jet pathways is expected as the only difference between the two pathways is the energy source that provides 14 % of the total heat and steam demand. This is in contrast to the LG bio-jet pathways, which require that all heat and steam demand is met by an external source of energy. These processes are more sensitive to the type of external energy source used. Net GWP of LG-HF bio-jet is 56 % lower than LG bio-jet pathway. FFU is 46 % lower in the LG-HF compared to the LG process.

Replacing natural gas with hog fuel reduces the GHGs released and fossil fuels used during the acquisition, production, and burning of natural gas. Using hog fuel does not completely eliminate all GHG emissions and fossil fuel use associated with heat and steam production. GHGs are released and fossil fuel fuels are consumed during the production and transportation of hog fuel. Replacing 1 MJ of natural gas with 1 MJ of hog fuel reduces the GWP CO_2 eq. by 60 g and fossil fuel use by 0.65 MJ. These results indicate that, from a life cycle impact standpoint, hog fuel is the preferred energy source for heat and steam generation in the biorefineries.

The hydrogen production method used is responsible for driving much of the difference in the bio-jet fuels life cycle GWPs and FFUs. The hydrogen process selected determines the amount of excess energy needed to meet the heat and steam demand of the biorefinery. If natural gas is used to meet the energy demand, the NGSR bio-jet process has a lower net GWP and FFU than LG bio-jet. NGSR bio-jet would be the preferred option. If hog fuel is used to meet the energy demand, LG-HF bio-jet simulation is the best option, not only between the two hog fuel simulations, but of all four simulations assessed. LG-HF bio-jet has significantly lower GWP and FFU values

than the other three bio-jet simulations (Table 1). Techno-economic assessment of these four bio-jet simulations, however, finds that gasifying lignin is more expensive and complicated than natural gas steam reforming. As technology improves gasifying lignin may become financially feasible, but at this time, the cheapest pathway to bio-jet fuel production with the lowest lifecycle impacts is using natural gas to produce hydrogen and hog fuel to meet the excess heat/steam demand [11].

The reductions of GWPs compared to petro-jet reported in this study are not as large as those reported in the literature (except for LG-HF) [4-8]. The system boundaries in this study include direct land use change emissions, and are partly responsible for the higher GWP values. If direct land use change emissions are removed from the system boundaries of this study, the GWP reductions for NGSR, NGSR-HF, LG, and LG-HF bio-jet pathways become 42 %, 49 %, 34 %, and 78 %, respectively, compared to petro-jet. These reductions are similar to the lower range of reductions reported for hydroprocessed seed oil (41% to 74%) [4,6,7], pyrolysis bio-jet fuels (55 % to 68 %) [6,7], and advanced fermentation of switchgrass to middle distillates (0.2 % to 78 %) [8]. LG-HF (without land use change) achieves a GWP similar to the Fischer-Tropsch bio-jet fuels that include carbon capture systems (74 % to 89 %) [4,5,7]. The incorporation of land use change models into bio-jet LCAs is important to understand the true impact these fuels could have on climate change.

Process designs specific to the bioconversion platform also drive differences in the GWP values of the biorefinery configurations simulated in this study versus those in the literature. The fermentation of switchgrass to ethanol and subsequent dehydration, oligomerization, and hydroprocessing in Staples et al. [8] is most similar to the

biorefinery design used in this study. In that report the GWP CO_2 eq. of jet fuel produced from switchgrass using an ethanol fermentation platform is found to be 11.7 g MJ^{-1} and increases by 2.9 g MJ^{-1} to 12.2 g MJ^{-1} if direct land use change emissions are included. This is lower than the GWP of NGSR, NGSR-HF, LG, and LG-HF simulations (Table 1). The choice of fermentation pathway is largely responsible for the difference in GWP values. Fermenting to acetic acid and then converting it to ethanol achieves a much higher yield compared to fermenting straight to ethanol, however hydrogen is required to convert the acetic acid to ethanol. 93 % of all hydrogen required in the NGSR and LG biorefinery simulations is needed to convert acetic acid to ethanol. Avoiding this step in the conversion of biomass to jet fuel would reduce GWP, but tradeoffs between final product yield and selling price need to be accounted for as well. A higher biofuel yield also reduces the amount of land needed. It is estimated that there is enough marginal/abandoned land to meet 26 % to 55 % of the current world liquid fuel demand using second generation biofuel production methods [21]. The acetogen pathway is approximated to produce 80% more ethanol than the ethanologen pathway and could increase the amount of liquid fuel produced from these agriculturally degraded lands [18]. This equates to a higher jet fuel yield per unit of land that is not possible from a traditional ethanologen fermentation pathway.

A commonality amongst bio-jet fuels from hydroprocessing of seed oils, pyrolysis, and bioconversion are the hydrogenation step(s) needed to produce the final product. Producing hydrogen is found to be a significant source of GHGs [4,7] and increased cost [22]. In previous studies it is assumed that this hydrogen would come from natural gas steam reforming [4,7]. In this research lignin gasification to produce

hydrogen is shown to have the potential to significantly reduce the GWP of hydrogen production if hog fuel is used to meet the heat and steam demand of the biorefinery. Future studies should assess the integration of other hydrogen production methods in biorefinery designs to determine their economic and environmental viability.

Conclusion

Bio-jet fuels produced from the bioconversion of poplar biomass reduce the GWP and FFU compared to petroleum based jet fuel. The production and use of hydrogen are identified as major contributors to the GWP and FFU of bio-jet fuel production. The hydrogen production method will dictate GHG emissions, FFU, and the degree to which these impacts can be reduced. LCA work in this study suggests that for biorefineries with integrated hydrogen production facilities, using hog fuel in place of natural gas to provide heat and steam will have reduced non-biogenic CO_2 emissions and FFU. Baseline biorefinery designs (NGSR and LG bio-jet) already include the infrastructure necessary for burning biomass, and addition of hog fuel to the burner/boiler would not drastically increase capital costs.

The LCA work presented here provides additional evidence that the GWP and FFU of the aviation sector will be reduced if biomass based drop-in jet fuels replace petroleum based jet fuels. However, this research is not complete as it only assesses impacts targeting climate change and use/dependence of fossil fuels. Additional research is needed to assess regional environmental impacts such as air quality and

water degradation. Locations of biorefineries and affected watersheds must be identified, however, to accurately address these impacts. Future work will report on these issues.

Methods

Environmental impacts considered are the 100 year Global Warming Potential (GWP) [23] and fossil fuel use. Fossil fuel use (FFU) is calculated by summing all fossil fuel inputs (coal, natural gas, crude oil) per MJ of jet fuel. Guidelines for conducting a LCA are set by ISO 14040 & 14044 [24, 25] and this research follows the ISO design. The LCAs in this research were developed using SimaPro v.8.0.

The bio-jet fuel life cycles are broken up into 4 sections: feedstock production and harvesting, ancillary chemicals, the biorefinery, and fuel distribution and use. Feedstock production and harvesting and fuel distribution and use are the same for each biorefinery configuration. Biorefinery process and ancillary chemical inputs will vary depending on the configuration. Descriptions of each life cycle section follow below. System boundary diagrams for each bioconversion pathway are displayed in Figures 6a and 6b.

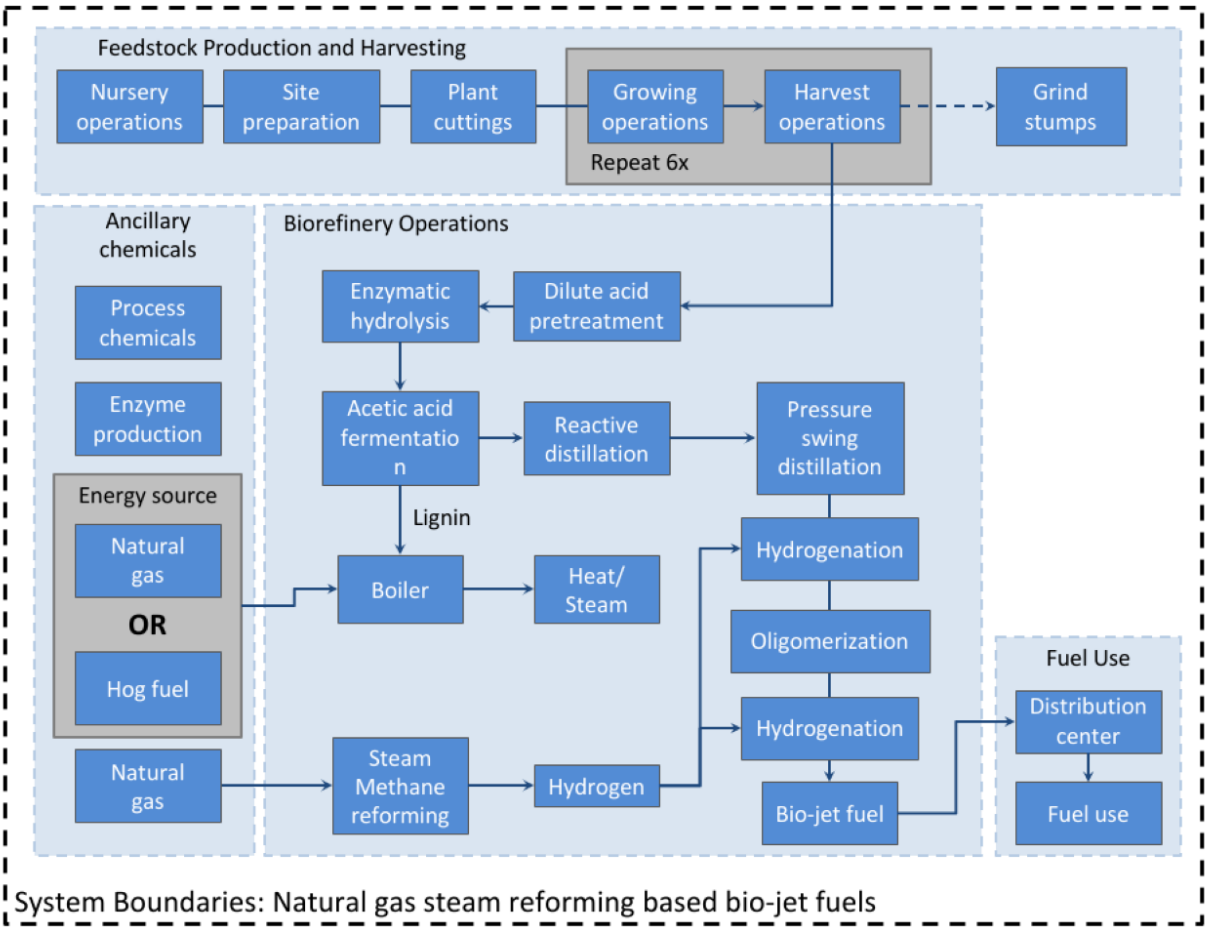

Figure 6a: Life cycle inventory system boundaries. Overview of the natural gas steam reforming based bio-jet fuel process. The type of energy source going to the boiler depends on the biorefinery simulation. NGSR bio-jet uses natural gas and lignin. NGSR-HF uses hog fuel and lignin. Not pictured, but included in the system boundaries are a waste water treatment facility, disposal of solid wastes, and an excess electricity by-product.

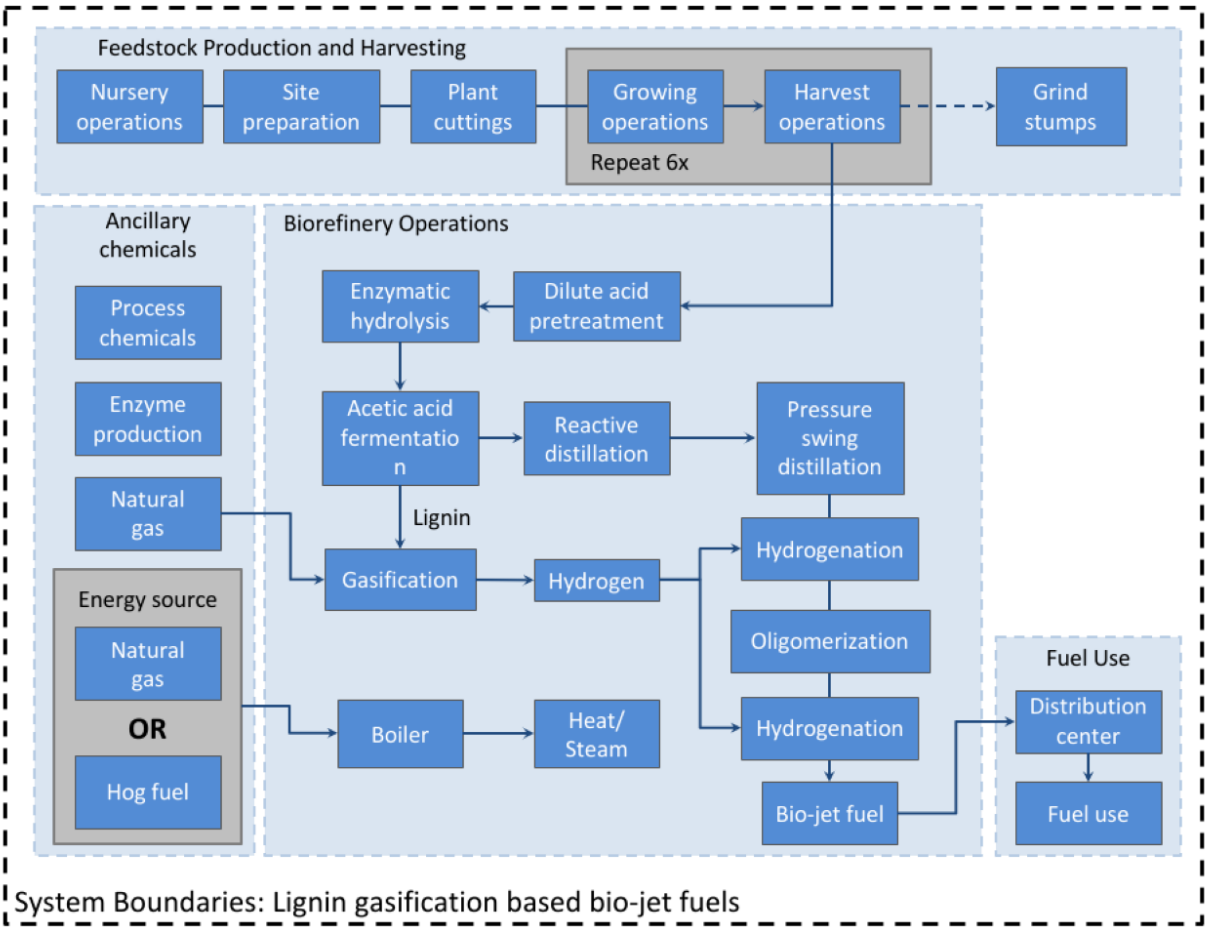

Figure 6b: Life cycle inventory system boundaries. Overview of the lignin gasification based bio-jet fuel process. The type of energy source going to the boiler depends on the biorefinery simulation. LG bio-jet uses natural gas. LG-HF uses hog fuel. Not pictured, but included in the system boundaries are a waste water treatment facility, disposal of solid wastes, and import of electricity.

Feedstock

The feedstock production and harvesting model is supported by operational data from industry (GreenWood Resources, personal communication, 2011-2014), literature [26], and LCA databases [27,28]. It is the same feedstock model used in [18] and is discussed in more detail that publication. The feedstock production and harvest model

is representative of a coppice harvest system, with the poplar trees being coppiced every 3 years for 6 cycles. The model includes all necessary site preparation, nursery operations, management of the poplar tree stands, harvest operations, and stump removal. Nitrogen fertilizer is applied in the spring following a harvest at a rate of 56 kg N per application. N_2O emissions from fertilizer and decaying biomass are calculated using the Farm Energy Analysis Tool [29]. Storage of carbon in the harvested poplar biomass as well as in below ground biomass (stump and roots) is included. The equivalent amount of CO_2 stored in the poplar wood is calculated using the stoichiometric relationship of CO_2 to carbon of 3.66 kg kg^{-1} and a carbon mass fraction of 51.7 % dry wood weight [30] (Table 2a & 2b). Direct land use change is included using the assumption that fallow land will be used for poplar plantations. Direct land use change associated with establishing the plantation is calculated using the Forest Industry Carbon Assessment Tool v.1.3.1.1. Indirect land use change is excluded from the system boundaries due to uncertainty associated with these models [31]. A transportation distance of 100 kilometers roundtrip is assumed to transport the harvested poplar biomass to the biorefinery gate. In total the feedstock production and harvest model covers a 21 year timespan [18].

	Mass fraction of bone dry poplar biomass (%)
Cellulose	42
Xylan	15.3
Lignin	25.8
C5SOLD	1.91
C6SOLD	5.73
Acetate	2.86
Extractives	4.5
Ash	1.91

Table 2a: Chemical mass fraction of bone dry poplar biomass. Xylan, five carbon polysaccharides (C5SOLD) (other than xylan), and six carbon polysaccharides (C6SOLD) combined represent the hemicellulose content [30].

Unit = kg	C	H	O	N	S
Cellulose	0.187	0.0262	0.207	0	0
Xylan	0.0695	0.00936	0.0741	0	0
Lignin	0.200	0.0234	0.0346	0	0
C5SOLD	0.00868	0.00117	0.00925	0	0
C6SOLD	0.0255	0.00357	0.0283	0	0
Acetate	0.0114	0.00192	0.0152	0	0
Extractives	0.00550	5.07E-05	0.0371	0.00235	4.09E-05
Total	0.507	0.0656	0.406	0.00235	4.09E-05
%	51.7	6.69	41.4	0.239	0.00417

Table 2b: Elemental composition bone dry poplar biomass. Xylan, five carbon polysaccharides (C5SOLD) (other than xylan), and six carbon polysaccharides (C6SOLD) combined represent the hemicellulose content [30].

Biorefinery

Currently no commercial facilities are producing bio-jet fuel from biomass via a bioconversion process. ASPEN-Plus chemical engineering software is used to simulate potential biorefinery process designs. The biorefinery simulations are designed to operate on 3200 tonnes of bone dry biomass per day. It is assumed that there is no biomass stored on site. Proposed poplar management schemes follow a just-in-time

harvest approach wherein poplar is harvested and delivered to the biorefinery as needed, this will avoid emissions associated with long term biomass storage. Simulation results show poplar biomass to bio-jet fuel conversion yields of 330 L t^{-1} for the natural steam gas reforming based processes and 305 L t^{-1} for the lignin gasification based processes. The biorefineries differ from each other in how hydrogen is acquired and the fuel source used to meet the energy demands of the facilities. The descriptions given below are overviews of the processes to convert poplar chips to jet fuel that were investigated. For in-depth descriptions of the biorefinery processes see the companion techno-economic analysis by Crawford et al. [11].

The biorefineries are similar in their process design, and have many of the same unit processes. The processes begin with dilute acid pretreatment and enzymatic hydrolysis. These steps are based on National Renewable Energy Laboratory (NREL) corn stover model, but modified to use a poplar feedstock [31]. Following enzymatic hydrolysis, glucose and xylose are fermented to acetic acid using *Moorella thermoacetica*. Acetic acid fermentation yield is projected to be 90 % and the titer 50 g L^{-1}. The yield and titer were supplied by industry partners developing an acetogen based biorefinery (Tim Eggeman, personal communication, 2014). The acetic acid undergoes reactive distillation, pressure swing distillation, hydrogenation, oligomerization, and one more hydrogenation step to become jet fuel. Biorefinery hydrogen requirement is 122 g L^{-1} of jet fuel. Hydrogen use for the first hydrogenation step, used to convert acetic acid to ethanol, is 114 g L^{-1} of jet fuel. The second hydrogenation step, converting unsaturated hydrocarbons to polymer fuel, uses 8 g L^{-1} jet fuel.

Waste water is treated onsite in a Waste Water Treatment (WWT) plant. The WWT design is based on Humbird et al. [32]. Methane generated during the anaerobic digestion stage is sent to the burner and combusted. All wastes are collected and sent to a landfill for disposal. Descriptions of the hydrogen production processes and energy sources for the four simulations follow below.

Simulation 1: Natural Gas Steam Reforming (NGSR bio-jet)

A natural gas steam reforming (NGSR) method is used to provide the hydrogen for the hydrogenation steps. The NGSR facility is integrated into the biorefinery to improve thermal efficiency. In this process lignin from the poplar biomass is combusted to provide heat and steam for the biorefinery. However, unlike second generation ethanol bioconversion facilities [32], the combustion of lignin cannot meet the entire heat and steam demand. Combustion of lignin and unreacted carbohydrates produces enough energy to meet 86 % of the heat/ steam demand. Natural gas is combusted to make up the remaining 14 % of the demand. Electricity is produced by converting high pressure steam into electricity via a multi-stage turbine. A small of amount excess electricity is generated during from process and is sold as a by-product. In the LCA this by-product is treated using the system expansion method per ISO 14044 guidelines [25]. An avoided production credit is generated for displacing electricity produced from natural gas, a likely candidate for marginal electricity [33]. Major process inputs and outputs for the NGSR bio-jet simulation are listed in Table 3.

Input	**NGSR Bio-jet**	**NGSR-HF Bio-jet**	**Unit**
Feedstock (bone dry)	81.4	81.4	g
Enzymes	0.683	0.683	g
Sulfuric Acid	1.46	1.46	g
Lime	2.43	2.43	g
Calcium carbonate	0.391	0.391	g
Carbon dioxide	0.172	0.172	g
Ammonia	1.03	1.03	g
Corn Steep Liquor	2.18	2.18	g
Sodium hydroxide	1.94	1.94	g
Natural gas - Steam reforming	0.0525	0.0525	MJ
Natural gas – Heat/steam	0.0937	0	MJ
Hog fuel – Heat/steam	0	8.23	g
Output			
Bio-jet fuel	1	1	MJ
Excess electricity	0.00254	0.00254	Kwh
CO_2 (biogenic)	87.5	102	g
CO_2 (non-biogenic)	32.6	27.9	g

Table 3: Natural Gas Steam Reforming based bio-jet processes – Major process inputs and outputs referenced to 1 MJ of NGSR and NGSR-HF bio-jet fuels.

Simulation 2: Natural Gas Steam Reforming with Hog Fuel (NGSR-HF bio-jet)

This process is similar to the NGSR bio-jet process, but attempts to reduce GHG emissions by reducing natural gas use. Natural gas needed to provide heat and steam is replaced with hog fuel. As a result, only biomass (lignin and hog fuel), are used to meet heat and steam demands. Major process inputs and outputs for the NGSR-HF bio-jet simulation are listed in Table 3. When the total amount of biomass used to produce bio-jet fuel is factored into yield calculations (poplar + hog fuel), the NGSR-HF bio-jet fuel yield is 300 L t^{-1}.

Simulation 3: Lignin Gasification (LG bio-jet)

In this process, lignin from the poplar biomass is recovered after fermentation and sent to a gasifier integrated into the biorefinery to produce hydrogen. The lignin gasification can only meet 75 % of the facilities hydrogen demand. Natural gas steam reforming is used to supplement the remaining 25 %. In the LG bio-jet process, all lignin is consumed in the gasification process and cannot be combusted to provide energy for the biorefinery. Natural gas is combusted in the burner/boiler of the biorefinery to provide the necessary heat and steam. High pressure steam is converted to electricity via a multi-stage turbine, but this alone cannot meet the entire biorefinery electricity demand. The remaining electricity demand is met by purchasing electricity. For the life cycle inventory work a unit process representing the average makeup of the 2012 U.S. national electrical grid is used to supply electricity [34]. Major process inputs and outputs for the LG bio-jet simulation are listed in Table 4.

Input	**LG Bio-jet**	**LG-HF Bio-jet**	**Unit**
Feedstock (bone dry)	88.4	88.4	g
Enzymes	0.743	0.743	g
Sulfuric Acid	1.59	1.59	g
Lime	2.64	2.64	g
Calcium carbonate	0.425	0.425	g
Carbon dioxide	0.187	0.187	g
Ammonia	1.12	1.12	g
Corn Steep Liquor	2.37	2.37	g
Sodium hydroxide	1.36	1.36	g
Natural gas - Supplemental hydrogen source	0.178	0.178	MJ
Natural gas – Heat/steam	0.506	0	MJ
Hog fuel – Heat/steam	0	44.5	g
Electricity	0.253	0.253	kwh
Output			
Bio-jet fuel	1	1	MJ
CO_2 (biogenic)	86.7	163	g
CO_2 (non-biogenic)	44.0	9.29	g

Table 4: Lignin gasification based bio-jet processes – Major process inputs and outputs referenced to 1 MJ of LG and LG-HF bio-jet fuels.

Simulation 4: Lignin Gasification with Hog Fuel (LG-HF bio-jet)

The LG-HF bio jet process is similar to the LG bio-jet process. The majority of the hydrogen demand is met via poplar lignin gasification. Natural gas steam reforming supplies the remaining hydrogen. Hog fuel is used to provide heat and steam for the facility. Major process inputs and outputs for the LG-HF bio-jet simulation are listed in Table 4. When the total amount of biomass used to produce bio-jet fuel is factored into yield calculations (poplar + hog fuel), the LG-HF bio-jet fuel yield is 200 L t^{-1}.

Ancillary chemicals

Each biorefinery process requires chemical inputs to convert the poplar biomass to jet fuel. The production of these chemicals is grouped into the ancillary chemicals section. Tables 3 and 4 list the major chemical inputs required by each biorefinery. Unit process data for the chemical inputs come from the USLCI [27], EcoInvent [28], literature, and the private sector. The electricity source in each unit process was set to come from a unit process representative of the 2012 U.S. national grid [34]. Data for enzyme production is supplied from Novozymes for their Cellic Ctec3 cellulases (Novozymes, personal communication, 2012). Transportation distances for each chemical are determined using the 2007 U.S. commodity flow survey [35].

Fuel distribution and use

The bio-jet fuel produced from each biorefinery is assumed to be transported 640 km to a distribution center (round trip). End use of the bio-jet fuel is combustion in a jet

engine. The bio-jet fuel produced in the biorefineries is assumed to be identical to petroleum based Jet-A fuel and will therefore have the same emissions when combusted in a jet engine. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) is used to provide jet engine emissions Model v1.2.0.11425 (GREET).

References

1. Borrion AL, McManus MC, Hammond GP. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. Renew Sustain Energ Rev 2012;16(7):4638-50.
2. Wiloso EI, Heijungs R, de Snoo GR. LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice. Renew Sustain Energ Rev 2012;16(7):5295-308.
3. Hileman JI, Stratton RW. Alternative jet fuel feasibility. Transport Policy 2014; 34:52-62.
4. Stratton RW, Wong HM, Hileman JI. Life cycle greenhouse gas emissions from alternative jet fuels. Cambridge (MA): Massachusetts Institute of Technology; 2010 June. PARTNER Project 28 Report PARTNER-COE-2010-001.
5. Agusdinata DB, Zhao F, Ilelji K, DeLaurentis D. Life cycle assessment of potential biojet fuel production in the United States. Environ Sci Technol 2011;45(21):9133-43.
6. Elgowainy A, Han J, Wang M, Carter N, Stratton R, Hileman J, et al. Life-cycle analysis of alternative aviation fuels in GREET. Lemont (IL): Argonne National Laboratory; 2012 June. 76 p. Technical Report ANL/ESD/12-8.
7. Han J, Elgowainy A, Cai H, Wang MQ. Life-cycle analysis of bio-based aviation fuels. Bioresource Tech. 2013;150:447-456.

8. Staples MD, Malina R, Olcay H, Pearlson MN, Hileman JI, Boies A, et al. Lifecycle greenhouse gas footprint and minimum selling price of renewable diesel and jet fuel from fermentation and advanced fermentation production technologies. Energy Environ. Sci. 2014;7:1545-1554.
9. Keoleian GA, Volk TA. Renewable energy from willow biomass crops: Life cycle energy, environmental and economic performance. Crit Rev Plant Sci 2005;24(5-6):385–406.
10. Hill J, Nelson E, Tilman D, Polasky S, Tiffany D. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. Proceedings of the National Academy of Sciences. 2006;103(30):11206-11210.
11. Crawford JT, Chin WS, Budsberg E, Bura R, Gustafson R. Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: Techno-economic assessment. Biotech. For Biofuels BBIO-D-16-00090. Accepted for publication May 2016 *Note to Editor – how should we cite this companion paper?*
12. Sassner P, Galbe M, Zacchi G. Steam pretreatment of Salix with and without SO2 impregnation for production of bioethanol. Appl Biochem Biotechnol 2005;121–124(1-3):1101–17
13. Mansfield SD, Mooney C, Saddler JN. Substrate and enzyme characteristics that limit cellulose hydrolysis. Biotechnol Prog 1999;15(5):804–16
14. Cherubini F, Stromman AH. Production of biofuels and biochemical from lignocellulosic biomass: Estimation of maximum theoretical yields and efficiencies using matrix algebra. Energ Fuel 2010;24(3):2657-66.
15. Andreesen JR, Schaupp A, Neurauter C, Brown A, Ljundahl LG. Fermentation of glucose, fructose, and xylose by *Clostridium thermoaceticum*: Effect of metals on growth yield, enzymes, and synthesis of acetate from CO_2. J of Bacteriology. 1973:114(2):743-51.
16. Ehsanipour M, Vajzovic Suko A, Bura R. Fermentation of lignocellulosic sugars to acetic acid by *Moorella thermoacetica*. Fermentation, cell culture and bioengineering. 2016; DOI 10.1007/s10295-016-1756-4.
17. Verser D, Eggeman TJ, inventors; ZeaChem Inc., assignee. Process for producing ethanol United States patent US 7964379. 2011 June 21.

18. Budsberg E, Crawford J, Gustafson R, Bura R, Puettmann M. Ethanologens vs. acetogens: Environmental impacts of two ethanol fermentation pathways. Biomass Bioenerg 2015;83(12):23-31.
19. Edwards T, Maurice LQ. Surrogate Mixtures to Represent Complex Aviation and Rocket Fuels. Journal of Propulsion and Power 2001; 17(2):462-466. DOI 10.2514/2.5765
20. Colket M, Edwards T, Williams S, Cernansky NP, Miller DL, Egolfopoulos F, Lindstedt P, Seshadri K, Dryer FL, Law CK, Friend D, Lenhert DB, Pitsch H, Sarofim A, Smooke M, Tsang W. Development of an Experimental Database and Kinetic Models for Surrogate Jet Fuels. 45th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV, USA. Paper No. AIAA 2007-770. January 2007. DOI 10.2514/6.2007-770
21. Cai X, Zhang X, Wang D. Land availability for biofuel production. Environ Sci Tech 2011;45(1):334-39.
22. Karatzos S, McMillan JD, Saddler JN. The potential and challenges of drop-in biofuels. Paris, France: International Energy Agency; 2014 July. 203 p. IEA Bioenergy Task 39 report T39-T1.
23. IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp, doi:10.1017/CBO9781107415324
24. Environmental management. Life cycle assessment - Principles and framework. Geneva, Switzerland: International Organization for Standardization; 2006. Report No.: ISO 14040:2006.
25. Environmental management. Life cycle assessment - Requirements and guidelines. Geneva, Switzerland: International Organization for Standardization; 2006. Report No.: ISO 14044:2006.
26. Caputo J, Balogh SB, Volk TA, Johnson L, Puettmann M, Lippke B, et al. Incorporating Uncertainty into a Life Cycle Assessment (LCA) Model of

Short-Rotation Willow Biomass (Salix spp.) Crops. Bioenerg Res 2014;7(1):48-59.

27. US life cycle inventory database [Internet]. Golden (CO): National Renewable Energy Laboratory. c2011 [cited 2012 September 5] Available from: http://www.nrel.gov/lci/.
28. Ecoinvent. Duebendorf, Switzerland: Swiss Center for life cycle inventories; 2009.
29. Farm Energy Analysis Tool [Internet]. University Park (PA): Camargo GGT, Ryan MR, Richard TL, Malcolm GM. c2015 [cited 2015 June] Available from: http://www.ecologicalmodels.psu.edu/agroecology/feat/.
30. Sannigrahi P, Ragauskas AJ, Tuskan GA. Poplar as a feedstock for biofuels: A review of compositional characteristics. Biofuels, Bioprod, Biorefin 2010;4(2):209-26.
31. Sanchez TS, Woods J, Akhurst M, Brander M, O'Hare M, Dawson TP, et al. Accounting for indirect land-use change in the life cycle assessment of biofuel supply chains. J R Soc Interface 2012;9(71):1105-19.
32. Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, et al. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol; Dilute-acid Pretreatment and Enzymatic Hydroylsis of Corn Stover. Golden (CO): National Renewable Energy Laboratory; 2011 May. 147 p. Technical Report NREL/TP-5100-47764 Contract No.: DE-AC36-08GO28308
33. Thomas CE. US marginal electricity grid mixes and EV greenhouse gas emissions. Int J of Hydrogen Energ 2012;37(24):19231-40.
34. Electric Power Annual [Internet]. Washington (DC): U.S. Department of Energy, Energy Information Administration. c2012 [cited 2013 December] Available from: http://www.eia.gov/electricity/annual/pdf/epa.pdf
35. 2007 Commodity Flow Survey. Washington (DC):U.S. Department of Transportation and U.S. Department of Commerce. c2010 [cited 2013 July 11]. Available from: http://www.census.gov/prod/2010pubs/ec07tcf-us.pdf

Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment of site specific impacts

Erik Budsberg, Nathan Parker, Prasad Bandaru, Renata Bura, Rick Gustafson

A note to the reader - the below article has been prepared for publication and follows the publication format as follows: Background, Results, Discussion, Conclusion, Methods.

Abstract

Background - Hydrocarbon drop-in bio-jet fuels could help to reduce greenhouse gas emissions within the aviation sector. The commercial scale production of these bio-jet fuels will require investments into new bioconversion facilities to convert biomass to hydrocarbon drop-in jet fuel. These conversion facilities will need dependable year-round supply of biomass feedstock. Large tracts of land will be required to grow this feedstock and the change in management of these lands could have substantial environmental impacts. This research investigates potential environmental impacts associated with converting land to grow poplar trees for conversion to drop-in bio-jet fuel. Spatial analysis and life cycle methodologies are used to evaluate changes to land use and management in 4 different regions within the western United States. The four regions are based around biorefineries proposed to be located near Pilchuck WA, Hayden ID, Jefferson OR, and Clarksburg CA. Each of the four regions would annually supply 125 million tonnes of poplar biomass to a biorefinery producing 380 million liters of bio-jet fuel. The amount of land converted is based off of predicted poplar yields for each region. The type of land converted to growing poplar, as well as the impacts associated with land use change will depend on regionally specific factors.

Results - The Clarksburg region is predicted to have the highest poplar yield and least amount of land converted. Of the land converted in the Clarksburg region, the majority of the land would come from croplands. Relative to the other regions, the conversion of intensively managed cropland to less intensively managed poplar production results in a decrease of fertilizer use and small increase in chemical inputs and fuel use. This translates to the lowest annual Global Warming Potential (GWP) for the Clarksburg region relative to the GWPs of Pilchuck, Jefferson, and Hayden. Conversely, the land in the Jefferson region would primarily come from unmanaged rangelands. Bringing this

rangeland into managed production results in a regional increase of nitrogen fertilizer use, chemical inputs, and fuel use, as well as the largest increase in GWP, relative to the other regions. The type of land converted isn't the only predictor for changes in agricultural inputs and GWP; total land converted also plays a substantial role as demonstrated by the Hayden region. Poplar yields are predicted to be lower in the Hayden region and more land must be converted to meet the biorefinery feedstock needs. The increased use of land leads to higher fuel use and greater greenhouse gas emissions in the Hayden region.

Conclusion - Combining life cycle assessment methodology with spatial analysis can help provide a more detailed view of the shifts in land use and resulting impacts. Feedstock growth and harvesting is a necessary and important process in the production for biofuels. The total contribution of feedstock production to the overall global warming potential lwill not be as substantial as downstreaming conversion and processing of biomass into biofuel, but changes to land use and management could result in changes at the local level that could result in unintended negative environmental consequences. It is important that these impacts to land use, along with greenhouse gas emissions, are modelled and evaluated to better understand the regional and local implications of building a biofuels industry.

Background

In the past decade there has been a substantial amount of Life Cycle Assessment (LCA) research focused on the commercial production of biofuels from lignocellulosic feedstocks (Borion et al. 2012, Wiloso et al. 2012, Stratton et al. 2010; Agusdinata et al. 2011; Elgowainy et al. 2012; Han et al. 2013; Staples et al. 2014). Many of these LCAs typically focus only on global impacts (i.e. greenhouse gas emissions and fossil fuel use), as biofuels are intended to help mitigate climate change effects by replacing petroleum based transportation fuels. Few of the biofuel LCA studies report on regional impacts (i.e. acidification, eutrophication, smog, water use, etc.) (Borrion et al. 2012, Wiloso et al. 2012, Nordberg et al. 2014, Kim et al. 2015) and

fewer still take into account the spatial variability of these impacts (Mutel et al. 2011, Nordberg et al. 2014). A major factor contributing to this issue is that regional impacts cannot be addressed when the location of a biorefinery and lands growing the lignocellulosic feedstock are unknown (Mutel et al. 2011). This has led to an incomplete view of life cycle impacts of producing biofuels (Nordberg et al. 2014).

Addressing regionally specific and non-global impacts requires LCAs incorporate spatial analyses within the scope of research. This approach has yet to become common practice, but research is now starting to be published that unify biofuel LCAs with geographical information systems (GIS) (Geyer et al. 2010, Gasol et al. 2011, Mutel et al. 2011, van der Hilst et al. 2012, Sinistore et al. 2015). In these studies, the LCA is used to calculate environmental impacts and GIS are used to spatially locate where the environmental impacts are generated. This allows researchers to identify hot spots and potentially develop solutions to reduce these impacts. Spatial LCAs can also be used to evaluate potential changes to an area when introducing a new biofuel production system. This is particularly important for systems that involve agricultural practices. Not only is there a lot of spatial variability in agricultural practices (Sinistore et al. 2015), but they also take up large areas of land, making land use change issues a concern. To address these impacts some researchers are beginning to use a spatial LCA approach to measure the net effect to environmental impacts that result from switching from one system to another in their respective regions.

Spatially explicit LCAs that are specific to the system and locations they evaluate have shown that when site specific factors are considered there can be substantial variability in LCA results (Gasol et al. 2011, Mutel et al. 2011, van der Hilst et al. 2012,

Sinistore et al. 2015). Agricultural practices are not static and can substantially vary from one region to the next (Norberg et al. 2014, Kim et al. 2015, Sinistore et al. 2015). For biofuel systems that use a feedstock(s) with a lower carbon footprint the effect of agricultural variability on total greenhouse gas emissions may be small, but for biofuels based on feedstocks with larger carbon footprints the overall variability could have a more pronounced effect. Spatially locating biofuel production can therefore help to reduce some of the variability and uncertainty in biofuel LCAs (Gasol et al. 2011, Mutel et al. 2011, van der Hilst et al. 2012, Sinistore et al. 2015). Conclusions from these studies further enforces the need to assess biofuel LCAs using spatially explicit LCAs.

In this research spatial analysis and life cycle methodologies are used to help identify regional land use changes and potential environmental impacts associated with converting lands from rangeland and croplands to growing poplar trees for biofuel production. This work builds on the LCA research presented in Budsberg et al. 2016 and uses the same biorefinery model that is designed to produce bio-jet fuel from poplar biomass. Cradle to biorefinery gate analyses for poplar bioenergy plantations are conducted for four regions in the western United States that could potentially host bio-jet fuel biorefineries. These regions are based around biorefineries simulated to be located in Pilchuck WA, Hayden ID, Jefferson OR, and Clarksburg CA. Within these regions, site suitability models identify lands that could potentially be converted to poplar crop production and feedstock transportation distances. Poplar crop management and site specific emissions are based on data collected from poplar pilot farms near each of the four proposed biorefinery locations. These results will help complete the picture of

potential life cycle environmental impacts resulting from a commercial scale biofuels industry in the western United States.

Results

The SWAP-AHB and GBSM models projected the types of lands and crops that could switch to growing to poplar at a selling price of $60 per tonne of poplar biomass. Results are presented in Tables 1 - 4. The Clarksburg region required the least amount of land to produce 1.25 million BDT of poplar chips per year, followed by Pilchuck, Jefferson, and Hayden, respectively. Compared to Clarskburg, Pilchuck required 30 % more land, Jefferson 54 % more land, and Hayden 137 % more land. The large range in land is due to the projected poplar yields for each region, with Clarksburg expected to have the highest biomass yields and Hayden the lowest. See Figure 1 for spatial overview of lands converted to growing poplar in each region.

Pilchuck		Hectares	%
Land use type converted to poplar	Rangeland	51260	73
	Cropland: Non-irrigated	9102	13
	Cropland: Irrigated	10177	14
	Total	70540	
Crops converted: Irrigated	Silage corn	2995	4
	Winter wheat	2957	4
	Tame hay (excludes alfalfa)	1721	2
	Barley	723	1
	Other crops	1781	3
Crops converted: Non-irrigated	Tame hay (excludes alfalfa)	4349	6
	Silage corn	3841	5
	Barley	480	1
	Other crops	431	<1

Table 1: Pilchuck land use and crop types converted to growing poplar. 'Other crops' are crops that individually represented less than 1 % of the land used to grow crops. Percent column is based off of total land use types converted to growing poplar.

Jefferson		Hectares	%
Land use type converted to poplar	Rangeland	77730	93
	Cropland: Non-irrigated	5164	6
	Cropland: Irrigated	389	<1
	Total	83282	
Crops converted: Non-irrigated	Tame hay (excludes alfalfa)	3922	5
	Oats	1065	1
	Other crops	177	<1

Table 2: Jefferson land use and crop types converted to growing poplar. 'Other crops' are crops that individually represented less than 1 % of the land used to grow crops. Percent column is based off of total land use types converted to growing poplar.

Hayden		Hectares	%
Land use type converted to poplar	Rangeland	75243	59
	Cropland: Non-irrigated	27816	22
	Cropland: Irrigated	25171	20
	Total	128229	
Crops converted: Irrigated	Dry edible beans (excludes lima)	18552	14
	Barley	1944	2
	Alfalfa hay	1934	2
	Tame hay (excludes alfalfa)	1542	1
	Other crops	1198	<1
Crops converted: Non-irrigated	Winter wheat	10935	9
	Tame hay (excludes alfalfa)	6252	5
	Alfalfa hay	5348	4
	Barley	2652	2
	Spring wheat	1932	2
	Other crops	697	<1

Table 3: Hayden land use and crop types converted to growing poplar. 'Other crops' are crops that individually represented less than 1 % of the land used to grow crops. Percent column is based off of total land use types converted to growing poplar.

Clarksburg		Hectares	%
Land use type converted to poplar	Rangeland	18737	35
	Cropland: Non-irrigated	1488	3
	Cropland: Irrigated	33956	63
	Total	54182	
Crops converted: Irrigated	Silage corn	12851	24
	Winter wheat	10695	20
	Grain corn	5104	9
	Barley	1998	4
	Dry edible beans (excludes lima)	1097	2
	Tame hay (excludes alfalfa)	756	1
	Other crops	1455	3
Crops converted: Non-irrigated	Tame hay (excludes alfalfa)	1067	2
	Other crops	421	<1

Table 4: Clarksburg land use and crop types converted to growing poplar. 'Other crops' are crops that individually represented less than 1 % of the land used to grow crops. Percent column is based off of total land use types converted to growing poplar.

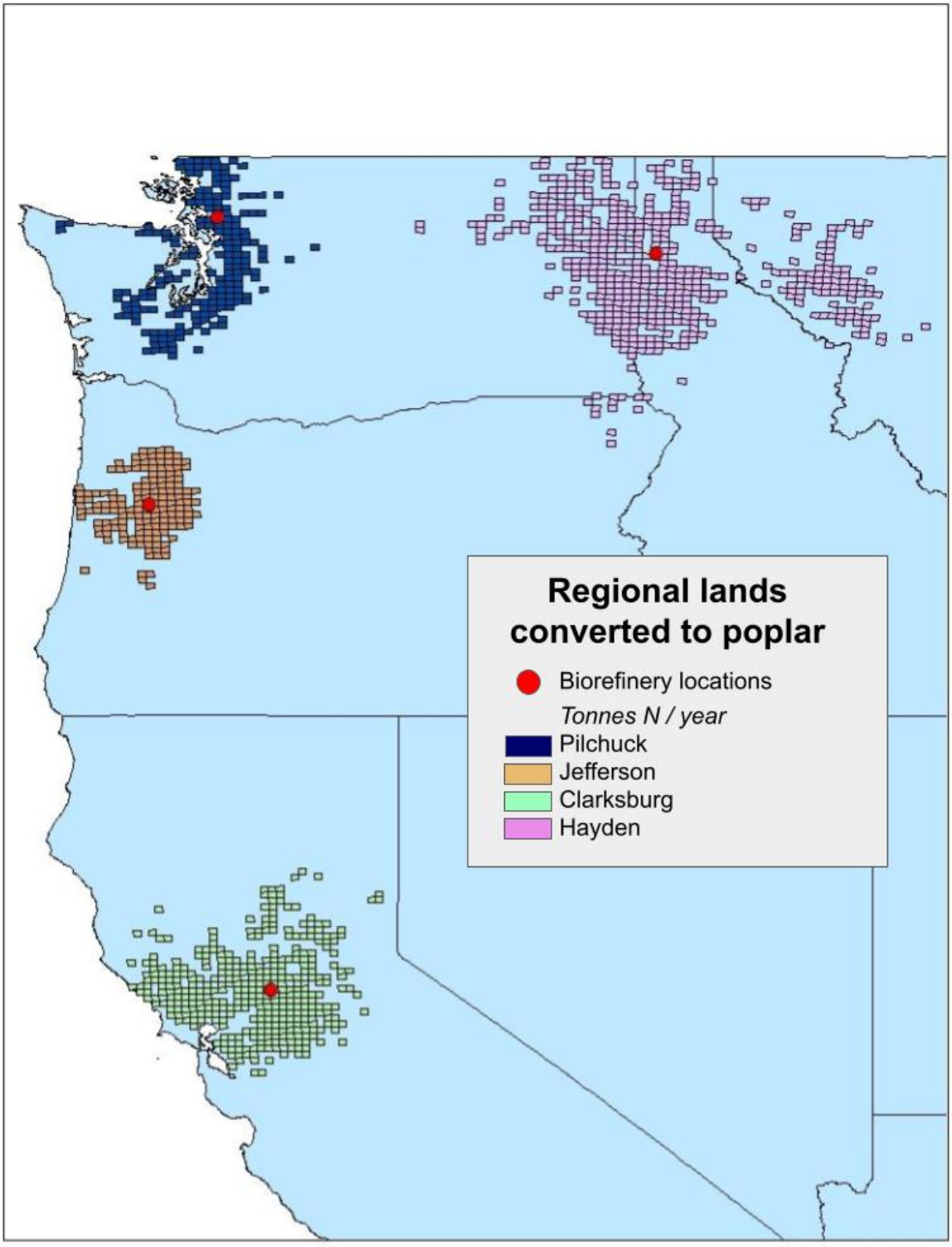
Regional lands converted to poplar
Biorefinery locations
Tonnes N / year
Pilchuck
Jefferson
Clarksburg
Hayden

Figure 1 - Areas where land could be converted to crowing poplar trees for bio-jet fuel. Each pixel is 8 km x 8km and contains at least one hectare of land than could be converted. The type of land converted in each pixel could be rangeland or cropland (irrigated and non-irrigated).

Regions also differed on the amount of pasture and cropland converted to growing poplar trees (Tables 1 - 4). The Jefferson region had the most amount of rangeland converted to growing poplar followed by Hayden, Pilchuck, and Clarksburg. On a percentage basis of land converted for each region almost all of the land in the Jefferson region projected to grow poplar trees would come from rangeland (93 %). In the Pilchuck, Hayden, and Clarksburg regions rangeland is projected to make up 73 %, 59 %, and 35 %, respectively, of the land used to grow poplar. Where croplands are converted to growing poplar, the type of crop converted to poplar differs for each region. In Jefferson the small amount of cropland converted to poplar is from non-irrigated tame hay (6 %) and oats (1 %). For the Pilchuck region the top crops converted include irrigated silage corn (4 %) and winter wheat (4 %), and non-irrigated tame hay (6 %) and silage corn (5 %). The main crops in the Hayden region are projected to come from irrigated beans (14 %), and non-irrigated winter wheat (9 %) and tame hay (5 %). In Clarksburg the top crops converted are irrigated silage corn (24 %), winter wheat (20 %), and grain corn (9 %). For a list of all crops converted for each region see Tables 1 - 4.

Nitrogen fertilizer was used in all four regions and is also expected to be used when growing poplar trees (Table 5). Under current active management practices, the Clarksburg region has the highest N fertilizer use, followed by Hayden, Pilchuck and lastly Jefferson. Under poplar management schemes N fertilizer use is projected to be

highest in the Hayden region, followed by Jefferson, Pilchuck and Clarksburg. When lands are converted from their current management state to poplar production the N fertilizer use decreases in three of the four regions: Clarksburg, Pilchuck, and Hayden regions are projected to see N fertilizer use decrease of 82 %, 45 %, and 17%, respectively. The average rate of application of N fertilizer on actively managed lands will also decrease in these three regions (Table 5). In the Jefferson region the N fertilizer average rate of application per hectare of actively managed land will decrease as well, however the total effect to the region will be a N fertilizer use increase of 239 %. The rate of N fertilizer application rate for poplar is less than the rate of N fertilizer for tame hay and oats in the Jefferson OR region, but by encouraging poplar growth, a large amount of rangeland (effectively unmanaged with no N fertilizer use) will become actively managed, thereby increasing the total amount N fertilizer use in the Jefferson region (Table 5). See Figure 2 for a spatial visualization of the change in N fertilizer use.

		Pilchuck	Jefferson	Hayden	Clarksburg
Nitrogen Fertilizer Use (tonnes/year)	Current practices	2613	482	3046	5549
	average use per hectare of cropland	*0.14*	*0.087*	*0.057*	*0.16*
	Poplar projection	1432	1633	2515	1063
	average use per hectare of land	*0.020*	*0.020*	*0.020*	*0.020*
	Change to region	-1181	1152	-531	-4487
	% Change to region	-45	239	-17	-81
Phosphorus Fertilizer Use (tonnes/year)	Current practices	965	170	2569	1493
	average use per hectare of cropland	*0.050*	*0.031*	*0.048*	*0.042*
	Poplar projection	0	0	0	0
	Change to region	-965	-170	-2569	-1493
	% Change to region	-100	-100	-100	-100
Potassium Fertilizer Use (tonnes/year)	Current practices	791	38	1235	52
	average use per hectare of cropland	*0.041*	*0.0068*	*0.023*	*0.0015*
	Poplar projection	0	0	0	0
	Change to region	-791	-38	-1235	-52
	% Change to region	-100	-100	-100	-100

Table 5: Fertilizer inputs per region.

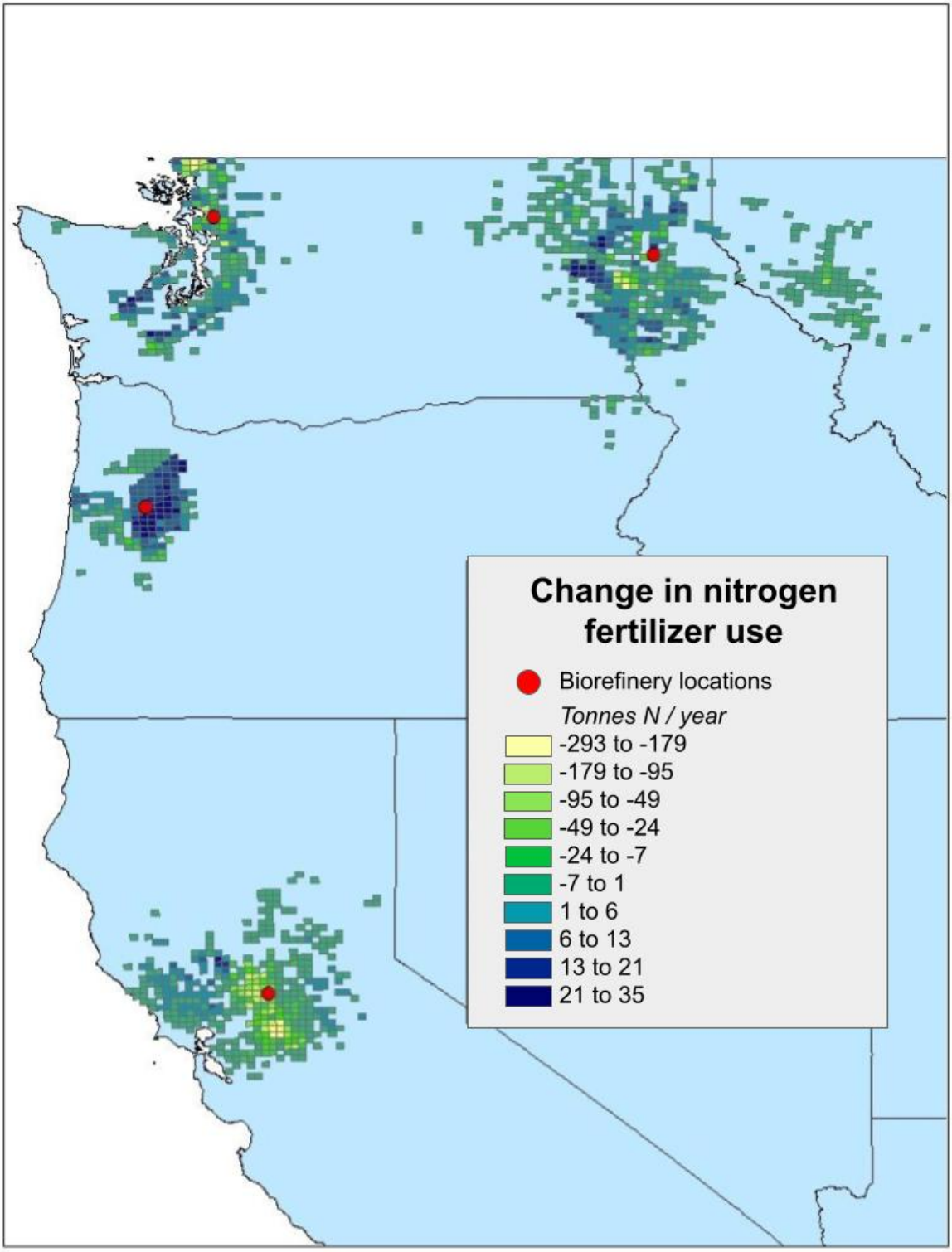
Change in nitrogen fertilizer use
Biorefinery locations
Tonnes N / year
-293 to -179
-179 to -95
-95 to -49
-49 to -24
-24 to -7
-7 to 1
1 to 6
6 to 13
13 to 21
21 to 35

Figure 2 - Change in nitrogen fertilizer use for each pixel as a result of switching from current practices to growing poplar trees for bio-jet fuel production. Green to yellow indicates a decrease in nitrogen use when switching to poplar. Light blue to dark blue indicates an increase in nitrogen use.

Phosphorus and potassium fertilizers are also currently used in all four regions for growing crops, although not as predominantly as N fertilizer as not all crops require their inputs. Neither phosphorus nor potassium are projected to be used when growing poplar, therefore switching to a poplar crop results in a 100 % decrease of phosphorus and potassium fertilizers in all four regions (Table 5). On an average rate of application per hectare the croplands in the Pilchuck region will see the biggest effect of ceasing the use phosphorus (on average 50 kg P per hectare of cropland per year) and potassium (on average 41 kg K per hectare of cropland per year). As an entire region, Hayden will see the biggest total effect where phosphorus and potassium use will go from 2569 tonnes per year and 1235 tonnes per year, respectively, to zero. See Figures 3 & 4 for a spatial visualization of the change in P and K fertilizer use.

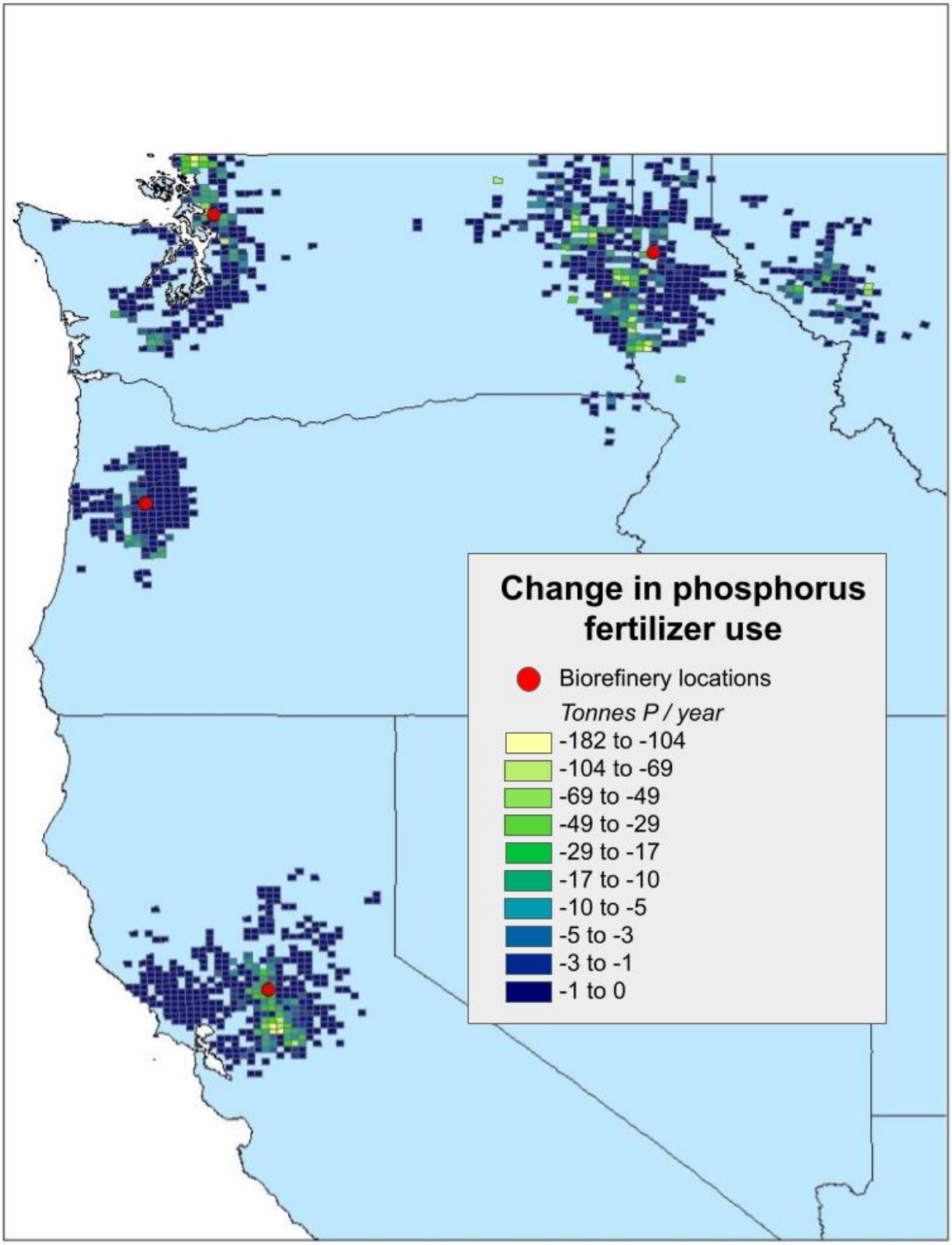
Change in phosphorus fertilizer use
Biorefinery locations
Tonnes P / year
-182 to -104
-104 to -69
-69 to -49
-49 to -29
-29 to -17
-17 to -10
-10 to -5
-5 to -3
-3 to -1
-1 to 0

Figure 3 - Change in phosphorus fertilizer use for each pixel as a result of switching from current practices to growing poplar trees for bio-jet fuel production. Phosphorus fertilizer is not expected to be used to grow poplar trees, therefore all pixels would see a decrease in use. Pixels that contain crops where phosphorus fertilizer is used would see the greatest reduction in use (light blue/ green to yellow). Pixels that predominantly contain rangeland that would be converted would see very little reduction in phosphorus use (dark blue).

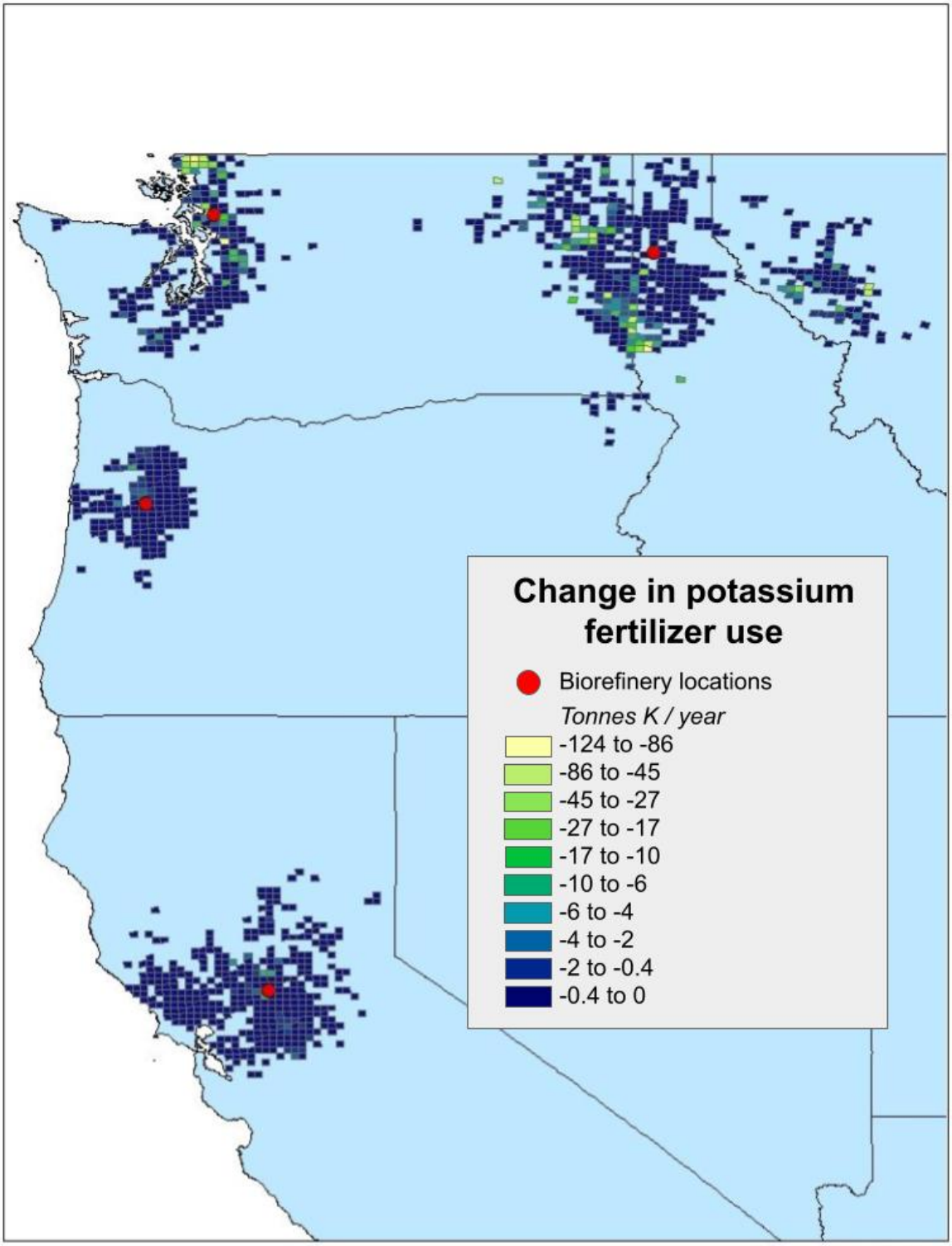
Change in potassium fertilizer use
Biorefinery locations
Tonnes K / year
-124 to -86
-86 to -45
-45 to -27
-27 to -17
-17 to -10
-10 to -6
-6 to -4
-4 to -2
-2 to -0.4
-0.4 to 0

Figure 4 - Change in potassium fertilizer use for each pixel as a result of switching from current practices to growing poplar trees for bio-jet fuel production. Potassium fertilizer is not expected to be used to grow poplar trees, therefore all pixels would see a decrease in use. Pixels that contain crops where potassium fertilizer is used would see the greatest reduction in use (light blue/ green to yellow). Pixels that predominantly contain rangeland that would be converted would see very little reduction in phosphorus use (dark blue)

Chemical usage, defined in this study as pesticides, insecticides, and herbicides, are used in all four regions for the management of current crops, as well as in the growth management of poplar trees (Table 6). For current actively managed croplands the total regional use of chemical controls is highest for Hayden, followed by Pilchuck, Clarksburg, and Jefferson. On an average per acre of cropland basis Hayden has the highest rate of chemical usage followed by Clarksburg, Jefferson, and Pilchuck. When lands are converted to growing poplar, the average rate of chemical usage remains the lowest in the Pilchuck region. Clarksburg and Jefferson also see a decrease in the average rate of chemical usage, while Hayden is projected to have an increase in the average rate of chemical inputs per hectare when converted to growing poplar. From a total annual regional standpoint Pilchuck is the only area that is expected to see an overall decrease in chemical inputs. Clarksburg, Hayden, and Jefferson will see regional increases of 18 %, 228 %, and 511 %, respectively (Table 6). See Figure 5 for a spatial visualization of the change in chemical pest control inputs.

		Pilchuck	Jefferson	Hayden	Clarksburg
Chemical inputs (tonnes/ year)	Current practices	187	18	240	124
	average use per hectare of cropland	*0.010*	*0.0033*	*0.0045*	*0.0035*
	Poplar projection	56	113	786	146
	average use per hectare of land	*0.00079*	*0.0014*	*0.0061*	*0.0027*
	Change to region	-132	94	546	22
	% Change to region	-70	511	228	18

Table 6: Chemical pest control inputs.

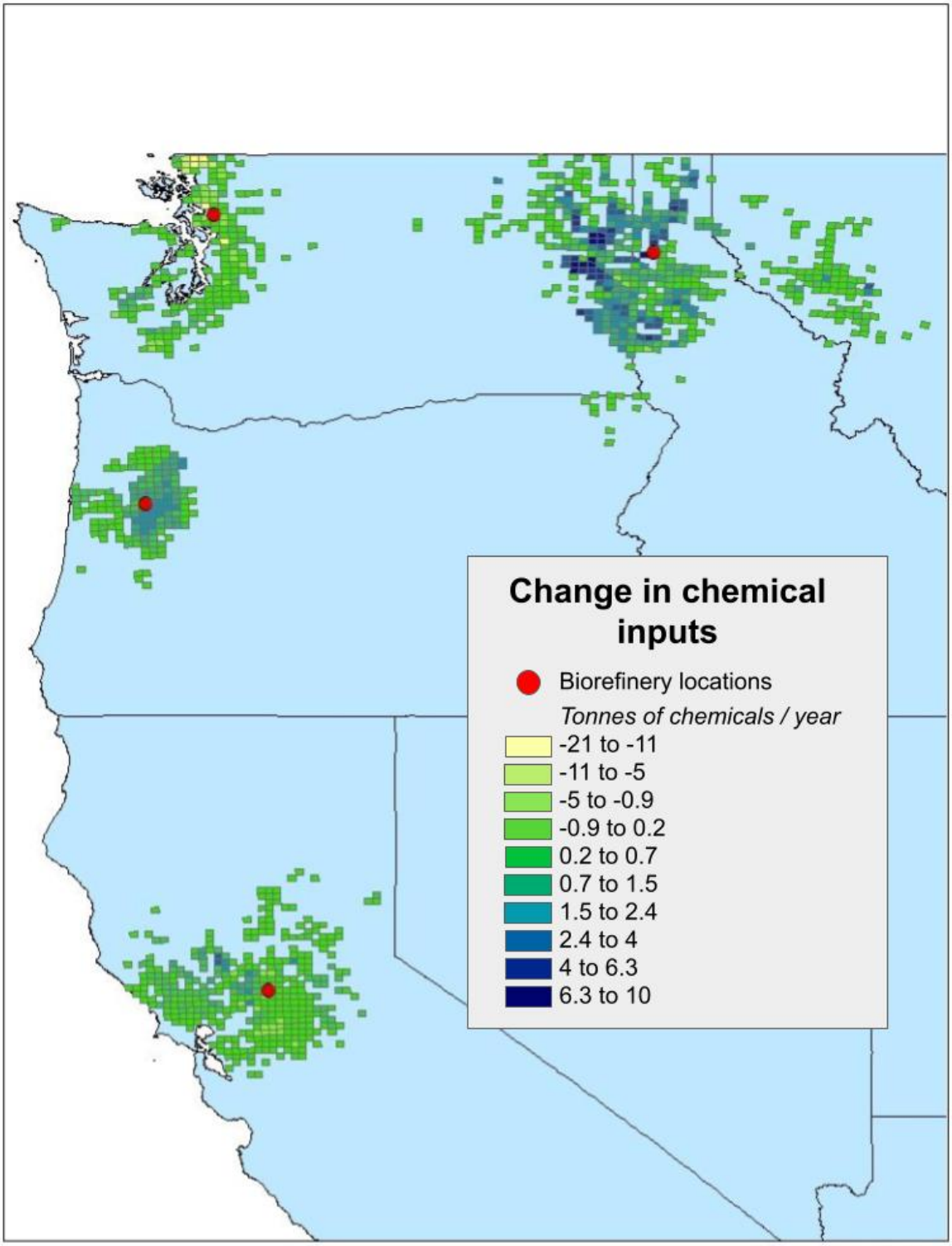
Change in chemical inputs
Biorefinery locations
Tonnes of chemicals / year
-21 to -11
-11 to -5
-5 to -0.9
-0.9 to 0.2
0.2 to 0.7
0.7 to 1.5
1.5 to 2.4
2.4 to 4
4 to 6.3
6.3 to 10

Figure 5 - Change in chemical inputs for each pixel as a result of switching from current practices to growing poplar trees for bio-jet fuel production. Chemical inputs include all pesticides, insecticides, and herbicides. Green to yellow indicates a decrease in chemical inputs when switching to poplar. Light blue to dark blue indicates an increase in chemical inputs.

The use of mechanical equipment, with its associated fuel usage, is required for the management of both current croplands and poplar tree farms (Table 7). Under current management practices the Hayden region sees the highest annual fuel use, followed by Clarksburg, Pilchuck and Jefferson. The average rate of use per hectare of cropland the fuel use is highest in the Clarksburg region while the average rate of fuel use is lower and fairly consistent in the other three regions (Table 7). Switching to a poplar tree crop results in a fuel use increase for all 4 regions with Jefferson seeing the highest increase (1,582 %) followed by Pilchuck (289 %), Hayden (181 %), and Clarksburg (28 %). The average rate of fuel use per hectare of land when growing poplar is approximately the same for all 4 regions (~ 3.7 MJ of fuel use per hectare per year). Compared to the average rate of fuel use for the actively managed crops, the average rate of use per hectare to produce poplar is somewhat similar. The increase of actively managed lands when switching from the current practices to poplar production results in higher fuel use for each region. See Figure 6 for a spatial visualization of the change of fuel use for each region.

		Pilchuck	Jefferson	Hayden	Clarksburg
Fuel Use (terajoules/ year)	Current practices - gasoline	10	5	18	8
	Current practices- diesel	60	14	145	140
	Current practices- total	70	18	163	148
	average use per hectare of cropland	*0.0036*	*0.0033*	*0.0031*	*0.0042*
	Poplar projection - diesel	271	308	459	191
	average use per hectare of land	0.0038	0.0037	0.0036	0.0035
	Change to region	201	289	295	42
	% Change to region	289	1582	181	28

Table 7: Fuel Use. Farm management only, no transportation of crops beyond farm exit gate.

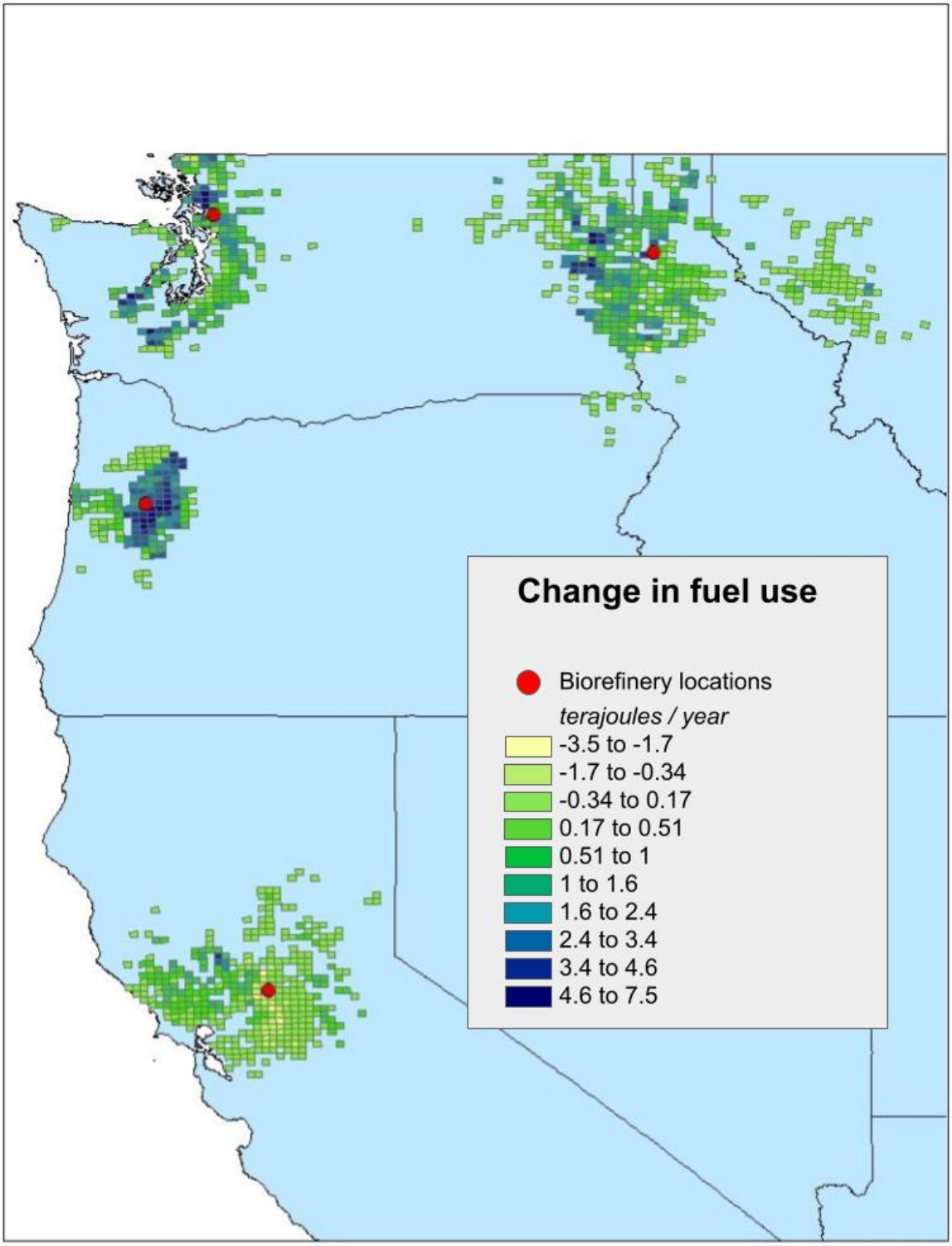
Change in fuel use
Biorefinery locations
terajoules / year
-3.5 to -1.7
-1.7 to -0.34
-0.34 to 0.17
0.17 to 0.51
0.51 to 1
1 to 1.6
1.6 to 2.4
2.4 to 3.4
3.4 to 4.6
4.6 to 7.5

Figure 6 - Change in fuel use for each pixel as a result of switching from current practices to growing poplar trees for bio-jet fuel production. Fuel use includes diesel and gasoline. Green to yellow indicates a decrease in fuel use when switching to poplar. Light blue to dark blue indicates an increase in fuel use.

Transportation distances from poplar tree farms to their respective biorefinery in each region are modelled using GBSM. The total distance and average distance the poplar chips must travel annually from farm to biorefinery differ for each region are shown in Table 8. Poplar chips travel the farthest in the Hayden region, followed by Clarksburg, and Jefferson. The distances travelled affects fuel needs to transport fuels and the combustion of these fuels ultimately affects the total energy needed to produce bio-jet fuel, as well as the GWP. Fuel use for poplar chip transportation for each region is reported in Table 8.

	Pilchuck	**Jefferson**	**Hayden**	**Clarksburg**
Total annual distance (km)	22666	10782	80457	38909
Average single-haul distance (km)	119	68	158	106
Projected annual fuel use (terajoules)	120	61	170	100

Table 8: Poplar chip transportation. Farm gate to biorefinery gate. Distances listed here are one-way. Round trip distances are used for assessing fuel use as part of the life cycle modelling.

GWPs for lands identified in this study, and the changes in their management/use, for all four regions are reported in Table 9. Under current land management practices Clarksburg has the highest GWP followed by Hayden, Pilchuck and Jefferson. The largest source of GHGs contributing to the GWP of the four regions is the manufacturing and use of nitrogen fertilizer followed by fuel use. Chemical inputs,

phosphorus, and potassium fertilizers add relatively small amounts to the GWPs of current practices.

Switching to poplar production has varying GWP effects depending on the region. Poplar projections for Pilchuck, Hayden, and Jefferson indicate increases in the regional GWP by 40 %, 137 %, and 710 %, respectively. Clarksburg GWP would decrease by 51 % if land was switched to poplar production (Table 9). When growing poplar, fuel use is the largest source of GHGs contributing to the GWP for all four regions followed by nitrogen fertilizer manufacturing and N_2O emissions resulting from its use (Table 9).

		Pilchuck		Jefferson		Hayden		Clarksburg	
		Current practices	Poplar projection	Current practices	Poplar projection	Current practices	Poplar projection	Current practices	Poplar projection
Annual GWP (tonnes of CO_2 eq)	Chemical inputs	1502	446	148	903	1927	6312	996	4
	Fuel Use	5938	23068	1558	26194	13904	39057	12641	16227
	Nitrogen	15286	8374	2817	9553	17818	14714	32463	6216
	N_2O emissions from N fert (FEAT)	15678	8589	2889	9798	18275	15092	33296	6375
	Phosphorous	0	0	0	0	0	0	0	0
	Potassium	0	0	0	0	0	0	0	0
	Farm gate total	22725	31888	4522	36650	33649	60083	46100	22448
	Change to region	NA	9162	NA	32128	NA	46179	NA	-23653
	% Change to region	NA	40	NA	710	NA	137	NA	-51
	Transportation to biorefinery	NA	8800	NA	4600	NA	13000	NA	7500
	Poplar total (includes transportation)	NA	40688	NA	41250	NA	73083	NA	29948

Table 9: Regional Global Warming Potentials

Direct land use change (DLUC) CO_2 emissions vary widely between the four regions and are dependent on the amount (total hectares converted, not percentage of land converted) of rangeland converted to growing poplar. Regions with more rangelands converted to growing poplar have higher initial carbon debts that must be paid off. The highest DLUC emissions are in Jefferson with 3,400,000 tonnes of CO_2 eq, followed by Hayden at 3,300,000 tonnes of CO_2 eq, Pilchuck at 2,300,000 tonnes of CO_2 eq, and Clarksburg at 820,000 tonnes of CO_2 eq (Table 10). These emissions contribute to the overall GWP for each region, but are onetime emissions, rather than related to annual emissions as the other impacts discussed above. The DLUC therefore creates a carbon 'debt' that must be paid off before the respective regional biorefinery systems can become carbon neutral or negative. This is discussed in more detail towards the end of the discussion section.

	Pilchuck	**Jefferson**	**Hayden**	**Clarksburg**
GWP (tonnes of CO_2 eq)	2,300,000	3,400,000	3,300,000	820,000

Table 10: Direct Land Use Change emissions

Discussion

The amount and type of land converted to growing poplar trees for conversion to bio-jet fuel is dependent on multiple variables including predicted poplar crop yield, types of crops being grown in the region, and the amount of rangeland available. As demonstrated in Figure 1 and Tables 1 - 4 there is a wide variation in the amount and type of land converted in each region. These differences in land used to grow poplar

trees dictate the differences in impacts observed in each region. Changes in fertilizers, chemical usage, and fuel use can have local impacts, as well as contribute to the overall GWP for each region. Understanding these site specific characteristics are important to develop a more detailed view of how changes to land management practices can impact a region when land use is switched from current management practices to poplar bioenergy farms.

In the Hayden, Pilchuck, and Jefferson regions the majority of land converted to growing poplar would come from rangeland, whereas the majority of land converted to growing poplar will come from croplands in the Clarksburg region (Tables 1 - 4). Rangeland is assumed to be effectively unmanaged (no fertilizer, chemical inputs, etc.) and converting this land into active poplar crop management will increase the use of fertilizers, chemical inputs, and fuel use which lead to regional and global environmental impacts. Where actively managed crops are replaced with poplar production, the net effect to the land will vary and is dependent on how those crops were managed prior to poplar conversion. For example, switching to poplar from crops that require more intensive management, such as grain corn, will result in a decrease in fertilizer use, chemical inputs, and fuel use. The displacement of food crops to produce bioenergy, and the potential observed benefit in reduction of fertilizers, chemical inputs, and fuel use, will likely add to the continuing debate of land use and food vs fuels, however the analysis of indirect land use change and its overall impact is beyond the scope of this study.

Under current land management practices nitrogen fertilizer use varied from region to region (Figure 2). The amount of fertilizer applied per hectare of managed

cropland depends on the region and the crops being grown there (Table 5). Converting to poplar production results in a decrease in fertilizer use in all regions except Jefferson. Actively managed croplands in the Jefferson region do not have the lowest average amount of nitrogen fertilizer use per hectare (compared to active croplands in other regions), but it does have the lowest total amount of nitrogen fertilizer use for the lands that are converted to poplar. Jefferson is the only region to see an increase in nitrogen fertilizer use when switching to poplar production because 93 % of the land in the region that would grow poplar is currently unmanaged pasture/rangeland. Rangeland does not receive any fertilizer treatments. Growing poplar on this land, and adding nitrogen fertilizer, substantially increases the amount of nitrogen fertilizer use in the region, even though the average amount of fertilizer applied to a hectare of land for poplar is less than the average rate of application for current actively managed croplands (Table 5). In the Clarksburg region the opposite effect is observed. A majority of the land projected to grow poplar is currently being used as cropland to grow corn and wheat (Table 4). These crops require higher nitrogen fertilizer use compared to growing poplar. Making the switch to poplar decreases the average amount of nitrogen fertilizer used per hectare and the total amount of nitrogen fertilizer used in the region. Both Pilchuck and Hayden regions see similar effects of decreasing nitrogen fertilizer use when switching to poplar, however the amount of tonnes of nitrogen saved varies per region (Table 5). Figure 2 displays the change in nitrogen fertilizer use and demonstrates the variability that exists region by region, and pixel by pixel. Even within a region there is a large range of variability with some pixels seeing an increase and others seeing a decrease. Phosphorus and potassium fertilizer use show similar trends

within the regions for current croplands. Both of these fertilizers are applied at lower rates than nitrogen fertilizer and their use does not differ as much within each region (Table 5, Figures 3 - 4). GreenWood Resources has indicated that they do not expect to use either of these fertilizers to grow poplar trees. Converting to poplar production cuts the use of potassium and phosphorus use in each region to zero. The discontinued use of these fertilizers reduces the impact associated with their production and use, but these do not have as big of an impact as the changes in nitrogen fertilizer use.

Chemical inputs used to control pests and promote crop growth (i.e. pesticides, herbicides, insecticides, etc.) vary from region to region (Figure 5). Jefferson, Hadyen, and Clarksburg regions are all expected to see increased use in chemical inputs when switching land use to poplar production (Table 6). Similar to the use of nitrogen fertilizer, Jefferson will see the largest increase in chemical inputs as much of the land converted to poplar is currently unmanaged. Under currently active practices the Hayden region has the highest use of chemical inputs and under a poplar management plan the region is still expected to use more than all other regions combined. This trend suggests that compared to the other regions, the Hayden region may be more susceptible to negative pest interactions and therefore a higher use of chemical inputs is required to maintain good crop yields. Pilchuck is the only region projected to have a decrease in chemical inputs when lands are converted to poplar production. Compared to other regions, croplands in the Pilchuck region have the highest application rate per hectare of land (average rate, not total use) (Table 6). However, when switched to poplar production, this region is expected to have the lowest average rate of use per

hectare of land. A substantial decrease in chemical use comes from the northern area of the Pilchuck region and this location also is predicted to see the largest decrease of fertilizer use as well, indicating an area of concentrated farmland that could switch to growing poplar and have a substantial effect on the region as a whole (Figure 5). Observing the variation in Figure 5 indicates that there is variation in chemical use from pixel to pixel in each region, but the variation is much more pronounced in the Pilchuck and Hayden regions vs the Clarksburg and Jefferson regions.

The average fuel use per hectare of current actively managed land is fairly consistent across all four regions, with Clarksburg seeing the highest fuel use (Figure 6). Total regional fuel use is directly related to the amount of land in cultivation and current fuel use for each region is consistent with this trend (Table 8). Jefferson has the least amount of land in cultivation followed by Pilchuck, Clarksburg, and Hayden (Tables 1 - 4), and total regional fuel use follows this same progression. The estimated fuel use for poplar management is expected to be the same regardless of region and all regions will see an increase in fuel use as more lands come under cultivation to grow poplar. As observed with nitrogen fertilizer use and chemical inputs, Jefferson has the highest increased fuel use as 93 % of the land to grow poplar will come from previously unmanaged lands. The variation of fuel use varies pixel by pixel in each region (Figure 6). Much of this variation is accounted for by the amount of land in each pixel coming under cultivation when switching to poplar production. For some areas, like the central Clarksburg region, fuel use could actually decrease as croplands are switched from fuel intensive crops (i.e. corn) to growing poplar (Figure 6).

The GWP for each region is affected by fertilizers, chemical inputs, fuel use, as well as the type of land converted to growing poplar. This results in a wide range of GWP values between the four regions (Table 9). Expected poplar yield and land use have been identified as key factors that determine the amount of inputs and land needed by region to produce poplar. The lower the expected poplar yield per hectare, the more land required to be converted to growing poplar to meet biorefinery feedstock demands. The more land used, the more inputs required, and therefore the higher regional GWP. Clarksburg requires the least amount of land to meet biorefinery needs, and therefore has the lowest GWP. Jefferson and Pilchuck have relatively similar total land needed, and have similar GWP. Hayden requires the most land and has the highest GWP. Looking at GWP alone though does not tell the whole story when addressing regional effects of feedstock growth and harvesting. The GWP savings must be evaluated to determine if a change in crop/ land use results in an increase or decrease in regional GWP values. Tradeoffs in current land management practices, as well as direct land use change factor into calculating the net effect on GWP for each region and these items are discussed below.

Compared to current land use practices Jefferson, Hayden, and Pilchuck regions would all see increases in GWP when switching to growing poplar (Table 9 - 'Farm Gate Total'. GWPs discussed here are for cradle to farm gate and do not include transportation. GWPs of poplar production with transportation to biorefinery are discussed further below). The increases in GWP are largely driven by a substantial increase in fuel use in each of these regions. Growing and harvesting poplar trees requires considerably more fuel than current farming operations, and even more so than

leaving the land unmanaged (i.e. converting rangelands to grow poplar). The Jefferson region is predicted to see a GWP increase of 710 % as a result of both increased fuel use and fertilizer use, compared to leaving the land in its current management state (almost entirely unmanaged rangeland). Although the fuel use is predicted to increase in the Clarksburg region when converting to growing poplar trees, the GWP will be lower compared to current land management practices. The decrease in Clarksburg GWP is a result of the reduction in regional fertilizer use (Table 9). From a GWP standpoint, the Clarksburg region sees the largest benefit in GHG reduction through the most efficient use of land (highest poplar yield) and through the conversion of high fertilizer input crops to lower fertilizer use for poplar production. If the goal of this study was to select one of the four regions to locate a biorefinery (rather than regional assessment of each area), it would be difficult to select a location other than Clarksburg.

Delivering poplar chips from the farm gate to the respective biorefineries is not without its impacts and there is variability between the four regions. Transportation distances are directly related to the poplar crop yields and land availability in each region. In regions where the annual poplar yield is projected to be lower, more hectares of land must be used to meet the yearly biorefinery feedstock needs. As more lands are converted to growing poplar, transportation distances from the farms to biorefinery also increases. Availability of farmland and pasture/rangeland at a selling price of $60/tonne also has an effect on transportation distances. If less land is locally available to grow poplar trees, then lands at farther distances will be used to grow poplar. These issues are demonstrated in Figure 1. The Jefferson region has a substantial amount of land available near the proposed biorefinery location (Table 8). In the Hayden region the

opposite is observed and the projected poplar yield is the lowest of the four regions so more lands must be used to meet biorefinery feedstock needs; farm to biorefinery transportation distances increase. As transportation distances increase, so does the fuel needed to operate the delivery trucks, and ultimately the emission of greenhouse gases and other associated tailpipe emissions (Table 9 - 'Transportation to biorefinery'). Within the distances travelled (Table 8), and associated emissions (Table 9 - 'Transportation to biorefinery'), there is variability between the 4 regions. Many biofuel LCA studies have assumed feedstock transportation distances of 100 km one way (Borrion et al. 2012). One size fits all models for transportation distances used in these studies may not accurately portray the effect of transportation in a region by either overestimating the farm to biorefinery transportation distances (i.e. Jefferson region) or by underestimating it (Hayden and Pilchuck regions). However, if regional data is not available an average one-way transportation distance of 100 km could be considered a reasonable assumption as this is about the average of all four locations.

An additional consideration when assessing GWP savings is the effect of direct land use change, which has a much more notable effect in regions where higher amounts of rangeland are converted to growing poplar (Table 10). Rangeland conversion shows much higher greenhouse gas emissions than those already in annual crop rotations. This initial carbon 'fee' or 'debt' associated with clearing lands has the potential to substantially increase greenhouse gas emissions associated with transitioning land use and can further influence regional GWP, and GWP savings. Not unexpectedly, the Jefferson GWP sees the biggest impact from DLUC, followed by Hayden, Pilchuck, and lastly Clarksburg. As discussed above, based on the GWP of

the four regions (Table 9) only Clarksburg shows a decrease in greenhouse gas emissions and therefore is the only region in which GWP savings are created when switching from current land management to a poplar bioenergy crop. With this GWP savings Clarksburg would be the only region in which the DLUC emissions debt could be 'paid back' (the point at which the difference in annual emissions between current land management practices and a poplar growth and harvesting system becomes greater than the GWP generated from the DLUC) . The GWP savings of Clarksburg could repay the DLUC carbon debt in 34.7 years. However, as discussed further below, the production of poplar is not the end point of this process and addressing the entire life cycle of the production of bio-jet fuel is necessary to fully understand the relative scale of the feedstock production process and calculation of DLUC carbon debt payoff.

The GWP of poplar production is only part of the greenhouse gas picture, and the GWP of feedstock production needs to be assessed in relation to the GWP of the biorefinery operations. Budsberg et al. 2016 reported annual cradle to grave life cycle GWP for producing bio-jet fuel from poplar biomass. The annual GWP was found to 710,000 tonnes of CO_2 eq from the production and use of 380,000,000 liters of bio-jet fuel (reported in Budsberg et al. 2016 as 54 g of CO_2 eq per MJ of bio jet). Direct land use change may be subtracted from the GWP values reported in Budsberg et al. 2016 to make direct comparisons with the work presented in this manuscript. Of the 710,000 tonnes of CO_2 eq, 76,000 tonnes of CO_2 eq (11% of the net GWP) were from the growth and harvesting of poplar biomass. The feedstock GWPs reported in this manuscript are lower than feedstock GWP reported in Budsberg et al. 2016. This is due to newer poplar feedstock production practices that were developed in response to regional

conditions at the GreenWood Resources pilot locations. Inserting the regional poplar growth and harvesting data into the full bio-jet fuel life cycle can help to complete the bigger picture of the regional effect on life cycle GWP. The full life annual cycle net GWP for each region would be 650,000 tonnes of CO_2 eq from Clarksburg, 660,000 tonnes of CO_2 eq at Pilchuck, 670,000 tonnes of CO_2 eq at Jefferson, and 690,000 tonnes of CO_2 eq at Hayden. The difference between the four regions is 40,000 tonnes of CO_2 eq, or about 4 %. In comparison to the net life cycle GWP for an equivalent amount of petroleum based jet fuel (380,000,000 liters), the GWP reductions for each region would be 47 % at Clarksburg, 46 % at Pilchuck and Jefferson, and 44 % at Hayden. The annual net GWP savings when replacing petroleum based jet fuel would be 570,000 tonnes of CO_2 eq at Clarksburg, 560,000 tonnes of CO_2 eq at Pilchuck and Jefferson, and 540,000 tonnes of CO_2 eq at Hayden. When looking at the complete life cycle for bio-jet fuel we observe relatively small differences in the overall net GWP and large GWP savings that can be attributed to each region where poplar is grown and converted to fuel. The substantial amount of entire lifecycle GWP savings can easily 'repay' the increase in carbon emissions when switching from current land management practices to growing poplar for biofuels.

Inserting DLUC back into the full LCA analysis of each region, these carbon savings can also be used to address the change in carbon debts that are estimated to be accrued in each region by converting land to growing poplar. All regions show that they will be able to repay the carbon debt accrued from DLUC within 1 to about 6 years. Clarksburg could repay the carbon debt in 1.4 years, Pilchuck in 4.1 years, and Hayden and Jefferson each in 6.1 years. For comparison, when DLUC is factored back into the

original study in Budsberg et al. 2016, the carbon debt could have been repaid in 6.4 years. Or in other words, bio-jet fuel produced from poplar in the Clarksburg region could be considered carbon neutral (and then carbon negative compared to petroleum based jet fuel) after 1.4 years, Pilchuck in 4.1 years, and Hayden and Jefferson in 6.1 years when considering the impacts of DLUC.

Conclusion

The Clarksburg region is predicted to have the highest poplar yield and least amount of land converted. Of the land converted in the Clarksburg region, the majority of the land would come from croplands. Relative to the other regions, the conversion of intensively managed cropland to less intensively managed poplar production results in a decrease of fertilizer use and small increase in chemical inputs and fuel use. This translates to the lowest annual GWP for the Clarksburg region relative to the GWPs of Pilchuck, Jefferson, and Hayden. Conversely, the land in the Jefferson region would primarily come from unmanaged rangelands. Bringing this rangeland into managed production results in a regional increase of nitrogen fertilizer use, chemical inputs, and fuel use, as well as the largest increase in GWP, relative to the other regions. The type of land converted isn't the only predictor for changes in agricultural inputs and GWP; total land converted also plays a substantial role as demonstrated by the Hayden region. Poplar yields are predicted to be lower in the Hayden region and more land must be converted to meet the biorefinery feedstock needs. The increased use of land leads to higher fuel use and greater greenhouse gas emissions in the Hayden region.

Agricultural practices are a dynamic process that change from region to region, and vary over time. The research presented here provides a snapshot in time and a comparison between regions. Variations in land use and management as well as climate play a major role in assessing the potential future of a robust biofuels industry. Ultimately though poplar feedstock production and harvesting makes up a small portion (approximately 10 %) of the overall GWP of bio-jet fuel production when compared to downstream processing and conversion, but other local impacts such as those associated with fertilizer use, chemical inputs, and fuel use could play an increasingly substantial role in the future development of bio-jet fuels industry.

Combining life cycle assessment methodology with spatial analysis helps to provide a more detailed view of the shifts in land use and resulting impacts. Feedstock growth and harvesting is a necessary and important process in the production for biofuels. The total contribution of feedstock production to the overall global warming potential likely will not be as substantial as downstreaming conversion and processing of biomass into biofuel, but changes to land use and management could result in unintended negative environmental consequences. It is important that these impacts to land use, along with greenhouse gas emissions, are modelled and evaluated to better understand the regional implications of building a biofuels industry.

Methods

Life cycle assessment methodology is used to assess cradle to biorefinery gate environmental impacts for the production of bio-jet fuel at 4 locations. The functional unit for each region is the annualized feedstock production and harvesting to support each respective biorefinery producing bio-jet fuel from a poplar feedstock. The biorefinery is assumed to produce 380 million liters (100 million gallons) of jet fuel from 1.25 million tonnes of poplar biomass, annually. Biorefinery design and process operations are described in detail in Crawford et al. 2016. To determine the average annual operations, the biorefinery is modelled to operate for 21 years and the data is then annualized. A 21 year time horizon is chosen so as to include the lifespan of a poplar tree farm (site preparation, nursery operations, and six – three year coppice cycles) (Budsberg et al. 2015). The study is not a complete LCA as work only addresses changes in the life cycle inventories within each region when a biorefinery is introduced into the area and poplar trees are grown to meet feedstock demands. The only characterization factors assessed are the 100 year global warming potential (IPCC 2013) and fossil fuel use, so as to make comparisons with a previous non-site specific LCA study that evaluated the same biorefinery design used in this research (Budsberg et al. 2016). Fossil fuel use (FFU) is calculated by summing all fossil fuel inputs (coal, natural gas, crude oil) used to convert the poplar into bio-jet fuel (Budsberg et al. 2016).

SimaPro v.8.0 is used to manage life cycle inventories. LCI data is combined with crop displacement data from researchers at UC Davis. These results are integrated and reported using regional maps created using ArcGIS v10 mapping

software. Physical boundaries are defined in each region by the lands converted to growing poplar for bio-jet fuel production. Resolution is 8 x 8 km grids and is defined by data parameters set by the crop displacement models. Life cycle analysis methods are used to calculate changes in land management and evaluate the change (net effect) to each grid block. These methods include conducting life cycle inventories of all crops that could be displaced for each region and then assigning this data to each crop located within a given grid block. Life cycle inventories are also completed for poplar crops for each region. See supplementary material for poplar growth and harvesting data for each region. These results are used to identify changes at the 8 km x 8 km grid level and combined to calculate the total impact to each region. Modeling tools and data collection are further described below.

Biorefinery locations & crop displacement modelling

We use a combination of models to simulate how an economically driven industry would organize to identify the locations of poplar plantations and the incumbent land uses displaced by these plantations. The simulation uses modelled yields of hybrid poplar that are spatially resolved to inform an agricultural economic model of land conversion of croplands to poplar plantations based on farm gate poplar prices. The Geospatial Bioenergy System Model (GBSM) is used to evaluate which combination of plantations will result in the lowest cost of fuel production while improving the economic outcomes for farmers over the current cropping pattern (Bandaru et al. 2015). The simulation results in a land use change pattern that would enable the continuous operation of a biorefinery that demands 1.25 million tonnes of poplar biomass per year. Each of these models are described in more detail below.

Poplar crop yields are dependent on local climate, soils, stocking density, and management practices. The yields are estimated using the 3PG-Coppice model (Hart et al. 2015) to capture the variations in these conditions across space. A 16 km^2 grid is used with soil parameters from STATSGO and climate represented as a repeated average year using data from 2000-2014 (Hart et al. 2015). The model simulates growth in the crop using monthly timesteps across the 21 year life of the plantation. Areas that are developed, forested, have slopes greater than 15% or salinity greater than 4 dS/m are excluded from the analysis. The poplar yields serve as inputs to cost of production budgets. These production budgets include all the operations needed to produce a crop. The poplar costs of production are taken from Chudy et al (2019). The site-specific costs in Chudy et al (2019) are generalized across the region by finding the average cost of operations on irrigated and non-irrigated plantations separately, and applying those costs to irrigated and non-irrigated potential poplar plantations.

Poplar adoption by landowners is modeled using a combination of a modified agricultural economic model (SWAP-AHB) and GBSM. SWAP-AHB determines the farm-gate prices required to induce a switch to poplar plantations. It is based on the SWAP model (Howitt et al, 2001) and uses a profit maximizing objective to allocate land and water resources between poplar and incumbent crops. Incumbent crop production functions are derived from state specific cost and returns studies for each crop. See the supplementary material for a list of data sources used to model each crop in each region. SWAP has been modified to expand the geographic scope and include poplar as a crop option.

GBSM is a profit maximizing model of the bioenergy system that sites, sizes, and allocates feedstock resources to biorefineries incorporating costs of feedstock procurement, transportation, biorefinery capital and operational costs. It finds the most profitable configuration of biorefinery sites and poplar plantations serving the biorefinery's demand given a selling price for the biofuel product. Biomass farm-gate prices are taken from SWAP-AHB and a separately calculated willingness-to-accept price for poplar on rangelands. See Parker et al (2010) and Parker (2012) for more detailed information regarding GBSM. Biorefinery operations are based on the Natural Gas Steam Reforming Bio-jet model in Crawford et al. 2016 and Budsberg et al. 2016. See these two publications for detailed descriptions and discussions regarding biorefinery design, operating parameters, and life cycle impacts. Through this analysis, the optimized biorefinery locations are Pilchuck Washington, Jefferson Oregon, Hayden Idaho, and Clarksburg California. Transportation distances are reported in the results section as one-way, but round trip distances were used for estimating fuel use for poplar chip delivery with the trucks assumed to be fully weighted for delivery and empty for return to poplar farms.

Crops that could potentially be displaced are listed in Table 11 and crop displacement is determined by profitability. For each given 8 x 8 km square, if poplar is identified as being more profitable than the current crops within that square, it is assumed poplar would replace that crop. Existing land use is taken from the Cropland Data Layer scaled up to 8 x 8 km grid and scaled to be consistent with the USDA Census of Agricultural crop areas by county as in Hart et al (2015). Two general lands types, rangelands and croplands, are identified as eligible for conversion to growing

poplar. Rangelands are defined as lands on which the indigenous vegetation is predominately grasses, grass-like plants, forbs, and possibly shrubs or dispersed trees (USDA NRCS - rangleand). Croplands are those in which adopted crops are grown for harvest (i.e. corn, wheat, peas, etc.) (USDA NRCS- cropland)

Land use / crop type
Tame hay (excluding alfalfa)
Alfalfa hay
Dry edible beans (excludes lima)
Dry edible lima beans
Grain corn
Silage corn
Haylage (excludes alfalfa)
Alfalfa haylage
Winter wheat
Spring wheat
Barley
Oats
Potatoes
Sugarbeets
Lentils
Rangeland

Table 11 – Potential crops and land use scenarios that could be converted to growing poplar.

To maintain consistency throughout the research, life cycle analysis of crop displacement uses the same data sources and assumptions as were used in the SWAP-AHB model. Maintaining this consistency is important as the SWAP-AHB model takes into account the economics surrounding crop management practices. Modelling decisions to replace a crop with poplar trees are based on the economics associated with data assumptions. Changing data sources and assumptions for the LCA work would introduce inconsistencies within the research as the assumptions for how each crop is managed is directly related to whether or not it would be displaced to grow poplar trees.

LCIs for crops in each region are developed using regional extension office data (extension office citations) and include the amount of fertilizer, pesticides, water, and fuel used annually to produce a given crop on a hectare of land. Fertilizer use is broken down by the amount of nitrogen, phosphorus, and potassium use. Chemical usage is calculated by aggregating all insecticides, herbicides, and pesticides (by weight) used for a given crop. Annual fuel use for each crop is measured by combining annual diesel and gasoline use (by energy content). As noted, crop management data for each region is largely based on data from an extension office for that region. Information detailing specific inputs for each displaced crop for each region and the data sources used is listed in the supplementary material.

Feedstock growth and harvesting

Poplar growth and management data is supported by operational data from GreenWood Resources and is representative of practices performed at the four poplar

demonstration farms located in Pilchuck WA, Jefferson OR, Hayden ID, and Clarksburg, CA. Regional differences in practices are observed at each location and noted, but in general growth and harvesting of poplar for bioenergy follows a similar management scheme. Poplar management practices are described in more detail in Budserg et al. 2015 and Budsberg et al. 2016. See those publications for further discussion. Below follows a general overview of poplar crop management. The feedstock production and harvesting life modelling is supported by operational data from industry (Greenwood resources, personal communication 2011 - 2015), literature (Caputo et al. 2014), and LCA databases (USLCI, EcoInvent). See the supplementary material for a complete list of inputs and management practices used within each region.

The first year of feedstock production includes growing poplar trees at a nursery and preparing the plantation location for poplar to be transplanted the following year. Nursery operations include herbicide, fertilizer, chemical and mechanical pest control (i.e. herbicides, mowing, etc.), and irrigation. Once large enough, the nursery stock poplar trees are turned into cuttings and transported to cold storage. Preparing the plantation location for the cuttings will depend on the site-specific characteristics, but in general the land will undergo heavy and finish disking, smoothing, row marking, and herbicide application. The cuttings are planted the following year and are grown for two years before the first coppicing, which will promote the growth of multiple stems per stump.

Following the first coppicing the trees are harvested every 3 years for 6 cycles. The poplar trees are harvested with a forage harvester and forage wagons are towed alongside the harvest to collect the chips. The chips are loaded into a chip van using a

silage blower and transported to the biorefinery. No storage of the poplar biomass is needed at the tree farm or biorefinery as the trees will be harvested year round, following a just-in-time harvest management scheme. Nitrogen fertilizer, and pest management processes (both chemical and mechanical) are used to promote poplar growth. Timing and rate of applying these chemical inputs is regionally dependent and reported in detail in the supplementary material. After 6 harvests (Year 21, counting site prep and nursery operations) the stumps are ground down on site and herbicide is applied to the soil. The system boundary for poplar crop management ends immediately after the below ground biomass is chipped and herbicide is applied. Greenwood Resources has shown both irrigated and non-irrigated to be viable practices for poplar growth depending on location. In this research irrigation is assumed to be used only if the previous crop was irrigated without a change to previous water use.

N_2O emissions from fertilizer and decaying biomass are calculated using two approaches. The Farm Energy Analysis Tool (FEAT) [34] is used for general estimates for all four regions. FEAT data is based on multiple poplar and willow growth management publications and provides non-regional specific information regarding greenhouse gas emissions, as well as other input and outputs. Below ground carbon stores, comprised of above ground stump (the part that remains after a harvest), below ground stump, and coarse roots, are included within the system boundaries.

Direct land use change (DLUC) associated with establishing the plantation on land that was previously pasture land is calculated using the Forest Industry Carbon Assessment Tool v.1.3.1.1 [35]. Tier 1 data [35] data is used to estimate the amount of carbon on these lands that would be released as CO_2 as a result of land use change.

More accurate data are not available as the grid resolution is 64 km^2 and it is unknown exactly how much biomass is on a given plot of land. IPCC values are used to approximate the relative impact of direct land use change on life cycle carbon emissions. Croplands converted to growing poplar are assumed to have a negligible amount of direct land use change as these are crops that are turned over annually and therefore any GHG emissions related to cropland for poplar cultivation would have occurred nevertheless as a result of the crop management scheme. DLUC is assumed to be a one time emission when the land is converted from its current state to growing poplar and is reported separately from the other data. All other aspects of either current land management practices or poplar growth and harvesting are assumed to occur on an ongoing basis, and from this an 'average' year of inputs and outputs can be calculated. This cannot be done with a one time emission like DLUC. DLUC is therefore reported separately and addressed by calculating a regional carbon debt payoff. The carbon debt payoff is the time it will take before the global warming potential savings from switching from current land use practices to poplar production can cancel out the global warming potential emissions generated from DLUC (assuming there are global warming potential savings from switching land use). Indirect land use change is not included in this analysis.

References

1. Borrion AL, McManus MC, Hammond GP. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. Renew Sustain Energ Rev 2012;16(7):4638-50.

2. Wiloso EI, Heijungs R, de Snoo GR. LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice. Renew Sustain Energ Rev 2012;16(7):5295-308.
3. Stratton RW, Wong HM, Hileman JI. Life cycle greenhouse gas emissions from alternative jet fuels. Cambridge (MA): Massachusetts Institute of Technology; 2010 June. PARTNER Project 28 Report PARTNER-COE-2010-001.
4. Agusdinata DB, Zhao F, Ilelji K, DeLaurentis D. Life cycle assessment of potential biojet fuel production in the United States. Environ Sci Technol 2011;45(21):9133-43.
5. Elgowainy A, Han J, Wang M, Carter N, Stratton R, Hileman J, et al. Life-cycle analysis of alternative aviation fuels in GREET. Lemont (IL): Argonne National Laboratory; 2012 June. 76 p. Technical Report ANL/ESD/12-8.
6. Han J, Elgowainy A, Cai H, Wang MQ. Life-cycle analysis of bio-based aviation fuels. Bioresource Tech. 2013;150:447-456.
7. Staples MD, Malina R, Olcay H, Pearlson MN, Hileman JI, Boies A, et al. Lifecycle greenhouse gas footprint and minimum selling price of renewable diesel and jet fuel from fermentation and advanced fermentation production technologies. Energy Environ. Sci. 2014;7:1545-1554.
8. Nordborg M, Cederberg C, Berndes G. Modeling Potential Freshwater Ecotoxicity Impacts Due to Pesticide Use in Biofuel Feedstock Production: The Cases of Maize, Rapeseed, Salix, Soybean, Sugar Cane, and Wheat. Environmental Science & Technology 2014 *48* (19), 11379-11388 DOI: 10.1021/es502497p
9. Kim J, Yalaltdinova A, Sirina N, Baranovskaya N. Integration of life cycle assessment and regional emission information in agricultural systems. *J Sci Food Agric*. 2015;95(12):2544-2553. doi:10.1002/jsfa.7149
10. Mutel CL, Pfister S, Hellweg S. GIS-Based Regionalized Life Cycle Assessment: How Big Is Small Enough? Methodology and Case Study of Electricity Generation. Environmental Science & Technology 2012 *46* (2), 1096-1103 DOI: 10.1021/es203117z

11. Geyer R, Stoms DM, Lindner JP, Davis FW, Wittstock B. Coupling GIS and LCA for biodiversity assessments of land use. *Int J Life Cycle Assess* 15, 454–467 (2010). https://doi.org/10.1007/s11367-010-0170-9
12. Gasol CM, Gabarrell X, Rigola M, González-García S, Rieradevall J. Environmental assessment: (LCA) and spatial modelling (GIS) of energy crop implementation on local scale. Biomass and Bioenergy 2011 (35);7 ISSN 0961-9534. https://doi.org/10.1016/j.biombioe.2011.03.041.
13. van der Hilst F, Lesschen JP, van Dam JMC, Riksen M, Verweij PM, Sanders JPM, Faaij APC. Spatial variation of environmental impacts of regional biomass chains. Renewable and Sustainable Energy Reviews 2012 (16); 4,ISSN 1364-0321, https://doi.org/10.1016/j.rser.2012.01.027.
14. Sinistore JC, Reinemann DJ, Izaurralde RC, Cronin KR, Meier PJ, Runge TM, Zhang X. Life Cycle Assessment of Switchgrass Cellulosic Ethanol Production in the Wisconsin and Michigan Agricultural Contexts. *Bioenerg. Res.* 8, 897–909 (2015). https://doi.org/10.1007/s12155-015-9611-4
15. Budsberg E, Crawford JT, Morgan H, Chin WS, Bura R, Gustafson R. Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment. Biotechnology for Biofuels 2016;9(170): DOI 10.1186/s13068-016-0582-2
16. Crawford JT, Chin WS, Budsberg E, Bura R, Gustafson R. Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: Techno-economic assessment. Biotechnology for Biofuels 2016;9(170): BBIO-D-16-00090.
17. Budsberg E, Crawford J, Gustafson R, Bura R, Puettmann M. Ethanologens vs. acetogens: Environmental impacts of two ethanol fermentation pathways. Biomass Bioenerg 2015;83(12):23-31.
18. IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp, doi:10.1017/CBO9781107415324

19. Bandaru V, Parker N, Hart Q, Jenner M, Yeo B, Crawford J, Li Y, Tittmann P, Rogers L, Kaffka S, Jenkins B. 2015. Economic sustainability modeling provides decision support for assessing hybrid poplar-based biofuel development in California. Calif Agr 69(3):171-176. https://doi.org/10.3733/ca.v069n03p171.
20. Hart QJ, Tittmann PW, Bandaru V, Jenkins BM. Modeling poplar growth as a short rotation woody crop for biofuels in the Pacific Northwest. Biomass and Bioenergy. 2015 (79) ISSN 0961-9534,https://doi.org/10.1016/j.biombioe.2015.05.004.
21. Chudy RP, Busby GM, Binkley CS, Stanton BJ. Biomass and Bioenergy. The economics of dedicated poplar biomass plantations in the western U.S. Biomass and Bioenergy. 2019. 124:114–124.
22. Howitt, R. E., K. B. Ward, and S. Msangi. "Statewide agricultural production model." University of California, Davis. Davis, California (2001).
23. Parker N, Tittmann P, Hart Q, Nelson R, Skog K, Schmidt A, Gray E. Development of a biorefinery optimized biofuel supply curve for the Western United States, Biomass and Bioenergy 2010 (34) 11, 1597-1607
24. Parker N. Spatially explicit projection of biofuel supply for meeting renewable fuel standard. Transportation research record 2012 2287 (1), 72-79
25. Range and Pasture [internet]. United States Department of Agriculture. Natural Resources Conservation Service. c2021 Available from https://www.nrcs.usda.gov/wps/portal/nrcs/main/national/landuse/rangepasture/
26. Cropland [internet]. United States Department of Agriculture. Natural Resources Conservation Service. c2021 Available from https://www.nrcs.usda.gov/wps/portal/nrcs/main/national/landuse/crops/
27. Crop enterprise data [internet]. Pullman (WA): Washington State University School of Economic Sciences. c2020 Available from http://ses.wsu.edu/enterprise_budgets/
28. Crop budgets [internet]. Moscow (ID): University of Idaho College of Agricultural and Life Sciences. c2020 Available from https://www.uidaho.edu/cals/idaho-agbiz/crop-budgets

29. Oregon Agricultural Enterprise Budgets [internet]. Corvallis (OR): Oregon State University College of Agricultural Sciences. c2020 Available from https://appliedecon.oregonstate.edu/oaeb
30. Farm Budget Generator [internet]. University of California Agriculture and Natural Resources; Agricultural Economics. C2020 Available from https://ucanr.edu/sites/Farm_Management/Farm_Budget_Generator/
31. Caputo J, Balogh SB, Volk TA, Johnson L, Puettmann M, Lippke B, et al. Incorporating Uncertainty into a Life Cycle Assessment (LCA) Model of Short-Rotation Willow Biomass (Salix spp.) Crops. Bioenerg Res 2014;7(1):48-59.
32. US life cycle inventory database [Internet]. Golden (CO): National Renewable Energy Laboratory. c2011 Available from: http://www.nrel.gov/lci/.
33. Ecoinvent. Duebendorf, Switzerland: Swiss Center for life cycle inventories; 2015.
34. Farm Energy Analysis Tool (FEAT) [Internet]. University Park (PA): Camargo GGT, Ryan MR, Richard TL, Malcolm GM. c2015 Available from: http://www.ecologicalmodels.psu.edu/agroecology/feat/.
35. Forest Industry Carbon Assessment Tool (FICAT) [Internet]. Cary (NC): National Council for Air and Stream Improvement. c2012 Available from: https://www.ncasi.org/resource/forest-industry-carbon-assessment-tool/

Supplementary materials - Poplar Growth and Harvesting

Poplar growth and Harvesting data. Data is provided by Greenwood Resources and is based on data collected from their four pilot sites located in Pilchuck WA, Jefferson OR, Hayden ID, and Clarksburg CA.

Pilchuck WA

Year	Data is per hectare of land	Operation	Number of entries	Fertilizer (kg N)	Pesticide/ herbicide (kg)	Pesticide/ herbicide (L)	Diesel (L)	Lubricant (kg)
0	Site Prep	Tillage	2	0	0	0	49.4	0.89
		Spraying	2	0	4.1775	0	2.96	0.0532
		Row Marking	1	0	0	0	7.41	0.133
1	Planting							
1	Crop establishment	Herbicide	1	0	2.75	0	3.71	0.0668
		Fertilizer	1	58	0	0	2.81	0.0445
2		herbicide by backpack	1	0	0.688	0	0	0
2	Establishment harvest	harvester	1	0	0	0	32.1	2.96
		Collection truck	1	0	0	0	128	
		Support vehicle	1	0	0	0	4.28	
3	Crop care 1.0	Post harvest cleanup	1	0	0	0	0.741	0.173
		Tillage	1	0	0.336	0	8.89	
		Fertilizer	1	58	0	0	2.81	0.0445
4	Crop care 1.1	Mowing	1	0	0	0	5.93	0.267
		Tillage	1	0	0	0	8.89	
		Herbicide by backpack	1	0	0.688	0	0	0
5	Crop care 1.2	Mowing	1	0	0	0	5.93	0.107
		Spraying by backpack	1	0	1.024	0	3.71	
5	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
6	Crop care 1.0	Post harvest cleanup	1	0	0	0	0.741	0.173
		Tillage	1	0	0.336	0	8.89	
		Fertilizer	1	58	0	0	2.81	0.0445
7	Crop care 1.1	Mowing	1	0	0	0	5.93	0.267

		Tillage	1	0	0	0	8.89	
		Herbicide by backpack	1	0	0.688	0	0	0
8	Crop care 1.2	Mowing	1	0	0	0	5.93	0.107
		Spraying by backpack	1	0	1.024	0	3.71	
8	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
9	Crop care 1.0	Post harvest cleanup	1	0	0	0	0.741	0.173
		Tillage	1	0	0.336	0	8.89	
		Fertilizer	1	58	0	0	2.81	0.0445
10	Crop care 1.1	Mowing	1	0	0	0	5.93	0.267
		Tillage	1	0	0	0	8.89	
		Herbicide by backpack	1	0	0.688	0	0	0
11	Crop care 1.2	Mowing	1	0	0	0	5.93	0.107
		Spraying by backpack	1	0	1.024	0	3.71	
11	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
12	Crop care 1.0	Post harvest cleanup	1	0	0	0	0.741	0.173
		Tillage	1	0	0.336	0	8.89	
		Fertilizer	1	58	0	0	2.81	0.0445
13	Crop care 1.1	Mowing	1	0	0	0	5.93	0.267
		Tillage	1	0	0	0	8.89	
		Herbicide by backpack	1	0	0.688	0	0	0
14	Crop care 1.2	Mowing	1	0	0	0	5.93	0.107
		Spraying by backpack	1	0	1.024	0	3.71	
14	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
15	Crop care 1.0	Post harvest cleanup	1	0	0	0	0.741	0.173

		Tillage	1	0	0.336	0	8.89	
		Fertilizer	1	58	0	0	2.81	0.0445
16	Crop care 1.1	Mowing	1	0	0	0	5.93	0.267
		Tillage	1	0	0	0	8.89	
		Herbicide by backpack	1	0	0.688	0	0	0
17	Crop care 1.2	Mowing	1	0	0	0	5.93	0.107
		Spraying by backpack	1	0	1.024	0	3.71	
17	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
18	Crop care 1.0	Post harvest cleanup	1	0	0	0	0.741	0.173
		Tillage	1	0	0.336	0	8.89	
		Fertilizer	1	58	0	0	2.81	0.0445
19	Crop care 1.1	Mowing	1	0	0	0	5.93	0.267
		Tillage	1	0	0	0	8.89	
		Herbicide by backpack	1	0	0.688	0	0	0
20	Crop care 1.2	Mowing	1	0	0	0	5.93	0.107
		Spraying by backpack	1	0	1.024	0	3.71	
20	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
20	Restoration	Disking	1	0	0	0	37	0.972
		Spraying	1	0	5.5	4.68	2.22	
		Grinding	1	0	0	0	14.8	

Jefferson OR

Year	Data is per hectare of land	Operation	Number of entries	Fertilizer (kg N)	Pesticide/ herbicide (kg)	Pesticide/ herbicide (L)	Diesel (L)	Lubricant (kg)
0	Site Prep	Tillage	2	0	0	0	24.6	0.442
		Spraying	1.5	0	4.1775	0	1.665	0.03
		Row Marking	1	0	0	0	9.26	0.167
1	Planting							
1	Crop establishment	Herbicide	1	0	0.688	0	4.54	0.0817
		Fertilizer	1	56	0	0	2.81	0.0445
2		herbicide by backpack	1	0	0.412	0	0	0
2	Establishment harvest	harvester	1	0	0	0	32.1	2.96
		Collection truck	1	0	0	0	128	
		Support vehicle	1	0	0	0	4.28	
3	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Spraying	1	0	2.785	0	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
4	Crop care 1.1	Mowing	1	0	0	0	4.54	0.148
		Tillage	1	0	0	0	3.71	
		Herbicide by backpack	1	0	1.3975	0	0	0
5	Crop care 1.2	Mowing	1	0	0	0	4.54	0.148
		Spraying	1	0	0.138	0	3.71	
5	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
6	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Spraying	1	0	2.785	0	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
7	Crop care 1.1	Mowing	1	0	0	0	4.54	0.148
		Tillage	1	0	0	0	3.71	
		Herbicide by backpack	1	0	1.3975	0	0	0
8	Crop care 1.2	Mowing	1	0	0	0	4.54	0.148
		Spraying	1	0	0.138	0	3.71	
8	Harvest	harvester	1	0	0	0	43.2	4.77

		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
9	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Spraying	1	0	2.785	0	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
10	Crop care 1.1	Mowing	1	0	0	0	4.54	0.148
		Tillage	1	0	0	0	3.71	
		Herbicide by backpack	1	0	1.3975	0	0	0
11	Crop care 1.2	Mowing	1	0	0	0	4.54	0.148
		Spraying	1	0	0.138	0	3.71	
11	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
12	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Spraying	1	0	2.785	0	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
13	Crop care 1.1	Mowing	1	0	0	0	4.54	0.148
		Tillage	1	0	0	0	3.71	
		Herbicide by backpack	1	0	1.3975	0	0	0
14	Crop care 1.2	Mowing	1	0	0	0	4.54	0.148
		Spraying	1	0	0.138	0	3.71	
14	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
15	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Spraying	1	0	2.785	0	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
16	Crop care 1.1	Mowing	1	0	0	0	4.54	0.148
		Tillage	1	0	0	0	3.71	
		Herbicide by backpack	1	0	1.3975	0	0	0
17	Crop care 1.2	Mowing	1	0	0	0	4.54	0.148
		Spraying	1	0	0.138	0	3.71	

17	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
18	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Spraying	1	0	2.785	0	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
19	Crop care 1.1	Mowing	1	0	0	0	4.54	0.148
		Tillage	1	0	0	0	3.71	
		Herbicide by backpack	1	0	1.3975	0	0	0
20	Crop care 1.2	Mowing	1	0	0	0	4.54	0.148
		Spraying	1	0	0.138	0	3.71	
20	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
20	Restoration	Disking	1	0	0	0	37	0.972
		Spraying	1	0	2.22	4.68	2.22	
		Grinding	1	0	0	0	14.8	

Hayden ID

Year	Data is per hectare of land	Operation	Number of entries	Fertilizer (kg N)	Pesticide/ herbicide (kg)	Pesticide/ herbicide (L)	Diesel (L)	Lubricant (kg)
0	Site Prep	Tillage	2	0	0	0	49.4	0.89
		Spraying	1	0	2.75	0.8775	1.11	0.02
		Pre-emergent herbicide	1	0	0	1.17	1.11	0.02
		Row Marking	1	0	0	0	30.9	0.556
1	Planting							
1	Crop establishment	Mowing	1	0	0	0	6.67	0.12
		Herbicide	1	0	2.06	18.485	6.67	0.28
		Tillage	1	0	0	0	8.89	
		Fertilizer	1	56	0	0	2.81	0.0445
2		herbicide by backpack	1	0	2.748	0	0	0

2	Establishment harvest	harvester	1	0	0	0	32.1	2.96
		Collection truck	1	0	0	0	128	
		Support vehicle	1	0	0	0	4.28	
3	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	6.88	2.34	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
4	Crop care 1.1	herbicide	1	0	1.38	0	0.889	0.016
		Herbicide by backpack	1	0	1.38	2.778	0	0
5	Crop care 1.2	Herbicide	1	0	1.38	0.438	3.71	0.107
5	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
6	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	6.88	2.34	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
7	Crop care 1.1	herbicide	1	0	1.38	0	0.889	0.016
		Herbicide by backpack	1	0	1.38	2.778	0	0
8	Crop care 1.2	Herbicide	1	0	1.38	0.438	3.71	0.107
8	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
9	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	6.88	2.34	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
10	Crop care 1.1	herbicide	1	0	1.38	0	0.889	0.016
		Herbicide by backpack	1	0	1.38	2.778	0	0
11	Crop care 1.2	Herbicide	1	0	1.38	0.438	3.71	0.107
11	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	

12	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	6.88	2.34	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
13	Crop care 1.1	herbicide	1	0	1.38	0	0.889	0.016
		Herbicide by backpack	1	0	1.38	2.778	0	0
14	Crop care 1.2	Herbicide	1	0	1.38	0.438	3.71	0.107
14	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
15	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	6.88	2.34	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
16	Crop care 1.1	herbicide	1	0	1.38	0	0.889	0.016
		Herbicide by backpack	1	0	1.38	2.778	0	0
17	Crop care 1.2	Herbicide	1	0	1.38	0.438	3.71	0.107
17	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
18	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	6.88	2.34	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
19	Crop care 1.1	herbicide	1	0	1.38	0	0.889	0.016
		Herbicide by backpack	1	0	1.38	2.778	0	0
20	Crop care 1.2	Herbicide	1	0	1.38	0.438	3.71	0.107
20	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
20	Restoration	Disking	1	0	0	0	44.5	1.12
		Spraying	1	0	5.5	4.68	2.96	
		Grinding	1	0	0	0	14.8	

Clarksburg CA

Year	Data is per hectare of land	Operation	Number of entries	Fertilizer (kg N)	Pesticide/ herbicide (kg)	Pesticide / herbicide (L)	Diesel (L)	Lubricant (kg)
0	Site Prep	Tillage	2	0	0	0	49.4	0.89
		Spraying	1	0	1.38	2.93	1.11	0.02
		Pre-emergent herbicide	1	0	0	1.17	57.9	1.047
		Ripping	1	0	0	0	12.3	0.221
		Row Marking	1	0	0	0	30.9	0.556
1	Planting							
1	Crop establishment	Mowing	0	0	0	0	0	0
		Herbicide	1	0	0	0	0	0
		Tillage	1	0	0	0	8.89	0.16
		Fertilizer	1	56	0	0	2.81	0.0445
2		herbicide by backpack	1	0	3.448	0	0	0
2	Establishment harvest	harvester	1	0	0	0	32.1	2.96
		Collection truck	1	0	0	0	128	
		Support vehicle	1	0	0	0	4.28	
3	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	3.575	1.4	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
4	Crop care 1.1	herbicide	1	0	1.38	0	0.556	0.01
		Herbicide by backpack	1	0	1.38	0	0	0
5	Crop care 1.2	Herbicide	1	0	0.688	0	0	0
5	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	

6	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	3.575	1.4	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
7	Crop care 1.1	herbicide	1	0	1.38	0	0.556	0.01
		Herbicide by backpack	1	0	1.38	0	0	0
8	Crop care 1.2	Herbicide	1	0	0.688	0	0	0
8	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
9	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	3.575	1.4	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
10	Crop care 1.1	herbicide	1	0	1.38	0	0.556	0.01
		Herbicide by backpack	1	0	1.38	0	0	0
11	Crop care 1.2	Herbicide	1	0	0.688	0	0	0
11	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
12	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	3.575	1.4	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
13	Crop care 1.1	herbicide	1	0	1.38	0	0.556	0.01
		Herbicide by backpack	1	0	1.38	0	0	0
14	Crop care 1.2	Herbicide	1	0	0.688	0	0	0
14	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	

15	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	3.575	1.4	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
16	Crop care 1.1	herbicide	1	0	1.38	0	0.556	0.01
		Herbicide by backpack	1	0	1.38	0	0	0
17	Crop care 1.2	Herbicide	1	0	0.688	0	0	0
17	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
18	Crop care 1.0	Post harvest cleanup	1	0	0	0	1.67	0.0833
		Sprayer	1	0	3.575	1.4	2.96	
		Fertilizer	1	56	0	0	2.81	0.0445
19	Crop care 1.1	herbicide	1	0	1.38	0	0.556	0.01
		Herbicide by backpack	1	0	1.38	0	0	0
20	Crop care 1.2	Herbicide	1	0	0.688	0	0	0
20	Harvest	harvester	1	0	0	0	43.2	4.77
		Collection truck	1	0	0	0	216	
		Support vehicle	1	0	0	0	5.76	
20	Restoration	Disking	1	0	0	0	44.5	1.12
		Spraying	1	0	5.5	4.68	2.96	
		Grinding	1	0	0	0	14.8	

Supplementary Material - Crop management inputs

Inputs for growing crops in each region. Inputs are assumed to be the same for both irrigated and non-irrigated crops. Data is based on crop enterprise budgets provided by university extension services located in each state. Washington State University School of Economic Sciences (cite), University of Idaho College of Agricultural and Life Sciences (cite), Oregon State University College of Agricultural Sciences (cite), and University of California Agricultural and Natural Resources (cite).

Pilchuck WA

		Annual amount per hectare			
Inputs	**Unit (per ha)**	**Silage Corn**	**Winter wheat**	**Tame hay**	**Barley**
Nitrogen (dry)	kg	235	101	101	67
P2O5 (dry)	kg	90	34	34	13
K2O	kg	112	0	0	0
Sulfur	kg	34	17	0	17
Pesticides (volume)	L	5	0	5	0
Pesticides (mass)	kg	14	7	0	7
Gasoline	L	12	0	34	0
Diesel	L	122	76	63	76

Jefferson OR

		Annual amount per hectare	
Inputs	**Unit**	**Tame hay**	**Oats**
Nitrogen (dry)	kg	101	81
P2O5 (dry)	kg	34	36
K2O	kg	0	36
Sulfur	kg	0	7
Pesticides (volume)	L	5	0
Pesticides (mass)	kg	0	0
Gasoline	L	34	0
Diesel	L	63	100

Hayden ID

		Annual amount per hectare					
Input	**Unit**	**Dry edible beans**	**Barley**	**Alfalfa**	**Tame hay**	**Winter wheat**	**Spring wheat**
Nitrogen (dry)	kg	28	67	22	101	101	85
P2O5 (dry)	kg	56	13	112	34	34	11
K2O	kg	34	0	84	0	0	0
Sulfur	kg	34	17	11	0	17	12
Zinc	kg	6	0	0	0	0	0
Pesticides (volume)	L	7	0	2	5	0	0
Pesticides (mass)	kg	0	7	0	0	7	1
Gasoline	L	14	0	0	34	0	0
Diesel	L	99	76	21	63	76	41

Clarksburg CA

		Annual amount per hectare					
Input	**Unit**	**Dry edible beans**	**Tame hay**	**Silage corn**	**Winter wheat**	**Grain corn**	**Barley**
Nitrogen (dry)	kg	28	52	184	157	237	67
P2O5 (dry)	kg	56	0	76	0	76	13
K2O	kg	34	0	0	0	0	0
Sulfur	kg	34	0	0	0	0	17
Zinc	kg	6	0	0	0	0	0
Pesticides (volume)	L	7	5	3	1	4	0
Pesticides (mass)	kg	0	0	0	0	1	7
Gasoline	L	14	34	6	6	6	0
Diesel	L	99	`	103	51	261	76

Production routes to bio-acetic acid: Life cycle assessment

Erik Budsberg, Rodrigo Morales-Vera, Jordan T Crawford, Renata Bura PhD, Rick Gustafson PhD

This article was published open access in Biotechnology for Biofuels in 2020. It can be found at:

Budsberg E, Morales-Vera R, Bura R, Gustafson R. Production routes to bio-acetic acid: life cycle assessment. Biotechnology for Biofuels 2020;13(154): 10.1186/s13068-020-01784

A note to the reader - the below article follows the publication format as required by the journal Biotechnology for Biofuels. The order is as follows: Background, Results, Discussion, Conclusion, Methods. The below version has been slightly modified for inclusion in this dissertation.

Abstract

Background – Similar to biofuels, numerous chemicals produced from petroleum resources can also be made from biomass. In this research we investigate cradle to biorefinery exit gate life cycle impacts of producing acetic acid from poplar biomass using a bioconversion process. A key step in developing acetic acid for commercial markets is producing a product with 99.8 % purity. This process has been shown to be potentially energy intensive and in this work two distillation and liquid-liquid extraction methods are evaluated to produce glacial bio-acetic acid. Method one uses ethyl acetate for extraction. Method two uses alamine and diisobutyl ketone. Additionally two different options for meeting energy demands at the biorefinery are modeled. Option one involves burning lignin and natural gas onsite to meet heat/steam and electricity

demands. Option two uses only natural gas onsite to meet heat/steam demands, purchases electricity from the grid to meet biorefinery needs, and sells lignin from the poplar biomass as a co-product to a coal burning power plant to be co-fired with coal. System expansion is used to account for byproducts and co-products for the main life cycle assessment. Allocation assessments are also performed to compare the life cycle tradeoffs of using system expansion, mass allocation, or economic allocation for bio-acetic acid production. Finally, a sensitivity analysis is conducted to determine potential effects of a decrease in the fermentation of glucose to acetic acid.

Results – Global warming potential (GWP) and fossil fuel use (FFU) for ethyl acetate extraction range from 1000 - 2500 kg CO_2eq. and 32 - 56 GJ per tonne of acetic acid, respectively. Alamine and diisobutyl ketone extraction method GWP and FFU ranges from -370 - 180 kg CO_2eq. and 15 - 25 GJ per tonne of acetic acid, respectively.

Conclusions – Overall the alamine/diisobutyl ketone extraction method results in lower GWP and FFU values compared to the ethyl acetate extraction method. Only the alamine/diisobutyl extraction method finds GWP and FFU values lower than those of petroleum based acetic acid. For both extraction methods, exporting lignin as a co-product produced larger GWPs and FFU values compared to burning the lignin at the biorefinery.

Background

There is significant interest in converting lignocellulosic biomass to biofuels with the goal of producing transportation fuels that reduce greenhouse gas emissions compared to petroleum based fuels. Many of these studies assessed the feasibility of converting this biomass to ethanol via fermentation methods [1-3]. Life cycle assessments have been performed to assess the environmental impacts of producing ethanol. Results from these LCA studies report that, while there is variability amongst the biofuel production methods related to feedstock type and fermentation method, ethanol biofuel will generally have a lower global warming potential lower than gasoline [2 – 4].

Similar conversion processes may be used to produce biochemicals which can displace petroleum based chemicals. Some of the chemicals recently proposed to be produced from lignocellulosic biomass include: polylactic acid [5 – 8], polyethylene [5], polyethylene terephthalate [8], polyhydroxyalkanote [6 – 7], succinic acid [9], butanediol [10] and starch based polymers [6 – 7]. LCA results on the production and use of these products differ, but in general bio-based chemicals are found to be superior in regards to lower global warming potentials compared to the petroleum based fuels they intend to replace [7]. Main sources of variation between biochemical LCAs can be traced to the source of electricity used in manufacturing, system boundaries, and allocation methods when more than one product is made during biochemical production [7].

A common issue in biochemical LCA studies is how to set the system boundaries [7]. Biofuel LCAs typically include full cradle to grave analysis. The use/disposal of fuel

is easy to identify (combustion) and emissions resulting from this can be readily tracked. Use and disposal of chemicals, especially platform chemicals, is much less straightforward. These chemicals are typically used in the synthesis of other chemicals. The use and disposal of these chemicals varies and can include large and/or undefined temporal scopes [6, 8, 11]. Addressing these issues can be complex and end of life scenarios can introduce uncertainty and variability in LCAs [6, 11]. To avoid end of life issues some researchers choose to set cradle to biorefinery gate system boundaries that include the manufacturing of the biochemical(s), but not use or disposal [6]. Others have performed full cradle to grave assessments by making assumptions of the use and disposal of the biochemical(s) [5 – 6, 8]. Those that include end of life scenarios found that it can have a significant effect on the global warming potential results, but these results are highly variable [6].

In this research, the petroleum based chemical targeted for replacement by a biochemical is acetic acid. Currently acetic acid is primarily made by methanol carbonylation [12]. The process works by reacting methanol with carbon monoxide in the presence of a metal carbonyl catalyst (Cativa process) [13]. Annual worldwide acetic acid demand in 2013 was 13.15 million tonnes and is expected to reach 17.3 million tonnes [14]. Acetic acid has a wide range of potential end uses and can be used to make products such as paints, plastics, adhesives, and food [12]. Carbonylation of methanol to produce acetic acid has a cradle to gate global warming potential of 1 kg CO_2 eq. / kg of acetic acid [15] and manufacturing acetic acid therefore contributed approximately 13.45 million tonnes of CO_2 eq. to the atmosphere in 2013. Reducing the

GWP of acetic acid production would be a positive step in mitigating the effect of chemical production on climate change.

Bio-based acetic acid can be produced from lignocellulosic biomass via a bioconversion process. Following pretreatment and hydrolysis an acetogen can be used in the fermentation step to produce acetic acid. Acetogens only produce acetic acid as they digest sugars and have a theoretical yield of 100 % [16]. To be widely marketable, acetic acid must be distilled to glacial purity (99.8% acetic acid). Distillation of acetic acid to glacial purity can be difficult if it is not in high concentration when fed to the recovery process [12]. Preliminary analysis in our research identified direct distillation as a major environmental and economic hurdle to producing bio-based acetic acid. Two potentially viable recovery processes for bio-based acetic acid have been proposed and are evaluated on a life cycle basis in this research. The first uses ethyl acetate extraction (EAX) to extract acetic acid from water. The second uses an alamine and diisobutyl ketone (DIBK) solvent to extract the acetic acid. Alamine/DIBK extraction is abbreviated as ADX within the text.

In addition to assessing the two extraction methods this work also seeks to identify life cycle tradeoffs in meeting biorefinery energy demands. Steam to operate the biorefinery can come from burning lignin supplemented with natural gas or purely from natural gas. Burning lignin has the advantage of lowering the GWP of the process and potentially producing renewable electricity which can be exported to further reduce the GWP (Borrion et al. 2012, Budsberg et al. 2015). The disadvantage to this approach is the high capital cost of a high pressure boiler that can burn lignin [17]. Alternatively the lignin may be sold for co-combustion in a coal fired plant [18]. If lignin is exported, only

natural gas would be used to produce the necessary steam for the biorefinery. This process would have a much lower capital cost but the GWP may be higher as fossil fuel use is increased at the biorefinery. To address this concern life cycle comparisons of burning lignin onsite versus exporting it as a co-product are included in this research

Four biorefinery designs are assessed in this research: EAX used to extract acetic acid with lignin and natural gas combusted onsite to provide steam (EAX OC), EAX used to extract acetic acid with natural gas burned onsite to provide steam and lignin exported to be co-fired with coal at a coal burning power plant (EAX LE), ADX used to extract acetic acid with lignin and natural gas combusted onsite to provide steam (ADX OC), and ADX used to extract acetic acid with natural gas burned onsite to provide steam and lignin exported to be co-fired with coal at a coal burning power plant (ADX LE). In the onsite combustion scenarios steam produced from burning lignin and natural gas is passed through a turbine to also produce electricity. Electricity generated from this process exceeds onsite demands and excess electricity is sold as byproduct of acetic acid production. In the lignin exporting scenarios only natural gas is burned at the biorefineries to meet steam demands and capital costs are minimized by using a lower pressure boiler and no turbine to produce electricity. Electricity needed to operate these biorefineries is assumed to be purchased from the grid.

Cradle to biorefinery exit gate system boundaries are used to evaluate acetic acid production. System expansion is used as the primary method to deal with either the production of an excess electricity by-product (when combusting lignin and natural gas onsite at the biorefineries) or the lignin co-product (when lignin is exported to a coal burning power plant). A functional unit of 1 tonne of acetic acid produced from a

biorefinery system with 21 year operating time frame is used in the analysis. Environmental impacts considered are the 100 year Global Warming Potential (GWP) [19], and Fossil Fuel Use (FFU). Scenario results are compared to each other as well as to petroleum based acetic acid produced by methanol carbonylation [15]. In addition to the four main scenarios described above, both an allocation assessment and a sensitivity analysis are conducted. The allocation assessment looks at the life cycle effects of the lignin co-product (lignin exporting scenarios) using both economic and mass allocation approaches. The sensitivity analysis tests the effect that the acetic acid yield has on life cycle impacts.

The work presented here is part of an investigation into the environmental and economic impacts of bio-acetic acid commercially produced via an advanced bioconversion pathway. The acetic acid is produced using a biorefinery design similar to the one reported by Crawford et al. [20] and Budsberg et al. [21] to produce hydro-carbon bio-jet fuel. The work is part of a collaboration between industry, government, and academia to develop a sustainable bio-fuels and biochemicals industry. In this article LCA is used to determine potential environmental impacts of bio-acetic acid production. A second article, also published in this journal, investigates the techno-economics of the proposed acetic acid production pathways and includes detailed descriptions of bioconversion and extraction processes [17].

Results

The life cycle assessment is broken up into the following categories to identify areas within the system boundaries that contribute to environmental impact categories:

- Carbon in biomass: CO_2 absorbed by photosynthesis in harvested chips, above ground and below ground stumps, and coarse roots over a 21 year time horizon.
- Poplar growth & harvesting: All technosphere processes associated with growing and harvesting poplar. Includes direct land use change emissions.
- Ancillary chemicals: All chemicals and inputs required for biorefinery operations, including natural gas.
- Purchased electricity: Electricity needed for biorefinery operations in scenarios where lignin is exported to coal fired power plants.
- Transportation: Includes transportation of poplar from farm to biorefinery gate, transportation associated with all chemical inputs, and transportation of lignin to coal plant (co-product scenarios).
- Biorefinery: All operations performed, raw materials used, and emissions from the biorefinery.
- Lignin at power plant: Emissions resulting from the combustion of lignin at a coal power plant (lignin co-product exporting scenarios).
- Avoided production: In the EAX OC and ADX OC scenarios an avoided production credit is earned from displacing electricity produced from natural gas with excess electricity produced at the biorefinery. In the EAX LE and ADX LE scenarios an avoided production credit is earned from displacing coal with lignin at a coal power plant.
- Petro-acetic acid: Cradle to refinery exit gate life cycle impacts for production of petroleum based acetic acid.

Global Warming Potential

The GWPs calculated from each bio-acetic acid production scenario and petroleum based acetic acid are presented in Figure 1. Net GWPs are listed in Table 1. For all scenarios, the biorefinery section is the largest source of greenhouse gases (GHGs) contributing to the GWP. Lignin combusted at the power plant is the second largest contributor to the GWP in the EAX LE and ADX LE scenarios. A significant proportion of the GHGs contributing to the GWP from the biorefinery operations, and all the GHGs from lignin combustion at the power plant, are from combustion of biomass and considered biogenic. The ancillary chemicals category is the second largest contributor to the GWP in the EAX OC and ADX OC scenarios, and third largest in the lignin export scenarios. All emissions contributing to the GWP from the ancillary chemicals category are from the use of fossil fuels and considered non-biogenic. Across all scenarios poplar growth and harvesting follows the ancillary chemicals category as the next largest contributor of GHGs to the GWP. Top sources of GHGs to the GWP from poplar growth and harvesting are direct land use change (276 kg CO_2 eq. per tonne of acetic acid) followed by nitrogen fertilizer production and N_2O emissions from its use (35 kg CO_2 eq. per tonne of acetic acid, combined), and diesel use in farm equipment (30 kg CO_2 eq. per tonne of acetic acid). Transportation and purchased electricity comprise only small percentages of the GWPs. The avoided production credit reduces the GWP of each scenario. In the EAX OC and ADX OC this credit is generated by exporting excess electricity and displacing electricity produced from natural gas. In the EAX LE and ADX LE scenarios the avoided production is for directly displacing coal at a coal burning facility with lignin. The type of fossil fuel displaced has

a notable effect on the avoided production credit generated. For every MJ of natural gas electricity that is displaced a credit of 0.19 kg of CO_2 eq. is earned. For every MJ of coal electricity displaced a credit of 0.32 kg of CO_2 eq. is earned. Per tonne of acetic acid, the avoided production credit decreases the CO_2 eq. of the net GWPs of EAX OC, EAX LE, ADX OC, and ADX LE by 1800 kg, 915 kg, 590 kg and 915 kg, respectively. The effect of the avoided production credit on the life cycle impacts of acetic acid production are evaluated below in the allocation section of the results.

Scenario	**Net GWP CO_2 eq. (kg t^{-1})**	**Net FFU (GJ t^{-1})**
EAX OC	1000	32
EAX LE	2500	56
ADX OC	-370	15
ADX LE	180	25
Petro-acetic acid	1000	44

Table 1: Global Warming Potential and Fossil Fuel Use results.

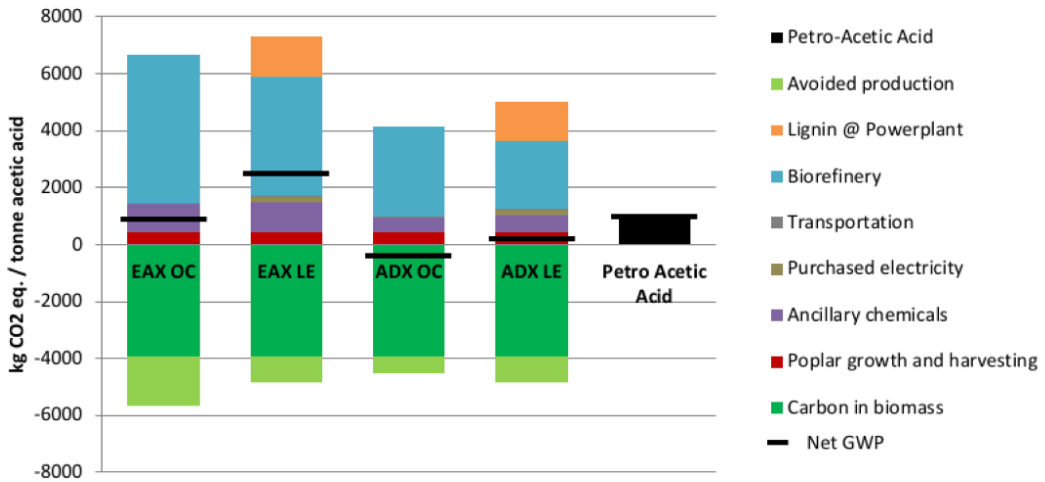

Figure 1: Global warming potentials of acetic acid production scenarios.

A breakdown of sources of GHGs within the biorefineries is presented in Figure 2. The two primary GHGs emitted from the biorefinery simulations are CO_2 and CH_4. CO_2 is emitted from the combustion of lignin, natural gas, biogas, and the aerobic stage of the wastewater treatment process. Fugitive CH_4 emissions result from small leaks of natural gas within the biorefinery system. In all scenarios natural gas combustion is the main non-biogenic source of greenhouse gases contributing to the GWP. In the EAX OC and ADX OC onsite lignin combustion is the second largest contributor to the GWP. A significantly higher natural gas use in the EAX scenarios compared to the ADX scenarios results in higher fugitive methane emissions at the biorefinery. Fugitive methane emissions are the second largest source of GHGs contributing to the GWP at the EAX LE biorefinery. In the ADX LE scenario, emissions from the combustion of biogas generated from the anaerobic stage of the wastewater treatment process is the

second largest source of GHGs contributing to the GWP. CO_2 emissions from the aerobic stage of the wastewater treatment process are similar in all four scenarios.

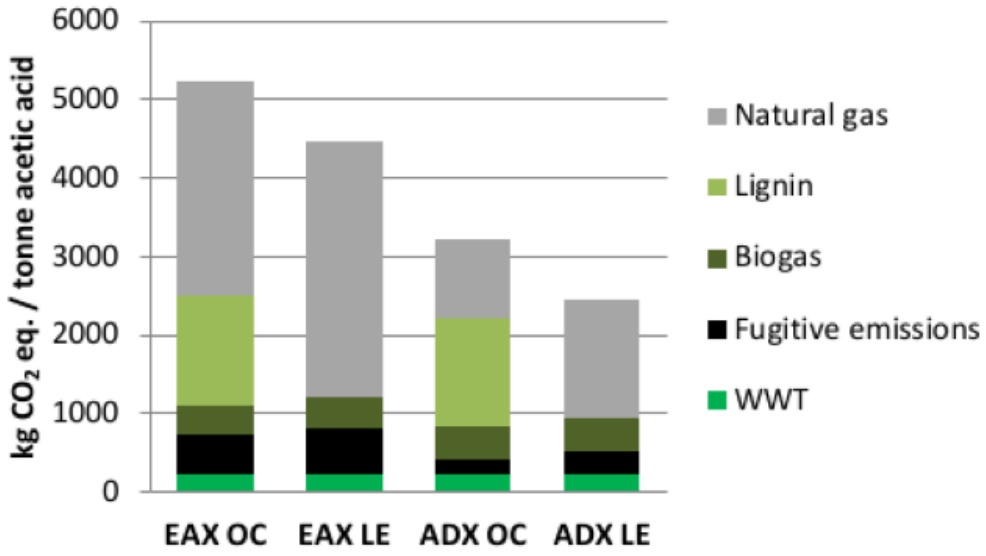

Figure 2: Sources contributing to the global warming potential of the biorefinery in each scenario. Global warming potentials for natural gas, lignin, and biogas are from the combustion of each fuel. Fugitive emissions are natural gas emissions that are assumed to leak/escape from various stages of biorefinery operations. Wastewater treatment (WWT) includes CO_2 emissions for both anaerobic digestion and aerobic digestion. Anaerobic digestion produces CH_4 which is sent to the boiler for combustion (and ultimately emitted as CO_2).

A breakdown of the GWP in the ancillary chemicals category is shown in Figure 3. In all scenarios the largest contributor to the GWP is natural gas production and acquisition followed by the manufacturing of enzymes, sodium hydroxide, and ammonia. The GWP effect of natural gas acquisition is more than two times greater in the EAX scenarios than in the ADX scenarios. This is a result of the ethyl acetate extraction

method demanding a higher heat/steam input than alamine/DIBK extraction. All other major chemical inputs and their GWP effect are the same across all scenarios (except for lime which is not required in lignin exporting scenarios as lime is used to remove sulfur emissions from combusting biomass – a process not performed in the biorefinery in the these scenarios). Both ethyl acetate and alamine/DIBK extractive chemicals have little effect on the GWP owing to high recycling rates within their respective biorefineries.

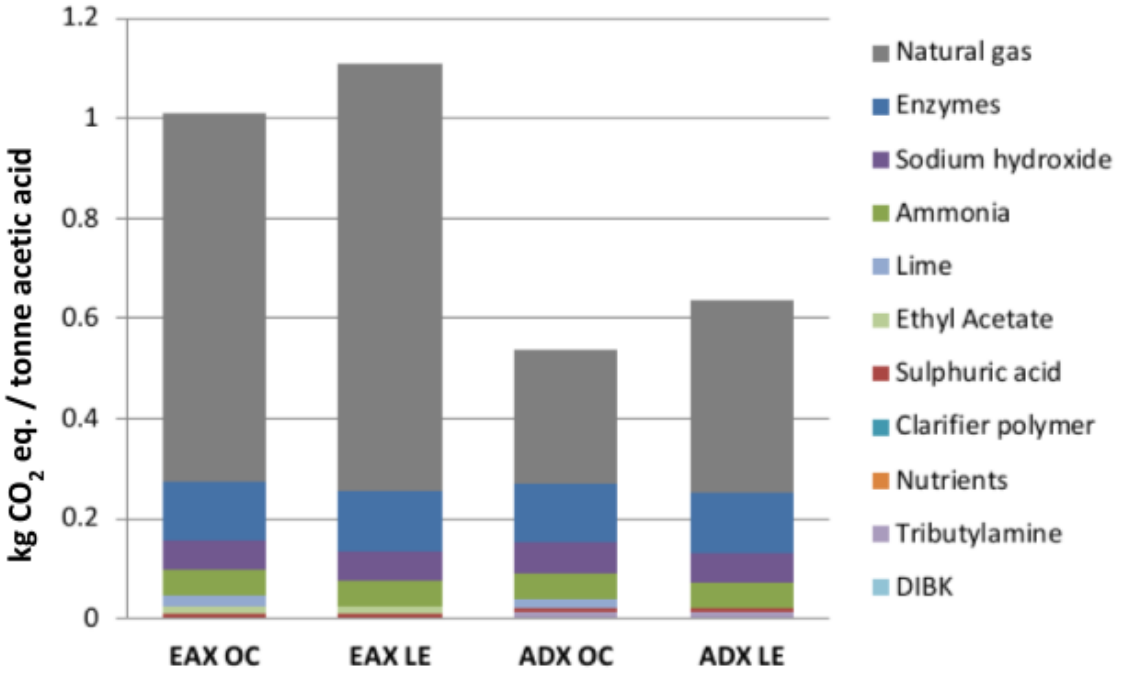

Figure 3: Sources contributing to the global warming potential of the ancillary chemicals category in each scenario.

The net GWPs are scenario dependent, but overall the EAX GWPs are higher than the ADX GWPs (Table 1, Figure 1). Compared to petroleum based acetic acid

EAX OC has an equivalent GWP while the GWP of EAX LE is 150% higher. The GWPs of ADX OC and ADX LE are 140 %, and 82 % lower than petro-acetic acid, respectively. For both EAX and ADX, the onsite lignin combustion scenarios achieve the lowest GWPs.

Fossil fuel use

FFU values were calculated for bio-acetic acid and petro-acetic acid production scenarios and are presented in Figure 4. Net FFU values are listed in Table 1. Compared to petro-acetic acid EAX LE uses 28 % more fossil fuels, while EAX OC, ADX OC, and ADX LE use 28 %, 65 %, and 43 % less fossil fuels, respectively. The acquisition/ manufacturing of products within the ancillary chemicals category are responsible for the majority of all fossil fuel use. Purchased electricity, transportation and poplar growth and harvesting are credited with only a minor amount of fossil fuel use. Avoided production credits reduce net fossil fuel use. Avoided production of marginal electricity production (natural gas) reduces FFU in EAX OC by 27 GJ $t^{-1}$and in ADX OC by 9.3 GJ t^{-1}. Avoided production of coal electricity reduces FFU in EAX LE and in ADX LE by 11 GJ t^{-1}.

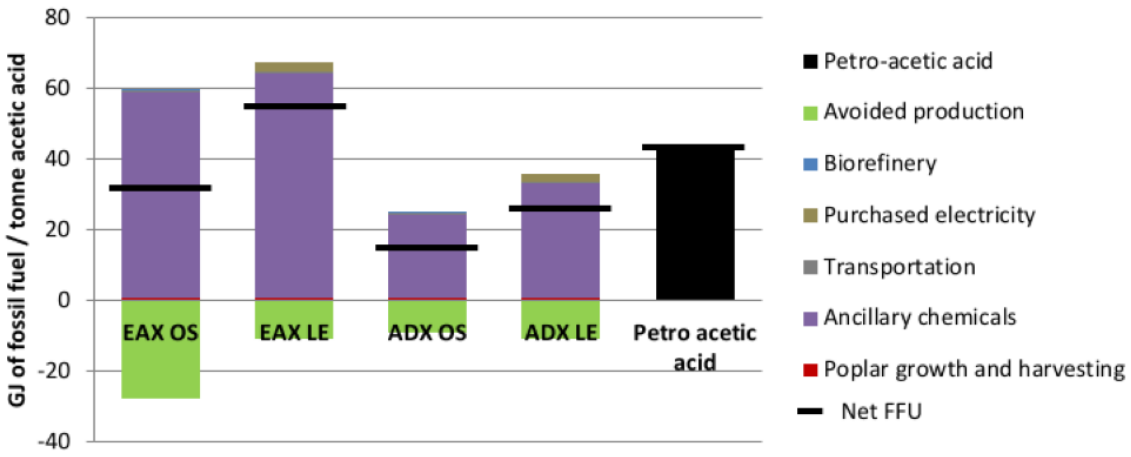

Figure 4: Fossil fuel use for each acetic acid production scenario.

For all scenarios natural gas acquisition / production is the largest user of fossil fuels within the ancillary chemicals category (Figure 5). Per tonne of acetic acid, natural gas FFU used in the production of acetic acid in the EAX OC, EAX LE, ADX OC, and ADX LE scenarios is 54 GJ, 63 GJ, 20 GJ, and 28 GJ, respectively. Manufacturing of enzymes is the second largest consumer of fossil fuels and is responsible for 1.8 GJ t^{-1} of acetic acid. All other products within the ancillary chemicals category combine to use approximately 2.4 GJ t^{-1} of acetic acid and individually represent 4 % to 10 % of the total fossil fuels used to make acetic acid.

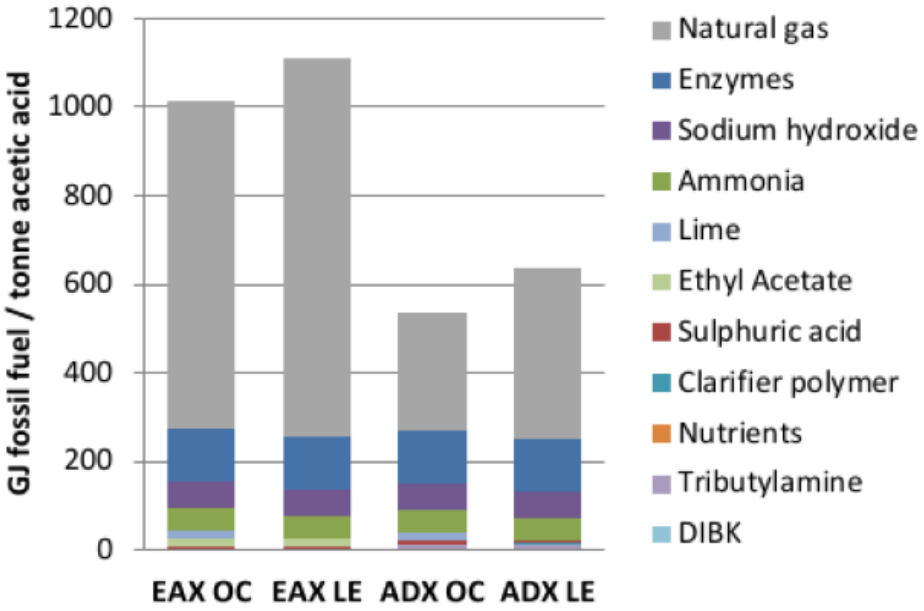

Figure 5: Fossil fuel use within the ancillary chemicals category of each scenario. Included in the calculations are the amount of fossil fuels needed to extract/produce/transport each chemical. For natural gas, this also includes the embodied fossil fuel energy in the gas itself.

Allocation and Sensitivity Analysis

Results of the allocation analysis are presented in Table 2. For both the EAX LE and ADX LE mass allocation assessments 69.5 % of the life cycle impacts are attributed to acetic acid production and 30.5 % of the impacts to the lignin co-product. Using economic allocation 95.5 % and 94.6 % of the impacts are attributed to acetic acid production in the EAX LE and ADX LE scenarios, respectively. The small difference in the economic allocation is due to the ADX scenarios having a calculated lower minimum selling price for acetic acid [17]. Compared to the system expansion approach

economic allocation results in higher GWP and FFU values for the EAX LE and ADX LE acetic acid life cycle scenarios. The effect of mass allocation is not as significant as economic allocation. In the case of EAX LE mass allocation actually reduces the net GWP and FFU compared to the system expansion approach. For ADX LE mass allocation results in an increase to the net GWP and no change to the net FFU compared to the system expansion approach.

Scenario	**Net GWP CO_2 eq. (kg t^{-1})**	**Net FFU (GJ t^{-1})**
EAX LE: System expansion	2500	56
EAX LE: Economic allocation	3200	64
EAX LE: Mass allocation	1900	47
ADX LE: System expansion	180	25
ADX LE: Economic allocation	960	34
ADX LE: Mass allocation	310	25

Table 2: Global Warming Potential and Fossil Fuel Use allocation results.

Sensitivity analysis results are presented in Table 3. Decreasing the glucose to acetic acid fermentation yield by 10% decreases the amount of acetic acid produced per tonne of biomass from 533 to 482 (~ 10 %). Decreasing the acetic acid yield does not change the rate of inputs to the biorefinery. Therefore, relative to a tonne of acetic acid, inputs to the biorefinery (ancillary chemicals) increase as acetic acid yield drops (i.e. same of amount of inputs, but a lower final product yield). Inputs to the biorefinery increase by 10 % to 11 %, except for natural gas use which only increases by 6 %.

Natural gas use does not increase as much as the other inputs within the ancillary chemicals category as a decrease in the conversion of glucose to acetic acid results in more biomass available to convert to bioenergy and less acetic acid to recover. The increase in available biomass for bioenergy also increases the amount of excess electricity produced by approximately 6 %. Combustion of the additional biomass increases biogenic CO_2 emissions at the biorefinery by 19 %. The total effect of decreasing the acetic acid yield, the relative increase in ancillary chemicals, and an increase in excess electricity are increases to the GWP and FFU of EAX OC and EAX LE. EAX OC GWP and FFU increase by 20 % and 6.3 %, respectively. EAX LE GWP and FFU increase by 12 % and 7.1 %, respectively.

Scenario	**Net GWP CO_2 eq. (kg t^{-1})**	**Change from base case (%)**	**Net FFU (GJ t^{-1})**	**Change from base case (%)**
EAX OC: -10% Fermentation yield	1200	20	34	6.3
EAX LE: -10% Fermentation yield	2800	12	60	7.1

Table 3: Global Warming Potential and Fossil Fuel Use sensitivity analyses.

Discussion

Poplar biomass can be used to produce acetic acid that has a lower GWP and uses less fossil fuels than petroleum based acetic acid produced via carbonylation, however it depends on the extraction method used to concentrate and purify the acetic

acid (Table 1). EAX OC results in lower FFU and an equivalent GWP compared to petroleum acetic acid. EAX LE has a GWP and FFU significantly higher than petro-acetic acid. On the other hand, ADX OC and ADX LE both have much lower GWPs and FFU values compared to petro-acetic acid. All poplar based acetic acid production scenarios benefit from large avoided production credits. The avoided production credits help to lower the net GWP and FFU for each scenario. Without the credits GWP and FFU values would be much larger, and when removed, ADX OC is the only scenario that would still have a GWP and FFU lower than petro-acetic acid.

Between the two extraction methods investigated here, the alamine/DIBK extraction method to produce acetic acid via bioconversion of poplar biomass achieves the lowest GWPs and FFU values. Compared to the EAX scenarios, ADX scenarios achieve GWP CO_2 eqs. that are 1370 kg t^{-1} lower when burning lignin onsite and 2320 kg t^{-1} lower when lignin is exported to a coal power plant. For FFU ADX values are 17 GJ t^{-1} lower when burning lignin onsite and 31 GJ t^{-1} lower when lignin is exported to a coal power plant. ADX scenarios show lower net GWPs and FFU values than the EAX platform because the ADX pathway requires less heat/steam and therefore less natural gas (Table 5, Figures 1 & 4). Natural gas use is 34 MJ lower in ADX OC vs EAX OC and 33 MJ lower in ADX LE vs EAX LE.

EAX OC has a lower GWP and FFU than EAX LE (Table 1). Drivers for this difference include changes to natural gas use, electricity purchasing, and the avoided production credit. The EAX OC biorefinery design includes a turbine onsite so that high pressure steam created from the combustion of lignin and natural gas can be used to produce electricity. In the EAX LE scenario lignin is exported to a coal burning facility

and biorefinery capital expenses are decreased by using a lower pressure boiler and foregoing a turbine. To make up for the loss in energy by exporting the lignin the EAX LE biorefinery must use more natural gas and purchase electricity, thereby increasing use of fossil fuel based resources compared to EAX OC. The decision to use a low pressure boiler and to not produce electricity onsite in the EAX LE scenario also results in lower thermal energy generation compared to EAX OC. In EAX OC electricity is not only produced from biomass and biogas, but also from steam produced from natural gas combustion. The total amount of excess electricity that can be used to displace electricity production elsewhere (and counted as an avoided production credit) is therefore larger than in EAX LE when just lignin is used to displace coal. It was originally hypothesized that EAX LE would result in a lower GWP because on a per unit of energy basis coal based electricity has a larger GWP than natural gas based electricity. It was assumed that this would result in an avoided production credit for EAX LE that would out-compete the loss in total energy production. The additional low carbon electricity produced in the EAX OC scenario, however, outweigh the benefits of coal displacement in the EAX LE scenario.

Similar to the EAX scenarios, ADX OC scenario finds a lower GWP and FFU than ADX LE. The demand for increased biorefinery natural gas use and purchased electricity in ADX LE help to drive up both the GWP and FFU. Unlike the EAX scenarios, however, the avoided production credit is greater in the lignin exporting model. ADX OC does not produce as much electricity as EAX OC and therefore there is not a significant loss in energy produced when comparing ADX OC to ADX LE. The increased avoided production credit in ADX LE results from the shift to displacing coal

based electricity instead of natural gas based electricity. Even with the greater avoided production credit, however, the ADX OC scenario has lower GWP and FFU values. The difference between the GWP and FFU values of ADX OC and ADX LE are not as large as the differences between EAX OC and EAX LE (Table 1).

Avoided production credits are identified as a significant benefit to the acetic acid production scenarios. Economic and mass allocation assessments were performed to determine the life cycle impacts associated with just acetic acid by removing the environmental burdens and benefits of the lignin co-product from the life cycle of acetic acid production and to compare environmental impacts using different LCA methodology. The economic value of lignin is small compared to acetic acid and based on economic allocation almost all life cycle process (except avoided production because it is downstream of acetic acid production) are attributed to acetic acid production. Mass allocation shares the environmental burdens between lignin and acetic acid more evenly with ~30 % attributed to the lignin co-product and ~70 % attributed to acetic acid. Economic allocation produces higher GWPs and FFU than mass allocation as more of the life cycle processes are associated with acetic acid production. In both economic and mass allocation displacement of coal by the lignin co-product is completely removed from acetic acid production. This process occurs downstream of the separation of lignin from the acetic acid production process and is therefore entirely attributed to the lignin co-product. For economic allocation, removal of the avoided production credit without the additional removal of environmental burdens from acetic acid life cycle results in large increases to the EAX LE and ADX LE GWPs and FFU values (Table 2). The effect of mass allocation has on the GWP and FFU differs for EAX

LE and ADX LE. Although mass allocation removes the benefit of the avoided production credit it also removes 30% of the environmental burdens from the respective acetic acid life cycles. For EAX LE this means the GWP and FFU are reduced compared to that obtained using system expansion. For ADX LE the GWP increases, but not as much as it does for economic allocation and FFU remains the same as the system expansion model. The reason for the GWP increase in ADX LE is the loss of the avoided production credit. In the ADX LE system expansion model the avoided production credit is relatively much larger to the overall GWP than it is for EAX LE (Figure 1). The loss of the avoided production credit when using an allocation approach is therefore much more pronounced. Even though 30% of the environmental burdens are removed from the acetic acid life cycle in the mass allocation model, it is not enough to make up for the loss in avoided production. The results of the allocation analysis indicate that for both EAX LE and ADX LE life cycle results can greatly vary depending on acetic acid production design and the allocation methodology. This further underscores the importance of transparency in LCAs, as choosing one methodology over another can significantly change the results of a study.

Sensitivity analyses were conducted to evaluate the effect of a varied acetic acid fermentation yield. Decreasing the fermentation yield of glucose to acetic acid by 10 % increased the EAX OC and EAX LE GWP by 20 % and 12 %, respectively (Table 3). There are two driving factors in the increase to GWP. First, decreasing the fermentation yield decreases acetic acid production, but requires roughly the same amount of inputs (feedstock and ancillary chemicals). Relative to a tonne of acetic acid the life cycle impacts associated with these impacts increases. Secondly, decreasing the acetic acid

yield decreases the amount of carbon stored in the acetic acid end product and increases the amount carbon released through combustion of unfermented carbohydrates. The increase of inputs required to make a tonne of acetic acid combined with less carbon stored in the final products results in a “double hit” to the GWP. In contrast EAX OC and EAX LE FFU only increase by 6.3 % and 7.1 %, respectively, because of the decreased fermentation yield. FFU values are not affected by stored carbon (or the lack thereof) and only the increase in inputs relative to acetic acid production is factored into its calculations. Additionally, in relation to the other biorefinery inputs, the increase in available biomass for bioenergy reduces the demand for natural gas (6 % increase of natural gas; 10 – 11 % increase for all other inputs). Natural gas is the largest contributor to FFU and identifying non fossil fuel based replacements for natural gas will be key to reducing the process sensitivity (and overall FFU) to yield.

Currently there are no LCAs for production of bio-acetic acid in the literature to make direct comparisons too. An approximate comparison can be made to a process to produce succinic acid from corn stover using a LLE technique [9]. The bio-succinic production process uses the pretreatment and hydrolysis process proposed by Humbird et al. [1] to release sugars for fermentation (same as in the bio-acetic acid process). The released sugars are fermented using yeast (*Actinobacillus succinogenes)* to produce succinic acid, and the succinic acid is extracted using tri-n-actylamine in a LLE column. Similar to the bio-acetic acid research presented here, natural gas use was found to be one of the largest sources of GHGs and fossil fuel use (26.6 GJ of natural gas used per tonne of succinic acid produced). GWP and FFU are found to be 692 kg CO_2 eq and

25.2 GJ per tonne of bio-succinic acid, respectively. The GWP and FFU for bio-succinic acid are lower than those calculated for the EAX scenarios and higher or equivalent than the GWP and FFU calculated for ADX scenarios. Similar to the ADX scenarios, bio-succinic acid GWP and FFU values are significantly lower than their petroleum based counterparts [9].

Conclusion

Both ethyl acetate (EAX) and alamine/DIBK (ADX) are identified as viable extraction methods to produce glacial acetic created from the bioconversion of poplar biomass. The acetic acid produced from this process is identical to acetic acid produced from petroleum and can serve as a bio-based alternative without a loss in product quality. A goal in developing a bio-acetic acid and testing different extraction methods is to identify processes that reduce the GWP and FFU compared to petro-acetic acid. Only the ADX method is able to achieve these goals. EAX would result in a GWP that is either equivalent to or higher than that of petro-acetic acid. Natural gas use is a major contributor to the GWP and FFU for both extraction methods. The ability of the ADX method to operate with lower steam demands, and therefore use less natural gas, is a major factor in its overall lower GWP and FFU values. Identifying effective methods to reduce or replace natural gas with a renewable will reduce environmental impacts in the production of acetic acid.

Using lignin onsite or exporting it for co-firing at coal power plant can also have a significant effect on GWP and FFU values. Choosing between onsite lignin combustion and exporting it off site will affect the avoided production credit, natural gas use, and the need to purchase electricity. Allocation analysis identified that removing avoided credits from the system boundaries of acetic acid production generally increases the GWP and FFU. Additionally, environmental impacts associated with acetic acid production are identified as being sensitive to changes in acetic acid fermentation yield. Future research should focus on how to maintain a high acetic acid yield to avoid reducing the environmental benefits producing bio-acetic acid. See the companion paper [17] for an in-depth techno-economic analysis of acetic acid production from poplar biomass.

Methods

In this study the production of acetic acid via the bioconversion of poplar biomass is evaluated using life cycle analysis. Models of acetic acid production plant with an annual biomass processing of 250,000 BDT/yr were simulated in ASPEN-Plus chemical engineering modeling software, producing 133,300 and 132,700 ton/yr of acetic acid for EAX and ADX solvent based scenarios, respectively. Total capital expenses were estimated at 245, 197, 223 and 187 million USD for EAX OC, EAX LE, ADX OC, and ADX LE, respectively [17]. Scenarios are assessed that measure the life cycle environmental tradeoffs between acetic acid distillation/extraction methods, and within these models looking at burning lignin onsite or using the lower capital cost approach of selling the lignin to a coal power plant. Cradle to biorefinery gate system boundaries

are set for acetic acid production to include the growth and harvesting of poplar biomass, biorefinery operations, and manufacturing of all necessary inputs (i.e. process chemicals, energy). Use and disposal of acetic acid is beyond the scope of this study. Environmental impacts to be assessed include the global warming potential, and fossil fuel use.

Cradle to biorefinery exit gate system boundaries are used to evaluate acetic acid production (Figures 6a&b). A functional unit of 1 tonne of acetic acid produced from a biorefinery system with 21 year operating time frame is used in the analysis. Environmental impacts considered are the 100 year Global Warming Potential (GWP) [19], and Fossil Fuel Use (FFU). FFU is calculated by summing all fossil fuel inputs (coal, natural gas, crude oil) per tonne of acetic acid. Guidelines for conducting a LCA are set by ISO 14040 [22] & 14044 [23] and this research follows the ISO design. LCAs in this research are developed using SimaPro v.8.0. Scenario results are compared to each other as well as to petroleum based acetic acid produced by methanol carbonylation [15]. A sensitivity analysis is conducted to investigate the effect of a decreased acetic acid yield. Additionally system expansion method for co-products is compared to both economic and mass allocation when lignin is exported to a coal burning facility.

The bio-acetic acid life cycles are broken up into 4 sections: feedstock production and harvesting, ancillary chemicals, the biorefinery, and lignin use (co-product scenarios). Feedstock production and harvesting is the same for each biorefinery configuration. Biorefinery process, ancillary chemical inputs, and lignin use will vary depending on the configuration. Descriptions of each life cycle section and allocation

methods for lignin use follow below. System boundary diagrams for each bioconversion pathway are displayed in Figures 6a&b.

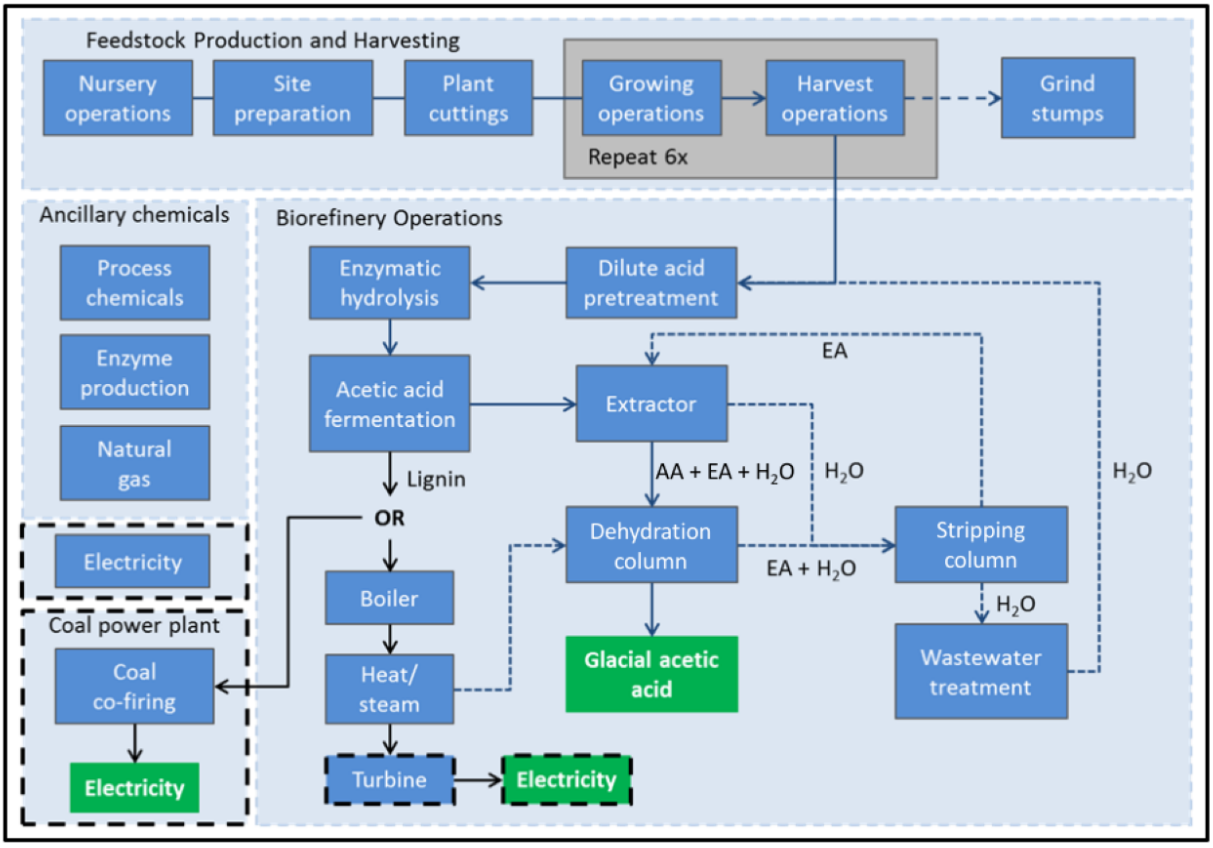

Figure 6a: Acetic acid (AA) extracted and distilled using ethyl acetate (EA). Both lignin scenarios are represented in the system boundaries figure. Black dashed line boxes indicate lignin scenario dependent operations. Lignin can either be burned onsite in the boiler to help produce heat/steam/electricity or sold to a coal power plant and co-fired with coal to produce electricity. If lignin is burned onsite, steam is run through a turbine to produce electricity. If lignin is exported to a coal power plant, no onsite electricity is made and electricity must be purchased from the grid for biorefinery operations. Green boxes highlight product made / energy produced.

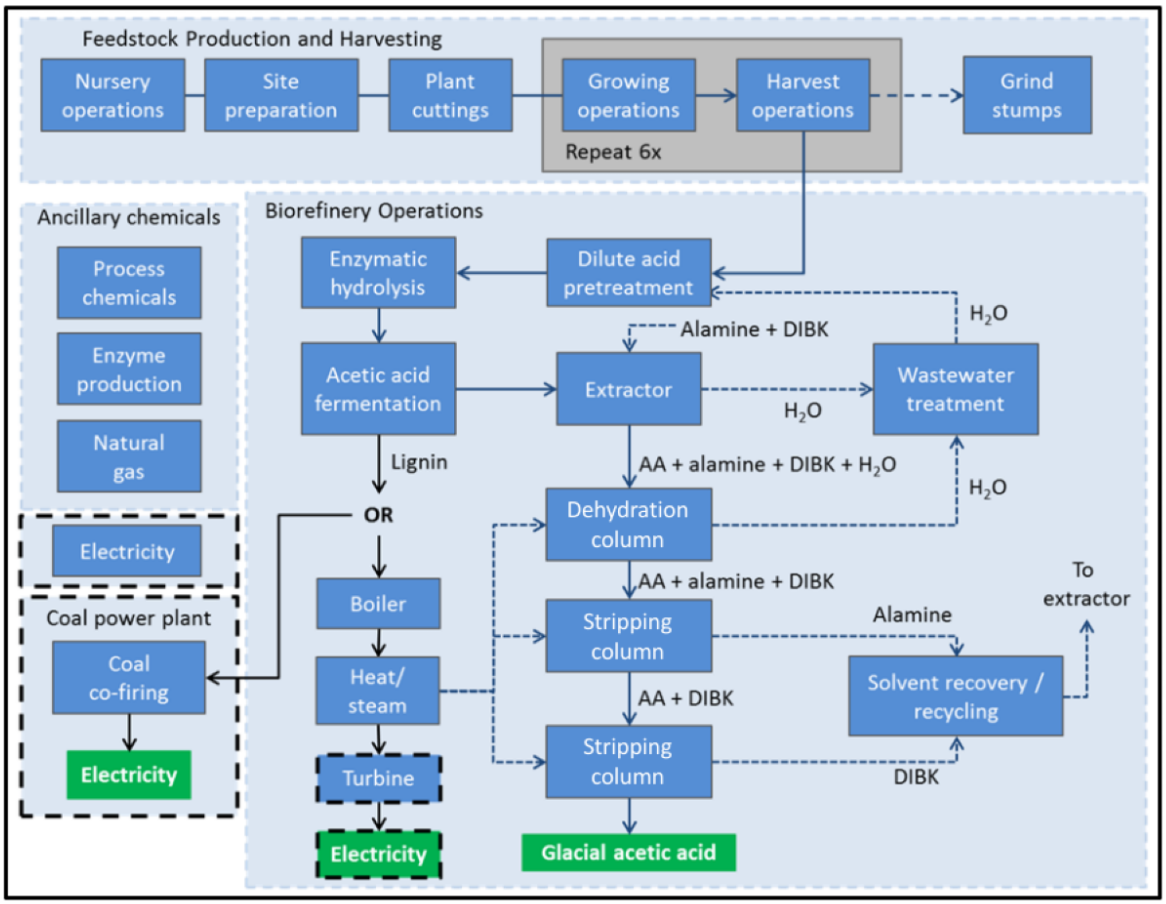

Figure 6b: Acetic acid (AA) extracted and distilled using an alamine and diisobutyl ketone solvent (ADX). Both lignin scenarios are represented in the system boundaries figure. Black dashed line boxes indicate lignin scenario dependent operations. Lignin can either be burned onsite in the boiler to help produce heat/steam/electricity or sold to a coal power plant and co-fired with coal to produce electricity. If lignin is burned onsite, steam is run through a turbine to produce electricity. If lignin is exported to a coal power plant, no onsite electricity is made and electricity must be purchased from the grid for biorefinery operations. Green boxes highlight product made / energy produced.

Feedstock

The feedstock production and harvesting model is supported by operational data from industry (GreenWood Resources, personal communication, 2011-2016), literature [24], and LCA databases [15, 25]. It is the same feedstock model used in [4] and is

discussed in more detail in that publication. A brief description is provided here. The feedstock production and harvest model is representative of a coppice harvest system, with the poplar trees being coppiced every 3 years for 6 cycles. The model includes all necessary site preparation, nursery operations, management of the poplar tree stands, harvest operations, and stump removal. Nitrogen fertilizer is applied in the spring following a harvest at a rate of 56 kg N per application. N_2O emissions from fertilizer and decaying biomass are calculated using the Farm Energy Analysis Tool [26]. Storage of carbon in the harvested poplar biomass as well as in below ground biomass (stump and roots) is included. The equivalent amount of CO_2 stored in the poplar wood is calculated using the stoichiometric relationship of CO_2 to carbon of 3.66 kg $kg^{-1}$and a carbon mass fraction of 51.7 % dry wood weight [27] (Table 2a & 2b). Direct land use change is included using the assumption that fallow land will be used for poplar plantations. Direct land use change associated with establishing the plantation is calculated using the Forest Industry Carbon Assessment Tool v.1.3.1.1. Indirect land use change is excluded from the system boundaries due to uncertainty associated with these models [28]. A transportation distance of 100 kilometers roundtrip is assumed to transport the harvested poplar biomass to the biorefinery gate. In total the feedstock production and harvest model covers a 21 year timespan [4].

Biorefinery

Currently no commercial facilities are using an acetogen fermentation pathway to produce biofuels and biochemicals. To assess the conversion impacts ASPEN-Plus

v.2004.1 chemical engineering software is used to simulate potential biorefinery process designs. The acetogen fermentation pathway ASPEN simulation is based on a combination of the NREL model [1], a proposed acetogen fermentation process [29], and laboratory work at the Biofuels and Bioproducts Laboratory at the University of Washington. The simulated biorefinery is assumed to operate on 250,000 tonnes of bone dry biomass per year.

Regardless of the product recovery method used (EAX or ADX), biorefinery operations begin with the same processes; dilute acid pretreatment, enzymatic hydrolysis, and fermentation. Pretreatment, hydrolysis, and fermentation conditions are presented in Table 4. These steps are based on National Renewable Energy Laboratory (NREL) corn stover model, but modified to use a poplar feedstock [1]. Following enzymatic hydrolysis, glucose and xylose are fermented to acetic acid using *Moorella thermoacetica*. The streams exiting the fermentation stage include a solid and liquid stream. Descriptions of the fate of these streams are described below. Incorporated into the biorefinery designs, and included in the LCAs is a wastewater treatment system. The WWT design is based on Humbird et al. [1]. Wastewater streams are treated in aerobic and anaerobic environments to produce clean process water, sludge, and methane. The sludge and methane are sent to the boiler. Solid waste produced from the biorefineries includes ash from the boiler and gypsum produced during acid neutralization after pretreatment. All wastes are collected and sent to a landfill for disposal.

Processing step	Process parameter	Value
Pretreatment	H_2SO_4 charge (gram of acid per gram of bone dry biomass)	0.01 1
	Temperature (°C)	200
	Xylan to xylose conversion (%)	75
Saccharification	Temperature (°C)	50
	Enzyme loading (miligram protein per gram cellulose)	20
	Cellulose to glucose conversion (%)	89
Fermentation	Fermentation temperature (°C)	58
	Glucose to acetic acid conversion (%)	92
	Xylose to acetic acid conversion (%)	92

Table 4: Process parameters for pretreatment, enzymatic hydrolysis, and fermentation.

The liquid stream exiting the fermentation is 5 wt % acetic acid and water. To be marketable acetic acid must be concentrated to 99.8 wt % (glacial acetic acid). When acetic acid concentrations are low (0.5 – 5 wt %) direct distillation of acetic acid from water is inefficient and liquid liquid extraction (LLE) is the preferred acetic acid recovery method [12]. In this research two LLE methods, both achieving acetic acid yields of 533 kg per bone dry tonne of biomass, are investigated to purify acetic acid. The first method uses ethyl acetate for extraction followed by distillation to recover the ethyl acetate (EAX). The second LLE method uses an alamine/DIBK extraction (ADX). These two extraction scenarios are described below. Major inputs and outputs for the biorefinery scenarios are presented in Table 5.

Ethyl acetate extraction

An overview of the ethyl acetate extraction (EAX) process is presented in Figure 1a. Following fermentation a mixture of water acetic acid (5% acetic acid by weight) is sent to a liquid-liquid extractor. Here it is mixed with ethyl acetate (EA) and the EA solubilizes the acetic acid. A mixture of acetic acid, EA, and a small amount of water are sent to a dehydration column operating at 118^{O}C. EA and the remaining water are distilled off and glacial acetic acid (99.8% acetic acid) is produced. Water and EA are sent to stripping column to recover the EA. EA exiting the stripping column is recycled back to the extractor. Water is sent to an onsite wastewater treatment facility before being cycled back through the process. Major inputs and outputs from the biorefinery are listed in Table 5.

Alamine/ Diisobutyl ketone *extraction*

An overview of the alamine/DIBK solvent extraction (ADX) process is presented in Figure 1b. After fermentation, acetic acid in water (5 % acetic acid by weight) is sent to an extractor. Acetic acid and water are mixed with alamine and DIBK. Acetic acid combines with alamine and DIBK and is removed from the water. This mixture is sent to a dehydration column (174^{o}C) to remove any residual water. Following dehydration the mixture of acetic acid, alamine, and DIBK is sent to a stripping column (190^{o}C). Alamine is removed and a mixture of acetic acid and DIBK is sent to a second stripping column (168 ^{o}C). DIBK is removed and glacial acetic acid is produced. DIBK and alamine are recovered and are recycled back into process. Water removed during

extraction/distillation is sent to wastewater treatment before being reused. Major inputs and outputs from the biorefinery are listed in Table 5.

In both extraction methods the solid stream separated out after the fermentation stage consists of lignin and other unfermented carbohydrates. To recover these solids and remove some of the residual water, the solid streams are filter pressed to 50 % solids (Figures 6a&b). Following concentration of the solids two potential downstream options for the solid stream are evaluated in this study. These are described in more detail below.

Onsite lignin combustion

Option one consists of combusting lignin onsite to produce heat/steam for the biorefinery operations and producing electricity by running high pressure steam through a steam turbine; using the moderate pressure steam exiting the turbine for the process. This practice is common in proposed biofuel biorefinery designs [1, 4] and pulp mills [30]. Compared to second generation lignocellulosic ethanol production, producing glacial acetic acid requires more heat/steam and combusting lignin alone cannot meet the entire energy demand. Extraction/distillation of acetic acid requires a significant amount of steam. To meet this demand, natural gas is imported and combusted with the lignin. To reach the temperatures needed for extraction/distillation moderate pressure steam would be required. However, techno-economic work has identified an economic benefit to instead first creating high pressure steam and passing it through a turbine to produce moderate and low pressure steam [17]. The conversion of high pressure steam to lower pressure steam through the turbine generates an amount of

electricity that exceeds the needs of the biorefinery. The excess electricity can be sold to the electrical grid to increase the revenue generated from the biomass. The production of excess electricity is greater in the ethyl acetate extraction process as this method has a greater steam demand and therefore more high pressure is passed through the turbine.

For the LCA of the onsite lignin combustion scenario, the electricity by-product is treated using system expansion per ISO standards [23]. The electricity by-product meets the requirements for using system expansion as it is currently produced from other sources and life cycle data for the production of electricity from these other sources can be obtained [31]. System expansion is the most common method used in biofuel LCAs to deal with an excess electricity by-product [32]. It is assumed that the electricity will be sold to the grid and displace electricity produced from natural gas, a likely candidate for the marginal electricity source [33]. An avoided production credit is generated for displacing this fossil fuel source of electricity with electricity produced from a renewable source.

Sell lignin to power plant

The second option for lignin is to export it to a coal power plant and co-fire with coal. This has been shown to be a viable option and can economically and environmentally benefit both the biorefinery and the coal power plant [18]. In this scenario lignin is considered a co-product to acetic acid production. It is dried to about 50% lignin by weight (50% water) and shipped to a nearby coal power plant and used in place of coal. The amount of coal displaced is based on the energy content of the

lignin. The moisture content of the lignin will affect the energy content and must be accounted for when calculating the amount of coal displaced (i.e. the energy required to remove water prior to combustion is included in the coal displacement calculation). In order to determine the coal displacement by selling the lignin as a co-product, the HHV of wet lignin (50% MC) was estimated using ASPEN. Lignin was modeled as vanillin $C_8H_8O_3$ with an HHV of 25.2 MJ / kg [1], similar to the experimental value of dilute acid pretreated lignin of 21.4 MJ / kg [34]. A heat stream from the burner was generated to determine the HHV of the wet lignin. Exporting lignin as a co-product requires that other forms of energy must be used to meet the needs of the biorefinery. Natural gas is assumed to combusted at the biorefinery to provide heat and steam. In this scenario it is assumed that a lower pressure boiler is used and the additional expense of a turbine to generate power would not be incurred. Natural gas boilers are more commonly used in the industry due to the relatively low capital cost in the range of $8–$23/kW [35] and their relatively small physical size. In contrast, biomass boilers are larger in size and have high capital cost ($94–$125/kW) [36] due to more complex design. Consequently, natural gas boilers are typically less expensive than those that would be suitable for combusting lignin. Exporting lignin and using natural gas as the sole driving fuel represents a lower cost alternative. A high pressure boiler with turbo-generator would be not be appropriate in such a biorefinery design approach. For the lignin export case the biorefinery electricity needs are assumed to be met by importing electricity from the U.S. national grid.

Input	**EAX OC**	**EAX LE**	**ADX OC**	**ADX LE**
Feedstock (bone dry) (t)	1.9	1.9	1.9	1.9
Enzymes (kg)	16	16	16	16
Sulfuric Acid (kg)	34	34	34	34
Ammonia (kg)	23	23	23	23
Sodium hydroxide (kg)	45	45	45	45
Clarifier polymer (kg)	1.1	1.1	1.1	1.1
Fermentation nutrients (kg)	50	50	50	50
Lime (kg)	26	0	26	0
Natural gas (GJ)	53	58	19	28
Ethyl acetate (kg)	5.2	5.2	NA	NA
Alamine (kg)	NA	NA	1.9	1.9
Diisobutyl ketone (DIBK) (kg)	NA	NA	1.9	1.9
Electricity (kwh)	0	320	0	300
Output				
Acetic acid (t)	1	1	1	1
Lignin (bone dry) (kg)	0	440	0	440
Electricity (kwh)	2600	0	860	0
CO_2 (from lignin) (t)	1.8	0	1.8	0
CO_2 (from natural gas) (t)	2.7	3.2	0.99	1.4

Table 5: Major inputs and outputs from the biorefinery of each scenario. Basis is 1 metric ton of acetic acid. EAX = ethyl acetate extraction. ADX = alamine/diisobutyl ketone extraction. OC = onsite combustion of lignin. LE = Lignin exported to a coal burning power plant. Extractants for each pathway (ethyl acetate for EAX, and alamine and diisobutyl ketone for ADX) are reported for their initial application rates per tonne of acetic acid. It is assumed that these extractants are reused at a 99 % recycling rate.

Ancillary chemicals

Biorefinery operations require chemical inputs to convert the poplar biomass to acetic acid. The production of these chemicals is grouped into the ancillary chemicals section. Unit process data for the chemical inputs come from the USLCI [15], EcoInvent [25], literature, and the private sector. The electricity source in each unit process is set to come from a unit process representative of the 2012 U.S. national grid [37]. Data for enzyme production is supplied from Novozymes for their Cellic Ctec3 cellulases [38]. Transportation distances for each chemical are determined using the 2007 U.S. commodity flow survey [39].

Allocation and Sensitivity Analysis

System expansion is used in evaluating the base case for the four bio-acetic acid production scenarios. As discussed above, this is deemed to be the appropriate treatment of the life cycle impacts for the product and excess electricity/lignin co-product. However, the results are also evaluated using mass and economic allocation methods to determine the life cycle effect of allocating life cycle impacts between acetic acid production and the lignin co-product (in the lignin exporting scenarios). Allocating the life cycle impacts between acetic acid and lignin divides the environmental benefits (i.e. carbon sequestration) and burdens (i.e. natural gas combustion) between acetic acid and the lignin co-product. To account for the movement of carbon within the biorefining systems the carbon sequestered in the poplar biomass is allocated to either acetic acid (i.e. glucose and xylose) or lignin.

Producing one tonne of acetic acid requires 1.8 tonnes of poplar biomass (dry weight). At a 51.7 % carbon content [27], 1.8 tonnes of poplar contain 930 kg of carbon. Through the bioconversion process 400 kg of this carbon will go into the acetic acid. 380 kg of the carbon is contained in the lignin. The 150 kg of carbon remaining in the system (carbohydrates in liquid streams) is divided between the acetic acid product and lignin co-product. The amount of this 150 kg assigned to either the acetic acid product or lignin co-product depends on the allocation method being assessed (mass or economic). From the acetic acid product view point, allocation also removes all processes that are downstream of the biorefinery - and tied to the lignin co-product - from the life cycle production of acetic acid; including coal displacement and emissions from lignin combustion at the coal burning facility.

The mass allocation approach divides the life cycle processes amongst acetic acid and lignin according to the mass of each product. For every tonne of acetic acid produced, 394 kg of lignin (dry weight) is exported. Economic allocation divides life cycle processes amongst acetic acid and lignin based on the economic values of these two products. The minimum selling price that was calculated in the accompanying techno/economic analysis [17] was used to establish the value of the acetic acid. In the EAX LE scenario techno-economic analysis identified the minimum selling price of acetic acid to be $819 per tonne and economic value of the lignin exported to the coal facility to be $39 per tonne (assuming $4.40 per MMBTU). In the ADX LE scenario the selling price for acetic acid is $677 per tonne and the value of the exported lignin to be $39 per tonne. More details regarding techno-economics can be found in the companion paper by [17].

A sensitivity analysis is conducted to test for model sensitivity to changes in fermentation yields. The fermentation yield of glucose to acetic acid in this research is set at 92%. Maintaining a fermentation yield of 92% may be difficult when operating at commercial scale and could likely fluctuate. If the fermentation yield decreases the amount of acetic acid produced would decrease and the amount unfermented carbohydrates, and therefore the amount of biomass available to burn, would increase. To test the effect of a decreased fermentation yield and to evaluate model sensitivity, a simulation is performed for the EAX OC and EAX LE scenarios in which the fermentation yield is decreased by 10 %. Only EAX is tested for sensitivity analysis as this system is more likely to be commercialized [17] and it is expected that the effect of a decreased acetic acid yield would be similar for both EAX and ADX.

References

1. Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, et al. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol; Dilute-acid Pretreatment and Enzymatic Hydroylsis of Corn Stover. Golden (CO): National Renewable Energy Laboratory; 2011 May. 147 p. Technical Report NREL/TP-5100-47764 Contract No.: DE-AC36-08GO28308
2. Borrion AL, McManus MC, Hammond GP. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. Renew Sustain Energ Rev 2012;16(7):4638-50.
3. Wiloso EI, Heijungs R, de Snoo GR. LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice. Renew Sustain Energ Rev 2012;16(7):5295-308.

4. Budsberg E, Crawford J, Gustafson R, Bura R, Puettmann M. Ethanologens vs. acetogens: Environmental impacts of two ethanol fermentation pathways. Biomass Bioenerg 2015;83(12):23-31.
5. Bos HL, Meesters KPH, Conijn SG, Corre WJ, Patel MK. Accounting for the constrained availability of land: a comparison of bio-based ethanol, polyethylene, and PLA with regard to non-renewable energy use and land use. Biofuels Bioproducts & Biorefining 2012;6(2):146-158.
6. Hottle TA, Bilec MM, Landis AE. Sustainability assessments of bio-based polymers. Polymer degradation and stability 2013;98:1898-1907.
7. Yates MR, Barlow CY. Life cycle assessments of biodegradable, commercial biopolymers – A critical review. Resources, Conservation and Recycling 2013;78:54-66
8. Papong S, Malakul P, Trungkavashirakun R, Wenunun P, Chom-in T, Nithitanakul M, Sarobol E. Comparative assessment of the environmental profile of PLA and PET drinking water bottles from a life cycle perspective. Journal of Cleaner Production 2014;65:539-550.
9. Dunn JB, Adom F, Sather N, Han J, Snyder S. Life-cycle analysis of Bioproducts and their conventional counterparts in GREET. Argonne (IL): Argonne National Laboratory; 2015 September. 90p. Technical Report ANL/ESD-14/9 Rev.
10. Forte A, Zucaro A, Basosi R, Fierro A. LCA of 1,4-butanediol produced via direct fermentation of sugars from wheat straw feedstock within a territorial biorefinery. Materials 2016;9:563 doi:10.3390
11. Pawelzik R, Carus M, Hotchkiss J, Narayan R, Selke S, Wellisch M, Weiss M, Wicke B, Patel MK. Critical aspects in the life cycle assessment (LCA) of bio-based materials – Reviewing methodologies and deriving recommendations. Resources Conservation and Recycling 2013;73:211-228.
12. Cheung H, Tanke RS, Torrence GP. 2012. "Acetic Acid", Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH.
13. Sunley GJ, Watson DJ. High productivity methanol carbonylation catalysis using iridium the cativa process for the manufacture of acetic acid. Catalysis 2000;58:293-307.
14. Aster N. Global Acetic Acid Production to Exceed 17.3 Mln Tonnes in 2018, According to In-demand Report by Merchant Research & Consulting. PRweb April 25, 2014. Accessed at http://www.prweb.com/releases/2014/04/prweb11797353.htm on 12/14/2015.

15. US life cycle inventory database [Internet]. Golden (CO): National Renewable Energy Laboratory. c2012 [cited 2017 March 13] Available from: http://www.nrel.gov/lci/.
16. Andreesen JR, Schaupp A, Neurauter C, Brown A, Ljundahl LG. Fermentation of glucose, fructose, and xylose by Clostridium thermoaceticum: Effect of metals on growth yield, enzymes, and synthesis of acetate from CO2. J of Bacteriology. 1973:114(2):743-51.
17. Morales-Vera R, Crawford J, Dou C, Bura R, Gustafson R. Techno-Economic Analysis of Producing Glacial Acetic Acid from Poplar Biomass via Bioconversion. Molecules. 2020;25(18):4328. Published 2020 Sep 21. doi:10.3390/molecules25184328
18. Galbreath KC. Subtask 2.1 - Effects of cofiring lignin and biosolids with coal on fireside performance and combustion products. Pittsburgh (PA): Prepared for U.S. Department of Energy, 2002. Cooperative Agreement No. DE-FC26-98FT41129. Access at http://www.osti.gov/scitech/servlets/purl/804937 on 12/14/15.
19. IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp, doi:10.1017/CBO9781107415324
20. Crawford JT, Chin WS, Budsberg E, Bura R, Gustafson R. Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: Techno-economic assessment. Biotech. For Biofuels BBIO-D-16-00090.
21. Budsberg E, Crawford JT, Morgan H, Chin WS, Bura R, Gustafson R. Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment. Biotechnology for Biofuels 2016;9(170): DOI 10.1186/s13068-016-0582-2
22. ISO 14040:2006 - Environmental management. Life cycle assessment - Principles and framework. Geneva, Switzerland: International Organization for Standardization; 2006. Report No.: ISO 14040:2006.
23. ISO 14044:2006 - Environmental management. Life cycle assessment - Requirements and guidelines. Geneva, Switzerland: International Organization for Standardization; 2006. Report No.: ISO 14044:2006.
24. Caputo J, Balogh SB, Volk TA, Johnson L, Puettmann M, Lippke B, et al. Incorporating Uncertainty into a Life Cycle Assessment (LCA) Model of Short-Rotation Willow Biomass (Salix spp.) Crops. Bioenerg Res 2014;7(1):48-59.
25. Ecoinvent. Duebendorf, Switzerland: Swiss Center for life cycle inventories; 2010.

26. Farm Energy Analysis Tool [Internet]. University Park (PA): Camargo GGT, Ryan MR, Richard TL, Malcolm GM. c2015 [cited 2015 June] Available from: http://www.ecologicalmodels.psu.edu/agroecology/feat/.
27. Sannigrahi P, Ragauskas AJ, Tuskan GA. Poplar as a feedstock for biofuels: A review of compositional characteristics. Biofuels, Bioprod, Biorefin 2010;4(2):209-26.
28. Sanchez TS, Woods J, Akhurst M, Brander M, O'Hare M, Dawson TP, et al. Accounting for indirect land-use change in the life cycle assessment of biofuel supply chains. J R Soc Interface 2012;9(71):1105-19.
29. Verser D, Eggeman TJ, inventors; ZeaChem Inc., assignee. Process for producing ethanol United States patent US 7964379. 2011 June 21.
30. Gustafson R, Raffaeli N. Washington state pulp and paper mill boilers: Current and potential renewable energy production. Bellevue (WA): State of Washington Department of Ecology; 2009. 45 pp Publication No. 09-07-048.
31. Ekvall T, Finnveden G. Allocation in ISO 14041 – A critical review. J Clean Prod 2001;9(3):197-208.
32. Gnansounou E, Dauriat A, Villegas J, Panichelli L. Life cycle assessment of biofuels: Energy and greenhouse gas balances. Bioresour Tech 2009;100(21): 4919-30.
33. Thomas CE. US marginal electricity grid mixes and EV greenhouse gas emissions. Int J of Hydrogen Energ 2012;37(24):19231-40.
34. Blunk SL, Jenkins BM. Combustion properties of lignin residue from lignocellulose fermentation. Davis (CA): Prepared for National Renewable Energy Laboratory by Department of Biological and Agricultural Engineering University of California, April 2002. NREL Subcontract ACG-8-18021-01.
35. Oskarsson K. A planner's guide for selecting clean-coal technologies for power plants. Washington, DC: The World Bank; 1997
36. Geletukha GG, Zhelyezna TA, Tishayev SV. Strategy of bioenergy development in Ukraine. In: 1st world conference on biomass for energy and industry, vol.2(7); 2000. p. 1260–3
37. Electric Power Annual [Internet]. Washington (DC): U.S. Department of Energy, Energy Information Administration. c2012 [cited 2013 December] Available from: http://www.eia.gov/electricity/annual/pdf/epa.pdf
38. Nielsen AM. Cellulase Life Cycle Assessment [Internet]. Message to: Budsberg E. 2012 Sept 7 [cited 2015 July 7].

39. Commodity Flow Survey. 2007. Washington (DC):U.S. Department of Transportation and U.S. Department of Commerce. c2010 [cited 2013 July 11]. Available from: http://www.census.gov/prod/2010pubs/ec07tcf-us.pdf

Conclusion

Bio-jet fuel and bio-acetic acid produced from a poplar feedstock have the potential to reduce life cycle impacts that contribute to climate change compared to the petroleum based jet fuel and acetic acid they are intended to replace. These potential reductions, and the degree to which GHG emissions and fossil fuel use are reduced, are dependent on multiple factors. GWPs and FFU are a direct result of the type of bio-product produced, the region from which the feedstock was sourced, the processes of bioconversion, and how waste products (i.e. lignin) are used and assessed.

All three studies presented in this dissertation are based around the use of life cycle methodology to evaluate the potential environmental impacts of bio-jet fuel and bio-acetic. LCA is a useful tool, but it is not without its concerns. The results of an LCA are only as good as the data used to model the process or system in question. For these studies LCA data was sourced from primary and secondary sources. The primary data for the growth and harvesting of poplar trees was collected by Greenwood Resources, as well as researchers at UC Davis and University of Idaho. ZeaChem and the Biofuels and Bioproducts Laboratory at the University of Washington provided primary data for the biorefinery systems. These primary sources of data were based on benchtop and pilot systems. They are accurate for the systems they represent. However, as we scale the growth and harvesting and biorefinery operations up to a commercial system, we also introduce variability and uncertainty. What works at pilot scale, may not work at commercial scale or be representative of operations when modelling a system in a different location (i.e growing poplar trees in wet climate vs a

dry climate, but still within the same region). Moving beyond the primary data sources, secondary data from life cycle inventory databases also have their own inherent issues. Secondary data, such as the USLCI and Ecoinvent were used to model processes where primary data was not available. Secondary data can help ease the process of building a full LCA, but it also introduces uncertainty as the unit process data may not be the best representation of the system under consideration and can only be used as an approximate estimate (i.e. crop production data or energy production from one area of the U.S. is not representative of production in another area). Taken together, the use of primary data and secondary data in this dissertation introduce uncertainty and the results presented should be viewed not as definitive numbers, but as reasonable approximations of the life cycle impacts of bio-jet fuel and bio-acetic acid production and use.

In regards to the bio-jet LCA study, the production and use of hydrogen are identified as major contributors to the GWP and FFU of bio-jet fuel production. The hydrogen production method will dictate GHG emissions, FFU, and the degree to which these impacts can be reduced. LCA work in this study suggests that for biorefineries with integrated hydrogen production facilities, using hog fuel in place of natural gas to provide heat and steam will have reduced non-biogenic CO_2 emissions and FFU. Baseline biorefinery designs (NGSR and LG bio-jet) already include the infrastructure necessary for burning biomass, and addition of hog fuel to the burner/boiler would not drastically increase capital costs.

The regional assessment of poplar crop adoption for a commercial scale biorefinery industry helps to complete the picture of potential changes to land

management, and the overall impacts of producing bio-jet fuel. Agricultural practices are a dynamic process that change from region to region, and vary over time, making spatial life cycle analysis research challenging. However, the amount of land needed to meet feedstock demands could be large and modelling potential changes in land use is an important consideration. Although, relative to bio-jet GWP, poplar feedstock production and harvesting makes up a small portion (approximately 10 %) of the overall GWP of bio-jet fuel production when compared to downstream processing and conversion, the regional assessment indicates that other local impacts such as those associated with fertilizer use, chemical inputs, and fuel use could play an increasingly significant role in the future development of bio-jet fuels industry.

As the interest in biofuels, and scaling up to commercial size, continues to draw interest it will be important to consider producing additional biochemicals from these biorefineries to diversify output. Both ethyl acetate (EAX) and alamine/DIBK (ADX) are identified as viable extraction methods to produce glacial acetic created from the bioconversion of poplar biomass. However, the LCA research in this study identified that only the ADX method is able to produce a bio-acetic acid that could have a GWP and FFU lower than petroleum based acetic acid. EAX would result in a GWP that is either equivalent to or higher than that of petro-acetic acid. Natural gas use is a major contributor to the GWP and FFU for both extraction methods. The ability of the ADX method to operate with lower steam demands, and therefore use less natural gas, is a major factor in its overall lower GWP and FFU values.

Also of consideration in designing and operating a biorefinery will be how to handle the remaining lignin after the cellulose and hemicellulose have been separated

from the biomass. Using lignin onsite or exporting it for co-firing at a coal power plant can also have a significant effect on GWP and FFU values. Choosing between onsite lignin combustion and exporting it off site will affect the avoided production credit, natural gas use, and the need to purchase electricity. Allocation analysis identified that removing avoided credits from the system boundaries of acetic acid production generally increases the GWP and FFU.

Both bio-jet fuel and bio-acetic bio-products have pathways to production that reduce GWPs, relative to petroleum based jet fuel and acetic acid, through the use of the poplar biomass feedstock. The substitution of lignocellulosic material as the carbon source for the jet fuel and acetic acid utilize the shorter carbon cycle of biogenic carbon, as opposed to the long lived carbon cycle of non-biogenic carbon, is a significant factor in reducing the GWP of these bio-based products. Furthermore, the reductions in FFU within the life cycles of bio-jet and bio-acetic acid help in the reduction in greenhouse gas emissions associated with FFU and add to their overall sustainability.

However, these bioproducts are not completely separated from reliance on fossil fuels. Fossil fuels are needed in the growth and harvesting of the poplar feedstock, and the transportation of poplar biomass (as well as other inputs) to the biorefineries, but use of fossil fuels may decrease as the biofuel industries expands. As biorefineries begin producing different types of drop-in biofuels, the use of fossil fuels in farming and transportation equipment could be phased out. The challenge to separate from fossil fuels is within the biorefineries themselves. Both bio-jet fuel and bio-acetic require natural gas, as either a hydrogen source for hydrogenation, and/or as a heat source. Future work should focus on how to produce these bioproducts without the need of

fossil fuel inputs. Switching to alternative, sustainable methods to replace natural gas could potentially decrease greenhouse gas emissions even further. Changes in technology and energy use may allow for future pathways to produce hydrogen without the use of natural gas or other fossil fuels, and in doing so could help to greatly reduce the GWP and FFU of bio-jet fuel production. Alternative hydrogen production, such as electrolysis, could have a significant impact on the life cycle emissions of bio-jet fuel, but would require a full LCA to evaluate the benefits of these systems. As research into biofuels and biochemicals continues to evolve, so does the prospect of reducing our dependence on fossil fuels.