Life Cycle Carbon Footprint of Ethanol and Potassium Acetate Produced from a Forest Product Wastewater Stream by a Co-Located Biorefinery

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S *Supporting Information*

ABSTRACT: Integrated production systems are designed on the concept of "minimum waste" to fully utilize natural resources by building industries next to each other when the waste of one is able to be the feedstock of another. A forest hardboard product wastewater stream contains wood extractives suspended in it that meet the input requirement of a cellulosic ethanol biorefinery facility. In addition, the biorefinery process partially substitutes for conventional wastewater treatment (WWT). A life cycle carbon footprint of fuel ethanol produced from a co-located biorefinery facility has been evaluated with a focus on greenhouse gas (GHG) emissions and compared with petroleum gasoline. The methodology takes into account changes to the original hardboard facility due to the presence of the integrated biorefinery. Three allocation methods (system expansion, mass allocation, and market value allocation) are applied in this study. Six scenarios are analyzed to evaluate the significance of several key variables. The basecase life cycle carbon footprint results show that ethanol produced from this biorefinery emits −27, 21, or 16 g of CO_2 eq/MJ using system expansion, mass, or market value allocation, respectively. The sources of energy employed have significant influence on the life cycle GHG emissions for ethanol and potassium acetate.

KEYWORDS: *Life cycle carbon footprint, Bioethanol, Integrated biorefinery, Energy sharing, GHG emissions, Potassium acetate*
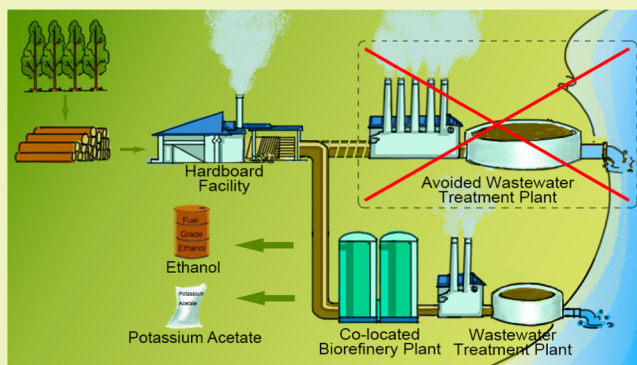
INTRODUCTION

The search for renewable liquid transportation fuels is motivated by concerns over energy security and climate change. In the United States transportation sector, the renewable liquid fuel market is led by corn ethanol.[1] But corn is also a food source, and therefore, alternative feedstocks are being considered for future biofuel production.

Potential Feedstocks for Biofuels. According to a recent report, future transportation biofuels will be produced in the United States, mainly from forest and agricultural resources.[2] Forest-derived resources include woody energy crops such as poplar or willow, forest residues and thinnings, mill residues, and pulping liquors. Agricultural resources include energy crops such as switchgrass and miscanthus and oil crops (for example, soybeans, rapeseed, canola, camelina), as well as agriculture residues (corn stover). In addition, woody components of municipal solid waste (MSW) and industrial waste may be suitable biofuel feedstocks. However, limited consideration has been given in the literature to feedstocks such as industrial and municipal wastes compared to forest and agricultural resources.

A few studies have looked into the technical feasibility of converting waste materials to biofuels and chemicals.[3−6] In working with an industrial partner, we have studied the process of converting hardboard manufacturing facility wastewater (containing suspended woody solids) into ethanol and potassium acetate. Furthermore, we estimate that production of ethanol from all United States hardboard facility wastewater may yield approximately 31 million gallons/yr. (see section 1.1, Supporting Information, for calculations leading to this ethanol yield estimate).

Life cycle assessment (LCA) is an accepted method to evaluate environmental performance of new products and processes, especially in recent years for biofuels.[1,7,8] The studied biomass raw materials include crop residues, energy crops, algae, and others.[1,9,10] Biofuels derived from dried solid waste or grass have often exhibited lower environmental impacts compared with traditional fossil fuels in terms of GHG emissions; however, this outcome is dependent on the specifics of each biofuel pathway.[1,8] More rare are life cycle assessments conducted on the conversion of organic materials in wastewaters to energy. One such approach is by bioelectrochemical systems (BESs), including (i) microbial fuel cell (MFC)
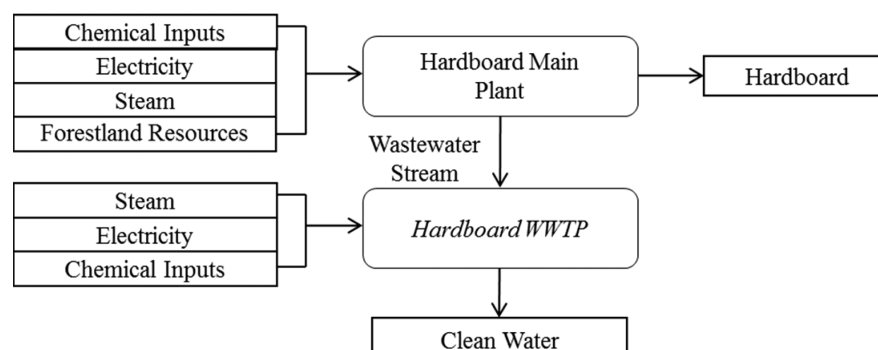
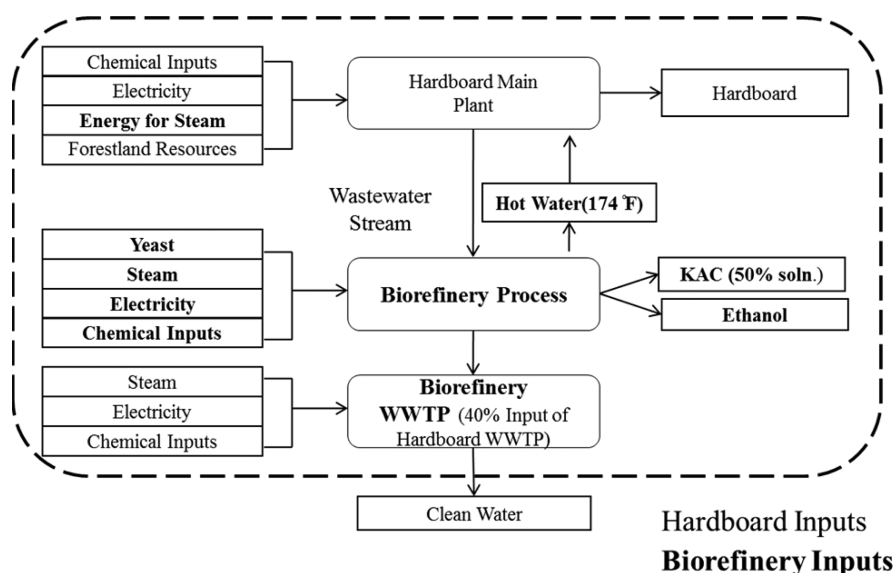**Figure 1.** Diagram of current hardboard manufacturing facility and its wastewater treatment process.

Figure 2. Co-located biorefinery utilizing wastewater from a hardboard facility showing a life cycle carbon footprint system boundary (dashed line).

treatment systems, (ii) microbial electrolysis cell (MEC) treatment systems, and (iii) microbial desalination cell (MDC) treatment systems.[11,12] However, LCAs of biorefineries processing wastewaters for production of liquid transportation biofuels and co-products are absent in the literature.

Biorefineries Co-Located with Industrial Facilities. The issue of system boundary is central to all biofuel LCAs, which follows directly from the goal and scope definition. In the carbon footprint analysis presented here, we deal with a specific case of industrial ecology[13,14] for production of a biofuel in which connections between the biorefinery and original hardboard facility are considered (see Methodology, Description of Process section). Questions such as the following are addressed: How will changes to the original hardboard facility due to sharing of process streams be included in the analysis? How will reductions in wastewater treatment inputs be assigned? Will upstream inputs for forest harvesting and hardboard processing be included due to use of wastewater as input to the biorefinery? Questions similar to these have been dealt with before in LCAs of biorefineries co-located with existing manufacturing facilities. For example, in a LCA of biofuel produced from gasification and catalytic upgrading of black liquor waste stream from pulp manufacturer,[15] all inputs to the biorefinery and changes to the original pulp facility were assigned to the biorefinery products in a consequential analysis. A study of ethanol produced from a biorefinery co-located with

a pulp mill utilized a system boundary encompassing both facilities and all products, such as biofuel and pulp in an attributional analysis.[16] Additional discussion of co-located biorefineries and consequential versus attributional LCA are presented in sections 1.2 and 1.3 of the Supporting Information.

METHODOLOGY

Goal, Scope, and Functional Unit Definition. The goal of this life cycle carbon footprint is to gain an understanding of how greenhouse gas (GHG) emissions are directly affected by biorefinery inputs and also indirectly affected by changes to inputs in the hardboard facility and wastewater treatment plant. This study approach will identify the most important process inputs and methodology assumptions. The system boundary will include biorefinery process units as well as affected units in the hardboard plant and wastewater treatment facility. The study is therefore a consequential analysis with the original hardboard facility as a baseline. As a result, all inputs to the co-located biorefinery and changes to inputs in the original hardboard facility and the wastewater treatment plant are assigned to the products of the biorefinery. Using this approach, the study will accomplish the stated goal of understanding the importance of key biorefinery inputs and will also include emissions due to changes of inputs beyond the biorefinery boundary limits. The wastewater from the hardboard facility is

considered a "waste" with no economic value, and therefore, it is not a product or co-product to which environmental burdens from the hardboard facility are assigned. This assumption is consistent with ISO 14040 and other biofuel carbon footprint guideline documents, although in LCA practice, there continues to be a question of whether a "waste is still a waste" if it becomes used for production of biofuels or other pro-educts.[17,18] Biorefinery infrastructure is not included in the scope of this analysis due to lack of data and because infrastructure impacts were shown to be negligible for high-throughput chemicals and transportation fuels.[19]

The carbon footprint analysis for ethanol is "cradle-to-grave", including ethanol combustion. However, the emissions of CO_2 from combustion of ethanol in engines are not counted toward the GHG inventory because the carbon atoms are biogenic in origin *and* we assume that all the carbon in the hardboard facility effluent would have been emitted as CO_2 during wastewater treatment and sludge combustion anyway (therefore, no change in emissions of CO_2 due to this assumption).[20−22] We neglect the final ethanol transportation step as well because it is generally considered negligible in most biofuels LCAs, for example, the GREET model shows that GHG emission for cellulosic ethanol distribution is only 1.2 g of CO_2 eq/MJ.[23] The analysis of potassium acetate is "cradle-to-gate" in order to make comparison to convention potassium acetate more direct. The basis for inputs into this life cycle carbon footprint analysis is one year of biorefinery operation (345 days), but the carbon footprint results are expressed on the basis of 1 MJ of ethanol and 1 kg of potassium acetate.

Description of Process. A conventional hardboard manufacturing process connected to a wastewater treatment plant (WWTP) is shown in Figure 1. This process involves material inputs like wood from forest resources, chemicals, and energy inputs such as steam and electricity. The wastewater stream containing wood fibers extracted from the wood chips needs to be treated in the WWTP, where more material and energy inputs are added. Figure 2 describes a configuration where the biorefinery process is co-located with the hardboard facility, with the bold font representing the changes in the material and energy flows to the original facility and inputs to the biorefinery, products, and recycled hot water. The co-located biorefinery employs a dilute acid hydrolysis process on the wastewater stream after increasing the total solids content of the wastewater using multiple-effect evaporation. Monomer sugars, including both hexoses and pentoses, are generated and then neutralized and fermented to produce ethanol. Acetic acid generated from dilute acid hydrolysis is concentrated and collected as 50% (wt) potassium acetate by reacting with potassium hydroxide. Hot water, a byproduct from the biorefinery, is sent to the hardboard plant to partially substitute for energy required for steam production there. Inputs to the remaining WWTP are reduced by 60% compared to the original plant (an estimate provided by the industrial partner based on engineering design calculations); however, there are inputs needed in the biorefinery process that are explained below.

Inputs and Inventory for Basecase Life Cycle Carbon Footprint. As shown in Figure 2 and Table 1, three categories of inputs to the carbon footprint are (i) inputs to the biorefinery, (ii) energy savings to the hardboard mill due to hot water return, and (iii) the original WWTP inputs. Inputs to the biorefinery are electricity, steam, and biorefinery chemicals including potassium hydroxide, lime, sulfuric acid, fertilizer,

Table 1. Inputs, Outputs, and Energy Savings[a]

	inputs to biorefinery	savings to hardboard mill	original WWTP
inputs			
electricity			
electricity (from Michigan grid) (MJ)	7.16×10^7	—	—
electricity (from WWTP mix) (MJ)	—	—	5.81×10^7
energy savings from hot H_2O return (MJ)	—	-7.98×10^7	—
steam			
steam for process heat from coal (MJ)	8.63×10^7	—	—
steam from WWTP mix (MJ)	—	—	5.07×10^7
chemical inputs			
KOH, 50% wt (kg)	2.18×10^6	—	—
lime (kg)	2.07×10^6	—	—
H_2SO_4 (kg)	2.80×10^6	—	—
fertilizer 5:1 N:P ratio (kg)	2.27×10^4	—	9.07×10^5
yeast (kg)	2.36×10^3	—	—
yeast extract (kg)	2.31×10^4	—	—
polymer flocculants (kg)	—	—	2.40×10^6
$Al_2(SO_4)_3$ (kg)	—	—	2.72×10^5
$Ca(NO_3)_2$ (kg)	—	—	5.90×10^4
Outputs			
KAc (50% soln) (kg)	3.84×10^6	—	—
ethanol (MJ)	6.04×10^7	—	—

[a]Based on annual operation of a co-located biorefinery in Michigan.

yeast, yeast extract, and nutrients for fermentation as shown in Table 1. Electricity to the biorefinery is assumed to be the Michigan grid (Tables S1 and S2, Supporting Information), and steam is generated in the biorefinery using hard coal because of its ready availability at the Michigan mill. Input data in Table 1 were obtained from an industry partner on this project. The inventory data for all of the inputs were obtained using ecoprofiles from the ecoinvent database in SimaPro (Table S3, Supporting Information).

Consistent with a consequential analysis, emission credits are assigned to the biorefinery products due to hot water (174 °F) returned to the hardboard facility to reduce coal for steam. The biorefinery design calls for a reduction in wastewater treatment inputs by 60% compared to the original facility (from the industrial partner based on engineering design calculations). Apart from the remaining 40% inputs for the wastewater treatment, the new inputs from the biorefinery are listed in the second column. Inputs to the original WWTP are shown in Table 1 (fourth column), which are categorized as electricity, steam, and chemical inputs. Power and steam for WWT are generated using the same energy resources as those in the hardboard manufacturing facility. Steam is generated by hard coal (65%), wood chips (30%), and WWTP sludge (5%). Hot water generated in the biorefinery that is transported back to the hardboard manufacturing facility is assumed to substitute for hard coal in this mix. The energy savings were calculated through the temperature and the amount of the hot water as shown in Section 2 of the Supporting Information. Although the production of ethanol from wastewater stream will decrease the portion of sludge in the energy mix, this influence is neglected because the percentage of sludge is small. According

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to the industry partner, these sources of energy, in the same ratios (65:30:5 for coal:wood chips:sludge), also make up 40% of the electricity needed in both the hardboard manufacturing facility and the WWTP. The remaining 60% of the power is provided from the Michigan grid. Main chemical inputs for the wastewater treatment include fertilizer, polymer flocculants, aluminum sulfate, and calcium nitrate as displayed in Table 1. Emission of N_2O and CH_4 from WWT are also considered (section 3, Supporting Information). For each m^3 of wastewater treated, 2 g N_2O are emitted to the air, and for each ton of solid in sludge treated, 200 kg CH_4 are emitted as per an IPCC report.[24] GHG emission of process water used in the biorefinery plant and the reduction of water input in the hardboard facility due to the hot water return are both neglected as the GHG emission of process water is much less than other inputs. For example, the GHG emission from process water in the biorefinery plant is less than 0.14 g of CO_2 eq/MJ ethanol (Section 4, Supporting Information)

Allocation Methods. Typical allocation methods used in biofuel life cycle carbon footprints include system expansion or are based on mass, volume, energy content, and economic value.[25] Due to the difference in function between ethanol and potassium acetate (ethanol is a fuel, while potassium acetate is a chemical), energy allocation is not appropriate.

Apart from the system expansion method, the base case approach in this analysis, two other methods were implemented: mass allocation and market value allocation. The system expansion method assigns all inventory data to the primary product bioethanol, while a credit is given for avoided emissions when the co-product potassium acetate (KAc) displaces the conventional KAc in the market. In the mass and market value allocation analyses, we retain the expanded system boundary and account for process changes to hardboard facility and WWTP but allocate those changes to inventory to both ethanol and KAc on the basis of output mass and market value, respectively. Thus, the mass and market value allocation approaches are hybrid attributional analyses due to the expanded system boundary. Hybrid allocation similar to this has been used before in biofuel LCAs.[26] The calculation of allocation factors are in Section 5 of the Supporting Information.

In the system expansion allocation method, credits due to energy savings from hot water return and WWTP savings, as well as a credit from the production of potassium acetate, are all assigned to ethanol. In mass and market value allocation methods, the emission credits for energy savings and WWTP savings are included in the allocation to ethanol and KAc.

Impact Assessment. The carbon footprint is evaluated using the impact assessment method of IPCC 2007 GWP 100a with SimaPro 7.3.3. In this method, global warming potentials (GWPs) for CO_2, CH_4, and N_2O are 1, 25, and 298, respectively, and other GWPs are included for compounds such as solvents and refrigerants that are part of the ecoprofile inventories.

The annual yield of ethanol and 50% potassium acetate are 2.28×10^6 and 3.84×10^6 kg/yr, respectively (Tables S5 and S7, Supporting Information). The prices of ethanol and 50% potassium acetate were found to be $2.50/gal[27] and $1.50/kg,[28] respectively according to current market price; thus, the mass allocation factor and market value allocation factor of ethanol are 0.54 and 0.4, respectively, as shown with the calculations in Tables S5 and S7 of the Supporting Information.

Scenarios. Consistent with the study goal and scope, we investigated several scenarios to understand impacts of model variables (input data, decisions, and assumptions) (Table 2 and

Table 2. Scenarios for Life Cycle Carbon Footprint Model Assumption Uncertainty

| scenario | allocation method | |
	system expansion method	market value allocation
1	alternative energy for biorefinery	alternative energy for biorefinery
	(a) natural gas	(a) natural gas
	(b) biomass	(b) biomass
2	alternative energy for WWTP	alternative energy for WWTP
	(a) natural gas	(a) natural gas
	(b) biomass	(b) biomass
3	±10% change in the yield of ethanol (6.64×10^7 MJ, 5.44×10^7 MJ)	±10% change in the yield of ethanol (6.64×10^7 MJ, 5.44×10^7 MJ)
4	±10% change in the yield of KAc (4.22×10^6 kg, 3.46×10^6 kg)	±10% change in the yield of KAc (4.22×10^6 kg, 3.46×10^6 kg)
5	savings to WWTP: basis of 60% to 50−70%	savings to WWTP: basis of 60% to 50−70%
6	N/A	price fluctuation
		(a) 25% increase to ethanol; 25% decrease to potassium acetate
		(b) 25% decrease to ethanol; 25% increase to potassium acetate

section 1.4, Supporting Information). Scenario 1 compares the environmental impact of design choices for using natural gas and mixed wood chips instead of coal to generate steam in the biorefinery. As discussed in the Results section for the basecase, savings of emissions from avoided WWTP emissions are significant because heat and power are largely from a mix where coal is dominant. Therefore, scenario 2 explores assumptions about WWTP energy usage that may apply to other hardboard facilities in the United States (depending on local situation), including two options. All electricity and heat are provided by (a) natural gas and (b) mixed wood chips. The ecoprofiles for the alternative sources of energy used in scenarios 1 and 2 are from the ecoinvent database in SimaPro (Table S8, Supporting Information). Yield of ethanol, yield of potassium acetate, and percentage reduction to the WWTP inputs, as well as price fluctuations were analyzed in scenarios 3−6. Scenario 3 analyzes the sensitivity of GHG emissions to the yield of ethanol ($\pm10\%$, which is 6.64×10^7 and 5.44×10^7 MJ for +10% and −10%, respectively), while all other inputs remain at base case values (Table 1). A similar strategy was applied to other inputs. Yield of KAc was increased or decreased by 10% in scenario 4 (4.22×10^6 and 3.46×10^6 kg for +10% and −10%, respectively). These variations of 10% in yield are expected to be in the range of uncertainty expected because of the approximate nature of engineering design calculations. Savings of WWT emissions is one of the biggest credits in the basecase life cycle carbon footprint, as will be shown next, so the influence of saving 50% or 70% of WWTP emissions was studied in scenario 5. Scenario 6 considers the influence of market price on market value allocation results.

■ RESULTS AND DISCUSSION

Basecase: Ethanol. Greenhouse gas (GHG) emissions for ethanol produced from the co-located biorefinery using basecase inputs are shown in Figure 3 for system expansion, mass allocation, and market value allocation. Life cycle carbon footprint results are displayed for each of the main inputs,
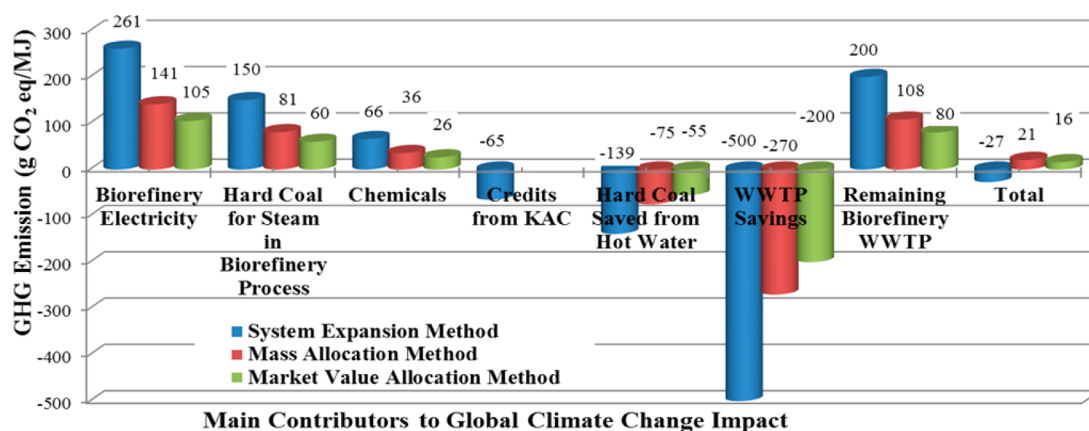
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Figure 3. Ethanol GHG emissions: System expansion, mass allocation, and market value allocation.
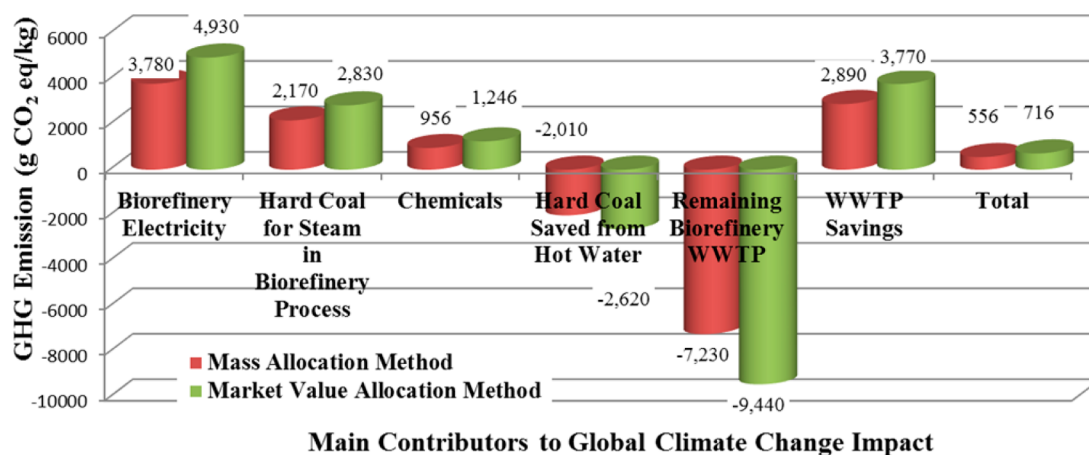

Figure 4. GHG impact from KAc with two allocation methods.
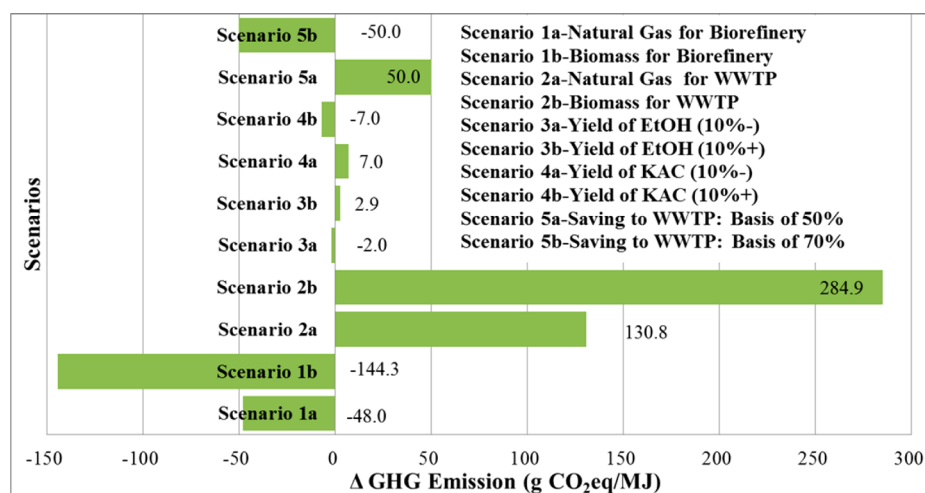

Figure 5. Scenario analyses of change in life cycle GHG emissions from ethanol produced in the co-located biorefinery using system expansion.

categories of inputs, or credits. Energy and steam to the both biorefinery and wastewater treatment plant are the main contributors to GHG emissions, while the savings from hot water return and avoided WWTP emissions are large credits. A key observation from this study is that a few large emission inputs and credits dominate the GHG emissions and that net GHG emissions (total in Figure 3) are very small in comparison. Of the three allocation methods, the system expansion method exhibits the lowest emissions, a negative life

cycle GHG emission to the environment of −27 g of CO_2 eq/ MJ ethanol. The mass and market value allocation methods resulted in emissions of 21 g and 16 g of CO_2 eq/MJ ethanol, respectively. These GHG emissions are much less compared to petroleum gasoline, whose emission is 90 g of CO_2 eq/MJ.[29]

Basecase: KAc. The GHG emissions of potassium acetate produced in the biorefinery (Figure 4) exhibit large emission inputs and credits, similar to ethanol in Figure 3. Net GHG emissions are 556 g of CO_2 eq/kg KAc for mass allocation and
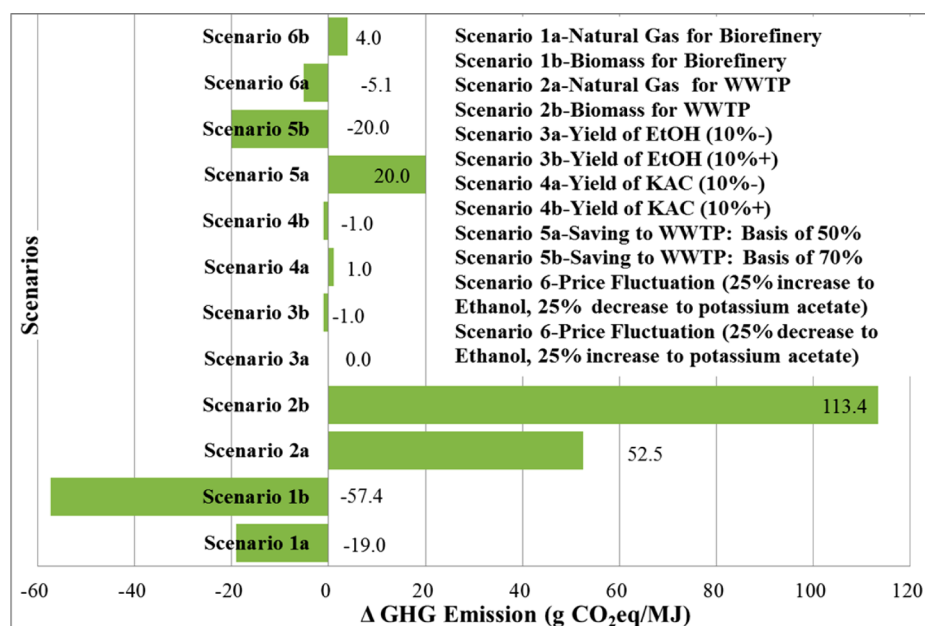
Figure 6. Scenario analysis of change in life cycle GHG emissions from ethanol produced in the co-located biorefinery using market value allocation.
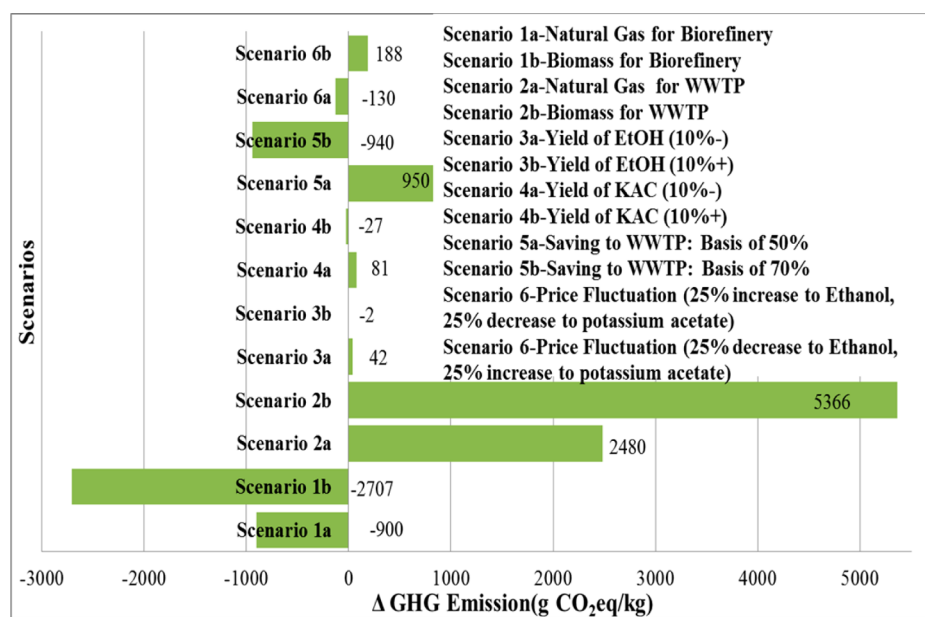

Figure 7. Scenario analyses of change in life cycle GHG emissions from KAc produced in the co-located biorefinery using market value allocation.

716 g of CO_2 eq/kg KAc for market value allocation. According to the ecoinvent database in Simarpo 7.3.3, conventional potassium acetate emits 1020 g of CO_2/kg KAc. On the basis of this preliminary analysis, in both the mass allocation and market value allocation methods, potassium acetate produced in the biorefinery process emits less GHG than from the current product in the market.

Scenario Analyses. The changes in net (total) GHG emissions for all six scenarios are shown in Figures 5, 6 and 7. Inputs that influence GHG emission the most are shown in these three figures as large positive and negative changes in emissions (scenarios 1, 2, and 5). Biomass as an alternative energy in scenario 1 and WWT savings of 70% in scenario 6 yield the greatest reduction in GHG emissions. Tables S5 and S6 in the Supporting Information list ethanol GHG emissions

in the basecase as well as the six scenarios in more detail and include the total emissions over the life cycle. The results are given for both system expansion and market value allocation methods. GHG emissions of co-product potassium acetate are shown in Table S11 of the Supporting Information for the scenarios with market value allocation.

Scenarios 1a and 1b: Alternative Energy for Biorefinery. When natural gas substitutes for coal for steam production in the biorefinery, GHG emissions are reduced by 48 g of CO_2 eq/MJ ethanol (Table S9, Supporting Information, Figure 5, system expansion). When steam is from mixed wood chips, net GHG emissions are reduced by 144 g of CO_2 eq/MJ. For the market value allocation method, GHG emissions are reduced by 19 and 57 g of CO_2 eq/MJ, respectively (Table S10, Supporting Information, Figure 6. GHG emissions for

potassium acetate were reduced by 900 and 2707 g of CO_2/kg KAc (Figure 7), respectively. The substitution of these alternative energy sources in the biorefinery makes a very large change to the life cycle carbon footprint of ethanol and KAc for both allocation methods.

Scenario 2: Alternative Energy Choices for WWT. The inputs for WWT have a large impact on GHG emissions for ethanol production in the co-located biorefinery in this study (Figure 3). WWT GHG emissions are dominated by sources of steam and electricity, which in the basecase are from coal, wood chips, and sludge burning. When we modeled the WWT process alone, the GHG emissions were 51.5 kg of CO_2 eq/m^3 of wastewater treated, which is a value that can be compared to the literature. For example, this emission factor can be compared to other wastewater treatment processes in the ecoinvent database, which range from 0.211 to 888 kg of CO_2 eq/m^3 depending on the source of wastewater. Furthermore, the hardboard WWT process modeled here is higher relative to wastewaters from similar forest products facilities such as fiber board waste effluent (0.329 to 12.5 kg of CO_2 eq/m^3) according the ecoinvent database.

According to the industry partner on this project, after the biorefinery is co-located with the hardboard facility, a WWT process is still needed but with only 40% of the original inputs. This reduction by 60% of the WWT process inputs are accounted for as an emissions credit in this life cycle carbon footprint analysis. If a lower GHG emission source of these WWT process inputs were to be used, then a smaller emission credit would be realized. When WWT electricity and steam are generated from natural gas, GHG emissions for ethanol increase by 130.8 and 52.5 g of CO_2 eq/MJ ethanol in the system expansion method and market value allocation methods, respectively (Figures 5 and 6). Use of biomass as an energy source in the original WWT process increases GHG emission by 284.9 and 113.4 g of CO_2 eq/MJ in the system expansion method and market value allocation method, respectively. GHG emissions of KAc show a similar trend as ethanol, with natural gas and biomass increasing GHG emissions by 2480 and 5366 g of CO_2 eq/kg, respectively (Figure 7). The results in this scenario show that inputs to the WWT process can have an overwhelming effect on the GHG emissions from a biorefinery co-located with a hardboard facility.

Scenario 3: Yield of EtOH. In this scenario, inputs remain at the basecase levels, but yield of ethanol increases or decreases by 10%. These changes in ethanol yield affect not only ethanol GHG results but also KAc results through allocation. For system expansion and market value allocation methods, changes in GHG emissions are relatively small compared to other scenarios (Figures 5−7). It can be concluded that product yield does not have a large effect on GHG results.

Scenario 4: Yield of KAc. These changes in KAc yield affect not only KAc GHG emissions but also ethanol results through allocation. In the system expansion method, ± 10% KAc yield changes GHG emission by ±7 g of CO_2 eq/MJ ethanol (Figure 5). Market value allocation results in smaller changes in this scenario: ± 1 g of CO_2 eq/MJ ethanol (Figure 6) and −27 and +81 g of CO_2 eq/kg KAc (Figure 7).

Scenario 5: WWT Savings. In the basecase analysis, we assume a reduction of WWT plant inputs to be 60% for the co-located biorefinery. When this replacement is changed ±10%, GHG emission differences are ±50 and ±20 g of CO_2 eq/MJ ethanol in the system expansion and market value allocation methods, respectively. The GHG emission fluctuation of KAc is

around ±950 g of CO_2 eq/kg KAc. Compared to other scenarios, uncertainty in the reduction in WWTP inputs for the co-located biorefinery is one of the most important.

Scenario 6: Price Fluctuation. The price fluctuation was assumed as 25% as discussed in Section 5.2 of the Supporting Information. When the price of ethanol increases by 25% while the price of KAc decreases by 25%, the market value allocation factor for ethanol increases from 0.42 to 0.52. Due to the change in the allocation factor, GHG emission is 4 g of CO_2 eq more per MJ of ethanol. When the price of ethanol drops by 25% while the price of KAc is 25% more, the allocation factor drops to 0.28. This drop in the allocation factor causes the GHG emission to decrease by 5 g of CO_2 eq/MJ ethanol. The GHG emission difference of KAc is 188 and −130 g of CO_2 eq/MJ, respectively.

In summary, the basecase consequential analysis shows that for both ethanol and potassium acetate large emissions from electricity and steam use in both the biorefinery and WWTP are counteracted by large credits from hot water return and avoided WWTP inputs in all three allocation methods. In the basecase consequential analysis, all emission credits are attributed to the biorefinery products and none to the original hardboard facility. It can be interpreted from our study that any "sharing" of these large emission credits with the hardboard facility would greatly increase emissions for ethanol and KAc. However, in our view, it is justified to attribute all credits to biorefinery products because no reduction in WWT would occur without the biorefinery.

Life cycle GHG emissions of ethanol in all allocation methods and with basecase inputs are much lower than that of petroleum gasoline, and in the system expansion method, GHG emissions are negative. The net GHG emissions of potassium acetate are similar to but slightly lower than the product existing in the market in both mass allocation and market value allocation methods. Results of scenario analyses show that key factors affecting the net GHG emission are the energy resources applied in both the biorefinery and WWTP. When cleaner energy resources like natural gas or biomass are utilized in the co-located biorefinery, the life cycle GHG impacts of both ethanol and potassium acetate are much reduced. However, when they are applied in the WWTP, the GHG emissions of both products greatly increase. The percentage reduction in WWTP inputs for a co-located biorefinery is also a highly relevant parameter. The variation of other life cycle carbon footprint assumptions, like yield of ethanol or potassium acetate, and the price of the product in the market are not likely to have much influence on the net GHG emissions based on our preliminary study.

■ FUTURE WORK

Future research will include an uncertainty analysis evaluating the effects of statistical uncertainty for each key input in Table 1.

■ CONCLUSION

An original cradle-to-grave life cycle footprint was conducted on a biorefinery co-located with a hardboard facility, with the avoided WWTP emissions and hot water return credits all allocated to the biorefinery products of ethanol and potassium acetate. Three allocation methods (system expansion, mass allocation, and market value allocation) were applied in this study. In the basecase, ethanol produced in a biorefinery co-

located with a hardboard facility achieves more than 60% reduction of GHG emissions compared to petroleum gasoline for all allocation methods. Potassium acetate produced in this biorefinery reduces GHG emissions compared to conventional potassium acetate by more than 30%. However, the GHG emissions are highly related to the GHG emission intensities of the energy resources utilized in both the biorefinery and WWTP and the percentage of the original WWT inputs a biorefinery is able to displace.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional introduction discussion and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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