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Hybrid thermochemical/biological processing: The economic hurdles and opportunities for biofuel production from bio-oil

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ABSTRACT

Hybrid thermochemical/biological processing encompasses several biofuel production pathways. Thermochemical conversion produces significant amounts of levoglucosan, an anhydrosugar that is a potential feedstock for liquid and gaseous biofuel production. However, few known microorganisms possess the ability to directly convert levoglucosan to biofuels. As a result, hydrolysis of levoglucosan to glucose is currently required ahead of fermentation. This has spurred research to engineer microorganisms capable of levoglucosan utilization. As research continues to produce such microorganisms, the economic opportunities for processing levoglucosan to biofuels must be assessed. An economic study was conducted to evaluate the production of ethanol, hydrogen, and methane from the fermentation of levoglucosan. Both direct bioconversion and fermentation of hydrolyzed levoglucosan were considered. Ethanol production by *Saccharomyces cerevisiae* was assumed, while hydrogen and methane were assumed to be produced by cultures of hydrogenogenic and methanogenic microbial communities, respectively. Direct conversion of levoglucosan to ethanol yielded the lowest minimum selling price (MSP) per gigajoule (GJ) of energy produced at \$15.33 GJ^{-1}, but represented a higher capital cost at \$9.03 MM. Hydrogen production from direct conversion of levoglucosan represented the minimum capital cost at \$3.49 MM but resulted in greater MSP. The greatest MSP, \$49.79 GJ^{-1}, was predicted for hydrogen production from hyrdrolyzed levoglucosan.

1. Introduction

Development of renewable fuels can reduce reliance on fossil fuels and may mitigate emission of greenhouse gases (GHG). In particular, renewable biofuels have garnered significant interest worldwide due to growing environmental awareness and regulatory incentives. Lignocellulosic biomass is a promising feedstock for biofuel production due to its abundance in forests, potential to be produced from dedicated bioenergy crops, and prevalence in agricultural and food processing wastes. Both biological and thermochemical approached exist for converting lignocellulosic biomass to biofuels. Biological conversion utilizes organisms and enzymes to digest and ferment substrates to fuel while thermochemical conversion employs extreme temperatures in the presence of limited or no oxygen to degrade biomass into fuels [1]. Combining these two processes into what is termed “hybrid processing” has gained interest [2,3]. Hybrid processing utilizes thermal degradation of lignocellulosic biomass to generate substrates that can be metabolized by microorganisms to produce fuels and other valuable compounds. Hybrid processing encompasses two pathways to fuel production; syngas fermentation and bio-oil fermentation. To date, syngas fermentation techno-economics have been more closely examined with less attention given to the economics of utilizing fast pyrolysis-based bio-oil for hybrid processing [4,5].

While the pursuit of hybrid processing has been gaining momentum within biofuels research, an economic analysis of biofuels derived from fermentation of pyrolysis bio-oil compounds has yet to be conducted. To understand how bio-oil-based hybrid processing might have an impact on the economics of fuel production at commercial-scale, it is useful to understand the current bottlenecks and limitations of the technology for various fuel end-products. Identification of cost-limiting steps in the hybrid processing pipeline can be used to direct additional translational research for process improvement. Furthermore, a techno-economic study can help identify which potential biofuel product presents the greatest economic opportunity for bio-oil hybrid

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processing with respect to various process variables. This may influence which particular biofuel is targeted in future hybrid processing research.

Currently, levoglucosan is the main substrate being considered for fermentation in hybrid processing due to its concentration in bio-oil, which can be as high as 5–12% of bio-oil mass (wet weight basis) [6]. The levoglucosan content in bio-oil following pyrolysis is directly affected by the biomass composition [7]. As an anhydrosugar of glucose, levoglucosan can be hydrolyzed using a strong acid to produce glucose at a 1:1 M ratio, which can be used for fermentation [8]. However, limited information exists regarding direct bioutilization of levoglucosan. Commonly cultured microorganisms are largely unable to metabolize levoglucosan, spurring development of an engineered *Escherichia coli* designed to uptake levoglucosan and produce ethanol [9]. Use of microorganisms for fermentation of bio-oil-derived levoglucosan is still challenged by the many biological inhibitors, such as butyric acid or 5-hydroxymethyl furfural, present in bio-oil that are retained in the aqueous phase of levoglucosan extracts [2,10]. While most of these inhibitors can be neutralized using an acid catalyst or overliming, this can significantly increase operating and capital costs for processing [3,8]. Therefore, there is a need to understand how process costs could be reduced if bio-oil-based hybrid processing is realized at commercial scale using bio-oil tolerant microorganisms that do not require hydrolysis or overliming prior to fermentation.

With several possible biofuel fermentation pathways that may be used in hybrid processing, it is useful to consider the unique aspects of each. Anaerobic digestion (AD) is a mature technology that uses microbial communities to convert organic substrates to methane [11]. Hydrogen production is an intermediate step within AD, with the hydrogen serving as a substrate for methanogenic microorganisms. Thus, AD can be repurposed for hydrogen production by removing or suppressing the activity of methane-producing microorganisms via modification of the organic loading rate, pH or temperature [12,13]. This form of hydrogen fermentation is referred to as dark fermentation [12,13]. Recently, direct utilization of aqueous pyrolysis liquor by an AD microbial community was demonstrated [14]. This research showed that AD microorganisms can metabolize levoglucosan for methane production. This work builds off other studies that have shown that AD communities can utilize exotic substrates, although limitations exist based on substrate concentration and inhibitor levels [15–17]. Nevertheless, more research is needed to determine if AD utilization of levoglucosan is affected by the composition of AD microorganisms and changes in bio-oil composition resulting from different pyrolysis conditions and substrates. Ethanol production from levoglucosan is another possibility that has been demonstrated using genetically engineered bacteria [9]. However, compatibility with bio-oil-derived levoglucosan will likely require significant engineering of metabolic pathways to overcome the broad array of inhibitors present. Despite the development of recombinant bacteria that can utilize levoglucosan at laboratory scale, the large-scale conversion of levoglucosan to ethanol still remains untested.

Process limitations that are not substrate-specific must also be considered when assessing possible fermentation processes for hybrid processing. For instance, methane production via AD can be limited by organic loading rate constraints and the rate of methanogenesis [18,19]. While AD production of methane has garnered a great deal of interest compared to hydrogen, hydrogen has a much greater energy density (122 MJ kg^{-1}) and can be easily stored as a metal hydride [20]. It is expected that if the selling price of hydrogen can reach \$2.00 – \$4.00 gallons of gasoline equivalent (\$0.53 – \$1.06 L of gasoline equivalent), it can be an economically competitive transportation fuel [21]. However, biological hydrogen production has been hampered by yields that are often low or highly variable [22].

The aim of this study was to provide a techno-economic assessment of three bioconversion strategies that can potentially utilize bio-oil derived levoglucosan as a substrate for biofuel production in hybrid processing. The process economics associated with ethanol, methane, and hydrogen production from fermentation of levoglucosan extracted from bio-oil were considered under conditions that current research is targeting for hybrid processing – direct fermentation of levoglucosan extracted from bio-oil in the presence of traditionally inhibitory pyrolysis compounds. The techno-economic model was used to provide an initial analysis of the economic opportunities for utilizing levoglucosan if these key technical hurdles are overcome. These results can provide insights into which potential biofuel end-products should be prioritized for further research based on the economic benefits that can be reaped if commercial production via hybrid processing is realized.

2. Methods

2.1. Model framework

The bioconversion processes evaluated did not consider redesign of the thermochemical processing element of the hybrid processing pipeline, as the evaluation aimed to understand the use of existing bio-oil streams for hybrid processing. As a result, this study utilized information from a prior thermochemical processing model by Wright et al. (2010) [23]. Using principles outlined in prior work, an early-stage economic analysis was performed considering only major unit operations and necessary operating supplies [24,25]. Fig. 1 defines the system boundary for the model and indicates the mass flows between the thermochemical process and the biological processes considered for the analysis. The system boundary was chosen to isolate the unique aspects between each bioconversion process in the context of being added to an existing thermochemical processing facility. Specifically, the system encompassed the purification of levoglucosan from bio-oil, fermentation of the levoglucosan to biofuel, and purification and upgrading of the biofuel. Both direct bioconversion of levoglucosan and hydrolysis of levoglucosan to glucose prior to bioconversion were considered to compare current and prospective methods and examine the economic trade-offs.

2.2. Cost estimation

Early-stage economic analysis is based on cost-scaling assumptions that are validated by historically acquired empirical data [26]. With the purpose of this work being to investigate the basic opportunities and limitations of various bioconversion processes for hybrid processing, many of these assumptions were incorporated into this study. Specifically, the use of Lang factors to estimate the total installed cost of equipment in this study, as described below, is expected to yield project cost estimations within +35%/−20% of actual values [27].

Bioreactor size was calculated to accommodate the levoglucosan output of the assumed pyrolysis plant according to Equation (1):

$$S_{n,B} = \frac{\dot{S} Y_P}{F_B \dot{P}} \quad (1)$$

where $S_{n,B}$ is the size of the new bioreactor (m^3), $\dot{S}$ is the rate of levoglucosan recovery from the pyrolysis plant, which is equivalent to the substrate loading rate for the bioreactor (kg day^{-1}), Y_P is the

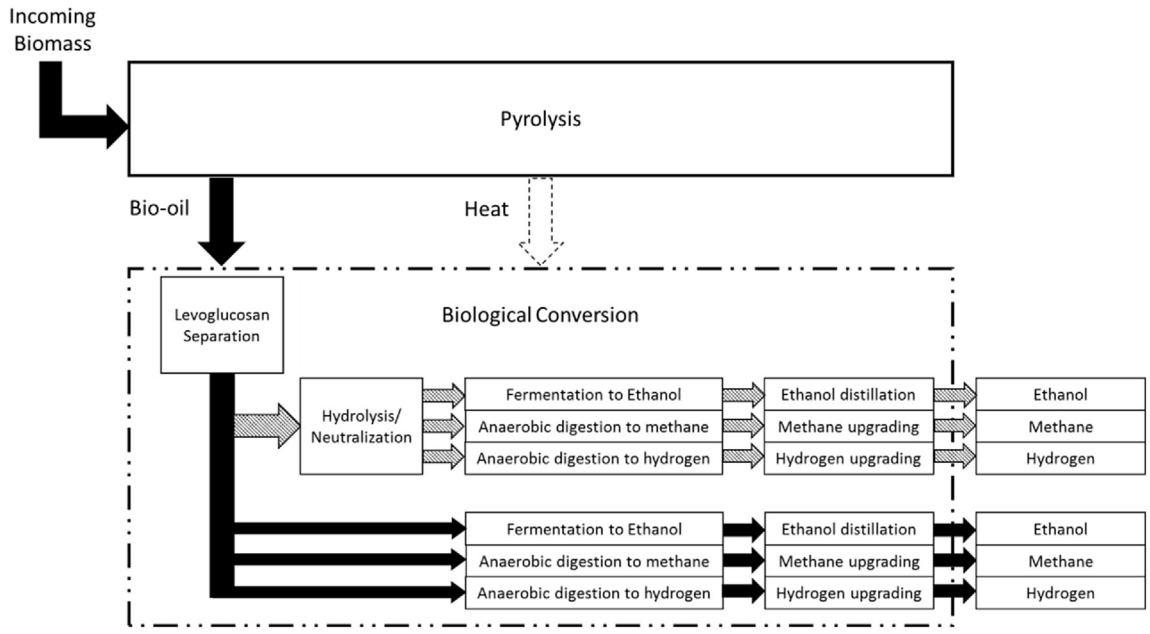

Fig. 1. Hybrid processing steps for production of ethanol, methane, or hydrogen from bio-oil levoglucosan. Grey arrows indicate the scenario where extracted levoglucosan is hydrolyzed to glucose ahead of bioconversion. Black arrows show the scenario of raw levoglucosan extract used for bioconversion. The area bounded by a dashed line outlines where the two processing scenarios deviate and represents steps analyzed and compared in the techno-economic model.

yield of biofuel (kg product (kg substrate)$^{-1}$), F_B is the useable fraction of the bioreactor (useable m^3/purchased m^3), which was assumed to be 80%, and $\dot{P}$ is the productivity (kg product (m^3)$^{-1}$ day^{-1}). If the predicted size of the bioreactor exceeded the maximum volume of currently available units (Table 1), two smaller bioreactors of equal size were selected to meet the required volume.

Cost estimates for bioreactors, tanks, centrifuges, and columns associated with the bioconversion processes were obtained from prior work and were adjusted to obtain the purchase cost of newly sized equipment according to Equation (2) [24].

$$C_n = \frac{S_n}{S_o} \times C_o^n \quad (2)$$

where C_n represents the cost of the newly sized equipment (United States dollars, USD); S_n is the size of the new equipment (m^3); S_o is the size of the equipment for which the cost is previously known (m^3); C_o is the cost of the previously characterized equipment (USD); and n is an empirically-derived exponent. These individual equipment cost exponents were taken from prior studies and several engineering cost estimation texts [24,28,29]. Previous cost and parameter information for bioreactors are listed in Table 1.

The installation and facilities costs were estimated using a lumped parameter known as the Lang Factor (f_L) [29]. The Lang Factor consolidates the estimated cost of buildings, piping, etc., into a single proportionality constant that can be used to predict installation and facilities costs as a multiple of the equipment cost. During the early-stages of new technology where minimal information exists regarding its implementation, f_L allows estimation of installation and facilities costs without detailed knowledge of the installation cost structure. Lang factor values used for the analysis are provided in Table 1. The installed cost of equipment was described using Equation (3), where C_I represents the total cost of purchasing and installing the equipment (USD).

$$C_I = f_L \times C_n \quad (3)$$

The C_I value for the estimated capital and installation cost comprised the fixed capital investment (FCI). Annual expenses for maintenance and repair, operating supplies, and patents and royalties were estimated at 5% of FCI, 1% of FCI, and 2% of FCI respectively. The total production cost (TPC) was calculated as the sum of the FCI and annual expenses. Annual general plant expenses associated with administration and product distribution were calculated as 10% of the TPC. Plant overhead was then calculated as 10% of the sum of TPC and plant expenses. The bioconversion facilities were expected to operate for 20 years with an internal rate of return of 10%. These assumptions agree with those typically used for early-stage techno-economic modeling [24,25].

A sensitivity analysis was conducted using the parameters and value ranges given in Table 2 to gauge their effect on the minimum

Table 1
Cost, sizing, and operational properties for bioreactors used to produce ethanol, methane, or hydrogen gas in the techno-economic model.

Parameter	Ethanol production	References	Methane/Hydrogen production	References
Maximum bioreactor volume (m^3)	3785	[64]	3100	[28]
Batch/Continuous	Batch		Continuous	
Reactor downtime (%)	20	[65]	–	
Previous size (S_o)	757	[64]	3067	[28]
Previous cost (C_o)	590,000	[64]	1,269,076	[28]
Cost exponent (n)	0.54	[64]	0.51	[28]
Lang factor	3	[43]	1.79	[47]

Table 2
Baseline and boundary values used to assess MSP sensitivity to various operational parameters.

Sensitivity analysis parameter	Low	Original[a]	High	Reference
Levoglucosan content in bio-oil (% of wet weight)	4.5	5	5.5	[6]
Productivity – Ethanol (g L^{-1} hr^{-1})	1.8	2	2.2	[43]
Productivity – Methane (g L^{-1} hr^{-1})	0.149	0.166	0.182	[46,66]
Productivity – Hydrogen (g L^{-1} hr^{-1})	0.321	0.357	0.393	[52]
Biomass daily rate (BDT)	1800	2000	2200	[23]
Operating days	296	329	362	[23]
Yield-Ethanol (g g^{-1} Levoglucosan)	0.46	0.51	0.56	Calculated
Yield – Methane (g g^{-1} Levoglucosan)	0.24	0.27	0.29	Calculated
Yield – Hydrogen (g g^{-1} Levoglucosan)	0.023	0.026	0.029	Calculated
Yield – Ethanol (g g^{-1} Glucose)	0.413	0.459	0.505	[39]
Yield – Methane (g g^{-1} Glucose)	0.216	0.24	0.264	[40]
Yield – Hydrogen (g g^{-1} Glucose)	0.021	0.0233	0.0257	[41]

[a] Biofuel yields from levoglucosan were calculated using yield values for glucose. The yield of biofuel per mole of substrate was assumed to be the same for both substrates. As a result, differences in yield values for the two substrates reflect the difference in molar mass between levoglucosan and glucose.

selling price (MSP) and capital costs for each fuel product. The range of values considered for each parameter was calculated as ±10% of the baseline parameter value.

2.3. Plant design

The hypothetical bioconversion facilities considered for the techno-economic model assumed that the bioconversion process was coupled with a 2000 bone-dry tonne per day fast pyrolysis facility (containing four 500 bone-dry tonne per day reactors) with an estimated 63% conversion efficiency of biomass to bio-oil. This facility size aligned with projections by the National Renewable Energy Laboratory regarding the size of future pyrolysis facilities [30]. Furthermore, the size and efficiency of the pyrolysis facility was consistent with a previous techno-economic model focused on biomass fast hydrolysis [23]. The levoglucosan content in the bio-oil was assumed to be 5% (wet weight basis) [6]. This was consistent with levoglucosan levels observed in bio-oil generated from pyrolysis at 350–500 °C [31,32].

The facilities were designed to extract levoglucosan using water at 90% efficiency at a concentration of 8.7% $w_{LG}/w_{mixture}$ [8]. A counterflow liquid-liquid extraction process was assumed. The size of the extraction column was estimated using a previously described model [24,33] based on the amount of bio-oil to be extracted, the distribution coefficient of levoglucosan in water (2.5), the mass fraction of levoglucosan in the extract, and the desired extraction yield (90%) [8,34]. Equations (2) and (3) were used to estimate the capital and installation costs of the extraction equipment using Lang factor, previous size, previous cost, and n values obtained from prior work [24].

For the baseline case of levoglucosan hydrolysis to glucose, a reactor prior to the fermentor or digester was estimated to operate at 125 °C using 0.5 M H_2SO_4 as the catalyst and a residence time of 44 minutes [8]. The reactor was sized by multiplying the average rate of bio-oil extract generation (453 L min^{-1}) by the necessary residence time (44 min) and then dividing by the useable volume fraction of the tank (0.95). Acid hydrolysis using sulfuric acid was selected because it is currently the most well characterized method to hydrolyze levoglucosan [8,35]. The purchase cost of sulfuric acid was assumed to be $55 per tonne [36]. The acid was assumed to be neutralized with molar equivalents of calcium carbonate ($100 per tonne) prior to fermentation [37]. The capital cost of the reactor was evaluated using CAPCOST [38].

The glucose (or levoglucosan in the case of direct bioconversion without hydrolysis) was considered to be the primary substrate for the organisms in the bioconversion step. Baseline bioconversion yields for each biofuel are presented in Table 2. The yield of ethanol from glucose was estimated as 90% of the theoretical yield in agreement with published values for the common fermentative yeast *Saccharomyces cerevisiae* [39]. For methane production from glucose, the reaction stoichiometry indicates a theoretical yield of 3 mol of methane and 3 mol of carbon dioxide per mole of glucose (i.e., 50% biogas quality). For the model, 90% of the theoretical methane yield was assumed, as prior research has shown that this is possible for glucose [40]. Published values were used for the yield of hydrogen from glucose [41]. Primary biofuel products were then assumed to be upgraded to transportation quality fuels as described in subsequent sections. The energy content of the refined fuels was evaluated using the lower heating value. While it is possible that other compounds within the aqueous bio-oil extracts, such as acetate, may contribute to biofuel production, these additional carbon sources were omitted from this early-stage analysis. The complete plant design model for each bioconversion process is provided in Supplementary File 1.

2.3.1. Ethanol

The ethanol plant considered in the analysis followed the same plant design as Claypool et al. [24], which has been validated to yield cost estimate results comparable to actual values. As the ethanol fermentation process is a sequence of batch reactions, surge tanks were used to accommodate the bio-oil output from the thermochemical process. Seed fermentors were sized as 10% of the size of the main fermentor (as determined using Equation (1)). The fermented broth from the main fermentor was then sent to another surge tank to convert the batch process back to continuous for biomass separation and subsequent distillation and purification of the ethanol. The size and number of centrifuges for biomass separation were determined using a previously described equation and assumptions for centrifuge properties [24]. The distillation process used an initial distillation column for large removal of water, followed by a rectifying column to bring the ethanol:water mixture to its azeotropic state. The azeotrope was then further dewatered using molecular sieve to bring ethanol to purity [42]. Equations (2) and (3) were used with calculated sizes and previously published size and cost data for centrifuges, distillation, and dewatering equipment to predict purchase and installation costs for these equipment [24,29]. It was assumed that all steam necessary for heating could be generated from the waste heat of the pyrolysis plant. The ethanol fermentation rate was assumed to be 2 g L^{-1} hr^{-1} with a 20% downtime in between batches to account for vessel emptying, filling, and sterilization [24]. The cost of the major equipment was adjusted to total installed cost with a Lang factor of 3 [43].

2.3.2. Anaerobic digestion – CH_4

Anaerobic digestion commonly utilizes a continuous process mode known as an upflow-anaerobic-sludge-blanket (UASB) that uses granular-based biofilms to perform methanogenesis. UASB digesters have been widely employed for treatment of wastewater [44]. While a variety of reactor designs exist for anaerobic digestion, the relatively high reaction rates and low hydraulic residence time (HRT) offered by UASB digesters make them attractive. UASB technology has the ability to separate HRT from the solids residence time (SRT). This results in decoupling of the biomass accumulation and effluent discharge rates, allowing for increased reaction rates, lower chances of washout, and greater substrate loading. Levoglucosan was assumed to be the sole carbon source for the methanogenic microbial communities. Although there is the potential for bioconversion of other major products such as acetate and other organic compounds present in the levoglucosan extract, consumption of these compounds was not considered in the model in order to isolate the techno-economics surrounding levoglucosan specifically. For upgrading, the gas produced from the bioreactor was assumed to be treated to remove hydrogen sulfide, water, CO_2, siloxanes, and then finally compressed to pipeline and transportation fuel pressures of 250psi and 4500psi, respectively. Capital and installation costs associated with gas upgrading were determined via a linear model relating the cost to the volume of gas processed [45]. Heating of the digester to 55 °C was assumed to be provided via waste heat from the pyrolysis plant. It was assumed that a specific methane productivity rate of 5.5 L L^{-1} day^{-1} (0.166 g L^{-1} hr^{-1}) could be achieved [46,66]. The cost of equipment was adjusted to total installed cost with a Lang factor of 1.79 [47].

2.3.3. Anaerobic digestion (Dark fermentation) – H_2

Biohydrogen production has garnered attention for research purposes, but has not been widely commercialized. Due to the lack of industrial data, the hydrogen production model was based on the CH_4 production scenario described previously, as UASB technology has also been applied to hydrogen production [48–51]. Heating of the vessel to mesophilic conditions was assumed to be provided by waste heat from the pyrolysis plant.

H_2 was assumed to be produced at 4 L L^{-1} hr^{-1} (0.357 g L^{-1} hr^{-1}) at an approximate gas quality of 44% H_2 with the remainder being CO_2 [52]. This rate lies within the wide range of production rates observed in previous work, which can be as high as 15 L L^{-1} hr^{-1} or less than 1 L L^{-1} hr^{-1} [52]. The cost of equipment was adjusted to total installed cost with a Lang factor of 1.79 [47].

3. Results and discussion

The complete techno-economic model, including inputted baseline values and corresponding model outputs, is presented in Supplementary File 1. In general, direct bioconversion of levoglucosan to biofuel resulted in a 1.3–3.1% reduction in capital costs compared to hydrolyzing the levoglucosan to glucose prior to fermentation. Likewise, direct bioconversion translated to a 26–46% decrease in MSP over the levoglucosan hydrolysis scenario depending on the bioconversion process (Table 3). This can be attributed to the increased operating costs associated with purchasing the sulfuric acid and calcium carbonate required for hydrolysis and neutralization, respectively. As seen in the sensitivity analysis (Fig. 2), adding the hydrolysis unit operation resulted in the MSP being more sensitive to the yield for all biofuels. This stems from the fact that there must be a greater increase in MSP to compensate for the added levoglucosan extraction costs when yield is lowered. Conversely, increasing the yield lowers the MSP by offsetting some the cost of the levoglucosan extraction process.

Producing ethanol via direct bioconversion of levoglucosan had the lowest MSP per unit energy produced at \$15.33 GJ^{-1}. The minimum capital cost for the bioconversion technologies considered was dark fermentation for H_2 production at \$3.49 million. The greatest energy yield, 257 TJ per operational year, was attained by ethanol fermentation. The major determinant of capital costs was the purchase of the bioreactor vessel for ethanol or methane production. Conversely, the biogas upgrading equipment cost was dominant for hydrogen production. Capital costs represented 27–40% of the MSP depending on the biofuel. The complete list of results is provided in Table 3.

Given the baseline ethanol production rate and yield, 296 annual batches would be required. The bioreactor volume was determined to be 906 m^3. A total fermentation cycle (including downtime) of 27 h was required to reach 44.47 g L^{-1} of ethanol in the fermentor. While typical starch-ethanol processes have fermentation times on the order of 40–50 h and produce closer to 100 g L^{-1}, the concentration of levoglucosan in aqueous extracts from bio-oil limited the final ethanol concentration. The ethanol process produced 9.53 Gg (1.99 MM gallons, 7.53 MM liters) of ethanol per year. The capital cost had the largest influence on the MSP of ethanol as the process scales best in the range of 55–73 MM gallons (208–276 MM liters) per year [53]. If the pyrolysis project is scaled up, the bio-oil yield from pyrolysis is increased, or the levoglucosan concentration within the bio-oil is increased, the MSP for ethanol production would improve. However, the MSP was overall more sensitive to decreases in substrate availability due to the relatively small scale of the ethanol fermentation plant. This sensitivity may create a risk for investment compared to larger ethanol projects since process perturbations could have a large negative impact on the MSP.

For methane, the HRT of 142 h (5.9 days) resulted in two twin-sized bioreactors of 2110 m^3. This HRT is consistent with that required for bioconversion of influents with high organic matter content in UASB reactors [54]. This process produced 6.96 million m^3 (245.7 MMCF) of methane under baseline conditions. The total annual energy captured in the methane was 8.6% less than that obtained from ethanol production. Relatively low production rates for methane required a large bioreactor size to accommodate the levoglucosan output from the pyrolysis plant. This resulted in a large increase in capital cost. The sensitivity analysis revealed that the MSP of the methane project was less sensitive to perturbations in yield, biomass daily rate, and bio-oil levoglucosan content compared to the ethanol project for the

Table 3
Estimated capital cost, cost per gigajoule (GJ), and annual energy yield values for each modeled bioconversion process.

	Biofuel product	Capital costs (MM\$)	MSP (\$/GJ)	Annual energy (TJ)
Non-hydrolysis	Ethanol	9.03	15.33	257
	CH_4	8.05	16.53	235
	H_2	3.49	26.78	58
Hydrolysis	Ethanol	9.23	20.77	257
	CH_4	8.16	22.23	235
	H_2	3.60	49.79	58

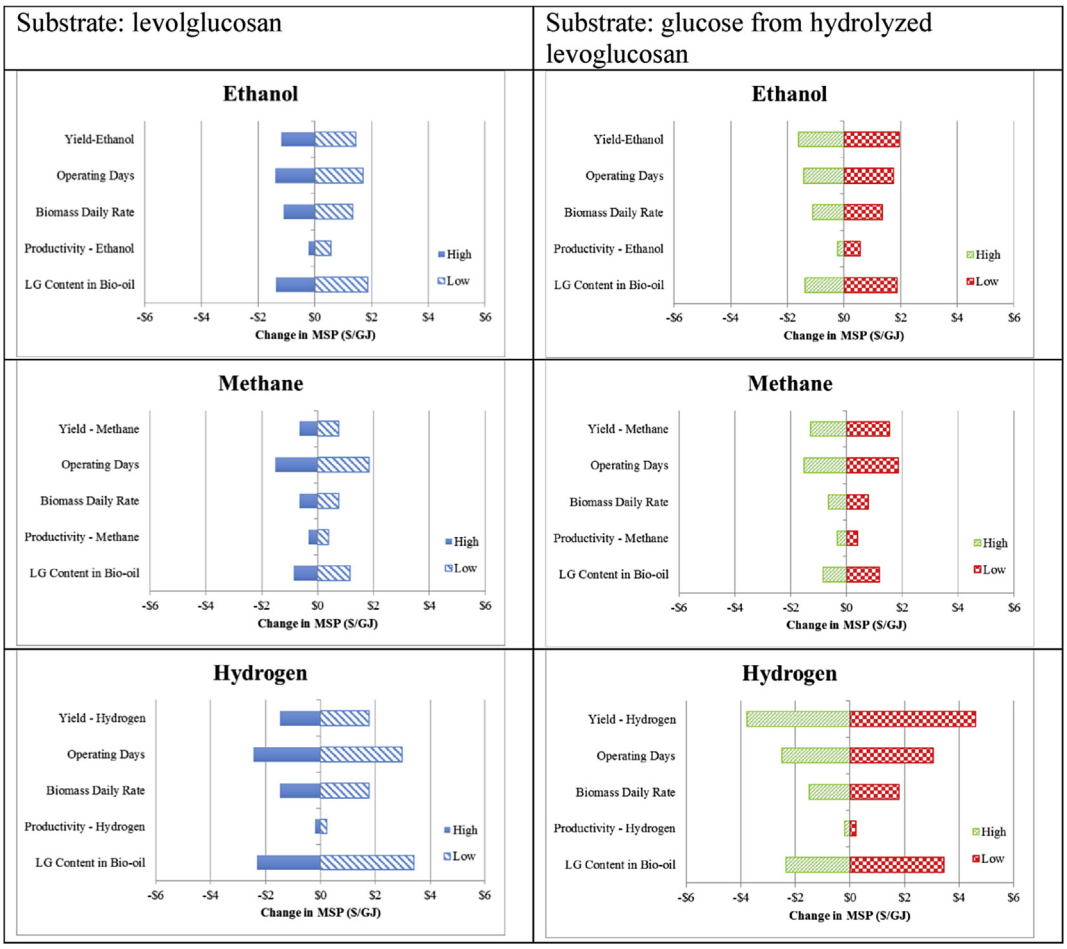

Fig. 2. Biofuel MSP sensitivity to various process variables. The left column corresponds to direct bioconversion of levoglucosan (LG) and the right column represents bioconversion of glucose generated from acid hydrolysis of levoglucosan.

range of values tested (Fig. 2). Notably, the MSP was relatively insensitive to the productivity, despite anaerobic digestion having the lowest productivity of the biofuels considered. This suggests that improvements in productivity greater than the 10% increase used for the sensitivity analysis are needed to decrease the capital cost of the large bioreactor volume and substantially lower the MSP.

The hydrogen process had a HRT of 6 h and required a bioreactor volume of 191 m^3. The total annual production of H_2 was 5.38 million m^3 (190 MMCF). The faster rate of hydrogen production relative to methanogenesis resulted in a smaller bioreactor volume and reduced capital costs. Moreover, the low yield of hydrogen compared to methane production led to a smaller quantity of gas to be upgraded. This resulted in a reduction in the size of the upgrading equipment and an additional decrease in capital costs over methane production. However, the low yields also led to a greater MSP for hydrogen compared to the other biofuels. The sensitivity analysis indicated that the MSP of hydrogen benefitted from the high rate of production and that changes in the productivity had a minor effect on MSP relative to other variables (Fig. 2). For the remaining variables examined, the low yield of hydrogen production resulted in these variables having a more pronounced effect on the MSP compared to the other biofuels. Accordingly, improving the yield of hydrogen, particularly in the case of levoglucosan hydrolysis prior to fermentation, would benefit the hydrogen MSP more than the other biofuels. Furthermore, elevating the quantity of available substrate, either through increasing the operating days, biomass daily rate or levoglucosan level in bio-oil, showed more potential to decrease the MSP in hydrogen compared to the other biofuel projects. The overall greater MSP sensitivity to process perturbations in the hydrogen project indicated more risk associated with this project than for the other biofuels.

3.1. Hurdles and opportunities for hybrid processing

The three technology scenarios examined here give insight into the relative benefits and differing challenges surrounding production of various biofuels from levoglucosan. The hurdles associated with fermentation of bio-oil levoglucosan are related to both the feedstock and the various bioconversion technologies. Many of the hurdles highlight opportunities to develop new technologies to improve the prospects of hybrid processing.

In terms of cost competitiveness, there were distinct differences between the three bioconversion scenarios. The MSP, expressed as $ per gallon or liter gas equivalent (gge, Lge), for ethanol, methane, and hydrogen were 1.88, 2.21, and 3.50 $ gge^{-1} (0.50, 0.59, and 0.93 $ Lge^{-1}), respectively, for the case of direct levoglucosan bioconversion. The current market prices for corn-grain ethanol, natural gas refined methane, and steam-reformed hydrogen are 2.10, 0.43, and 2.14 $ gge^{-1} (0.55, 0.11, 0.57 $ Lge^{-1}) respectively [55–57]. Ethanol was the only product with an MSP that was cost-competitive with current commercial prices (for corn-grain

ethanol) under baseline conditions. Despite the MSP of hydrogen being greater than the current commercial price, the high energy density of hydrogen compensated for the low production yields to push the MSP of hydrogen produced via direct bioconversion into the viability range of \$2.00 – \$4.00 gge^{-1} (\$0.53 – \$1.06 Lge^{-1}) as designated by the U.S. Department of Energy [21]. These results highlight the potential to produce cost-competitive ethanol and hydrogen if direct bioconversion processes are developed with yields and productivities similar to those achieved with glucose substrate.

The biofuels examined here may better compete with their commercial counterparts under certain conditions. Developing microorganisms with improved bio-oil inhibitor tolerance and levoglucosan utilization, either through further adaptation of existing levoglucosan-utilizing communities or via synthetic biology, can help decrease MSP if the engineered microorganisms achieve production rates that equal or exceed those previously obtained on other more conventional substrates [14]. While genetic engineering has conferred levoglucosan utilization and stress tolerance pathways to common fermentative microorgansisms, these traits have not yet been combined into a single organism for the purpose of fermenting aqueous bio-oil extracts to ethanol [9,58]. As the MSP for methane production from levoglucosan was most removed from current commercial values, methanogenic anaerobic digestion can potentially benefit most from improved microbial community function, particularly greater production rates. While anaerobic digestion of levoglucosan in extracts from pyrolysis liquor has been demonstrated, the loading rate was limited by inhibitors in the extract [14]. These results were obtained from a non-adapted microbial community. Enhanced production rates and adaptation of the communities to bio-oil inhibitors via enrichment culture or synthetic biology may eventually overcome these barriers [59].

In addition to the unique biological challenges associated with using bio-oil levoglucosan as a feedstock, there are also considerations that are more broadly associated with each bioconversion technology. While the ethanol production scenario presented the least cost per unit energy produced, it required the most capital. This is reflective of ethanol fermentation requiring equipment, such as centrifuges for the separation of solids from the fermentation broth, that are not needed for methane and hydrogen production. Adoption of certain practices, such as the use of membrane technology for water-ethanol separation, may help lower capital and operating costs by improving productivity (thus decreasing the required bioreactor size) and reducing energy demand [60]. In addition to the greatest capital costs, ethanol production had considerable volatility in MSP according to the sensitivity analysis. Scaling up the project could mitigate some of the MSP volatility, but would be constrained by the scale of the thermochemical process, which was already assumed to operate at a large commercial scale. As a result, the most feasible way to scale up the ethanol process would be to increase the concentration of levoglucosan in the bio-oil. However, additional research into the relationship between feedstock properties, pyrolysis conditions, and bio-oil levoglucosan content is needed to enable this strategy.

Hydrogen production yielded the lowest capital costs, which may mitigate upfront risk to investment. However, the annual energy captured in the hydrogen was lowest among the bioconversion processes analyzed. Hydrogen production via dark fermentation also faces notable technical challenges. These include low yields, the need to control the partial pressure of H_2 in the reactor to prevent product inhibition, and management issues for the byproducts created during fermentation [61,62]. Some have proposed use of cell-free systems to improve bioprocess yields, including that from biohydrogen production [63]. However, such cell-free systems are currently much less mature than conventional fermentation processes and additional research is needed to develop and scale them. While the low yields were represented in the techno-economic model, byproduct management may negatively impact the process economics presented here if reactor effluent must be treated for disposal. However, opportunities exist to utilize volatile fatty acid byproducts from dark fermentation for biological upgrading to polyhydroxyalkanoates (PHA) or for methane production via anaerobic digestion [61]. While these technologies were not integrated into this modeling effort, it is worth noting the potential to address waste management issues in hydrogen production through co-product development.

4. Conclusions

If direct bioconversion of levoglucosan to biofuels can be achieved with production rates and yields comparable to those obtained with glucose substrate, the MSPs for ethanol and hydrogen production approach current commercial prices. Realizing the opportunities for direct biofuel production from bio-oil levoglucosan will require overcoming several technical hurdles. These include discovering or engineering microorganisms or microbial communities that can metabolize levoglucosan while also tolerating inhibitors carried by the bio-oil. However, the analysis presented here motivates research in these areas, as direct utilization provides economic advantages compared to currently feasible conversion methods based on hydrolysis of the levoglucosan to glucose ahead of fermentation. By indicating the energy generation potential and operational sensitivities for several potential biofuels, the analysis presented here can inform decisions regarding future research efforts to advance direct fermentation of bio-oil levoglucosan or to instead pursue upgrading of levoglucosan to other value-added chemicals.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.renene.2016.04.095.

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