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Guiding Optimal Biofuels:
A Comparative Analysis of the Biochemical Production of Ethanol and Fatty Acid Ethyl Esters from Switchgrass

Scott M. Paap, Todd H. West, Dawn K. Manley, Eric J. Steen, Harry R. Beller, Jay D. Keasling, Dean C. Dibble, Shiyan Chang, Blake A. Simmons

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Scott M. Paap, Todd H. West, Dawn K. Manley, Dean C. Dibble, Blake A. Simmons
Sandia National Laboratories
P.O. Box 969 Livermore, CA 94551

Eric J. Steen
Joint BioEnergy Institute, 5885 Hollis Avenue, Emeryville, CA 94608

Harry R. Beller, Jay D. Keasling
Joint BioEnergy Institute and
Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Shiyan Chang
China Automotive Energy Research Center (CAERC), Tsinghua University
Beijing 100084, PR China

Abstract

In the current study, processes to produce either ethanol or a representative fatty acid ethyl ester (FAEE) via the fermentation of sugars liberated from lignocellulosic materials pretreated in acid or alkaline environments are analyzed in terms of economic and environmental metrics. Simplified process models are introduced and employed to estimate process performance, and Monte Carlo analyses were carried out to identify key sources of uncertainty and variability. We find that the near-term performance of processes to produce FAEE is significantly worse than that of ethanol production processes for all metrics considered, primarily due to poor fermentation yields and higher electricity demands for aerobic fermentation. In the longer term, the reduced cost and energy requirements of FAEE separation processes will be at least partially offset by inherent limitations in the relevant metabolic pathways that constrain the maximum yield potential of FAEE from biomass-derived sugars.

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NOMENCLATURE

AFEX	ammonia fiber expansion
CAFI	Consortium for Applied Fundamentals and Innovation
DA	dilute acid
FAEE	fatty acid ethyl ester
GHG	greenhouse gas
HHV	higher heating value
LAP	laboratory analytical procedure
MFSP	minimum fuel selling price
SHF	separate (or sequential) hydrolysis and fermentation
SNL	Sandia National Laboratories

1. INTRODUCTION

The utilization of lignocellulosic materials for biofuels production will be necessary if biomass-derived transportation fuels are to be produced on a large enough scale to make meaningful reductions to fossil fuel use in the transportation sector [1], and the liberation and microbial conversion of sugars from these feedstocks has been pursued as one potential route to industrial-scale biofuels production [2-4]. Ethanol is currently the only commercially relevant fuel derived from plant sugars, and its long history of industrial fermentative production made it an obvious choice for initial efforts to produce fuels from cellulosic materials. After decades of technology development, the past several years have seen the emergence of a nascent cellulosic ethanol industry, with commercial- or demonstration-scale plants now operating in North America, Europe, and China [5]. A range of proposed biochemical processes to convert lignocellulosic biomass to ethanol have been analyzed by numerous researchers, in the form of case studies based on detailed techno-economic models [6-8], life-cycle analyses [9], and comparisons between competing process configurations and technologies [10-12].

Despite ethanol's process technology maturity and efficient production in microbes [13], it suffers from a relatively low energy density (23.5 MJ/L versus 34.7 MJ/L for gasoline), and its corrosivity and miscibility with water presents challenges for the use of existing gasoline distribution infrastructure for ethanol-rich fuel blends. These well-known shortcomings have driven interest in the production of alternative high energy density, infrastructure-compatible fuel molecules from plant-derived sugars, commonly referred to as "drop-in" or "fungible" fuels, which has become possible with recent advances in metabolic engineering [14]. Prominent examples of candidate molecules include short-chain (C4 and C5) alcohols [15], isoprenoid derivatives such as farnesene (a precursor to farnesane) [16], and fatty acid derivatives such as alkanes [17] and fatty acid ethyl esters (FAEE) [18]. The water-immiscibility of these so-called "advanced biofuels" may significantly reduce the need for distillation operations for product recovery, potentially reducing the energy requirements of the fuel production process. However, claims that advanced biofuels will offer superior performance to cellulosic ethanol must be supported by comparative analyses of the respective production processes in terms of relevant economic and environmental metrics. To date such studies are lacking in the literature, with the work of Huang and Zhang [19] comparing the energetics of the microbial production of ethanol, butanol, fatty acid ethyl ester, and hydrogen serving as one of the few exceptions. The current paper attempts to address this gap by pursuing the following objectives: (1) conduct an assessment of the relative economic and environmental performance of representative processes to produce ethanol and a water-immiscible biofuel from lignocellulosic material under the current state of technology development, (2) investigate the effect of uncertainty and variability in process parameters and the relative importance of these parameters in determining the process performance by conducting a Monte Carlo analysis of the relevant processes, and (3) explore the long-term prospects for improving the performance of the fermentation and product recovery sections of the water-immiscible biofuel production processes, and the implications for their relative competitiveness versus the pathways for producing cellulosic ethanol.

In support of these objectives, a simplified process model representing the biochemical production of ethanol and a FAEE from acid- and alkaline-pretreated switchgrass was

constructed in Microsoft® Excel, based largely on detailed models of biofuels production constructed in chemical process simulation software packages [6, 8, 20]. Construction of a simplified model in Excel enabled the incorporation of multiple pathways from biomass to biofuel within a unified framework, and facilitated comprehensive Monte Carlo analysis in a fraction of the time that would be required using detailed models in process simulation software. The Monte Carlo analyses in turn provided valuable insight into the relative impacts of process parameters based on both their intrinsic influence on the model as well as the variability and uncertainty in their values. The ability to conduct this type of sensitivity analysis is crucial for identifying key parameters and process steps in early-stage technologies such as those currently under consideration, for which performance at scale is uncertain. The analytical approach taken here is similar to that presented by Spatari and coworkers [9], who employed a stochastic model of ethanol production based on acid and alkaline pretreatment methods in an analysis yielding life cycle environmental metrics. This approach was extended to include both environmental and economic metrics, as well as an evaluation of technologies to produce FAEE from lignocellulosic biomass.

2. SCOPE OF ANALYSIS

The current analysis encompasses biofuel production pathways that have been recognized in the literature as leading candidates for commercialization, and that have been the subject of intensive research efforts within government, industry, and academia. The choices of feedstock, process technologies, and fuels are not intended to represent the full scope of biochemical pathways from biomass to biofuels under development, and do not reflect the authors' endorsement of the chosen pathways.

2.1 Feedstock

Switchgrass (*Panicum virgatum*) was selected as the model feedstock for the current analysis. This highly productive perennial warm-season grass is native to the eastern U.S. and is one of the most widely studied examples of a potential dedicated energy crop [21, 22]. Composition ranges in terms of key chemical components are listed in Table 1, along with estimated costs, higher heating values (HHV), and moisture content values representative of a single late-fall (October) harvest with field drying. The greenhouse gas (GHG) emissions associated with the production, harvest, and transportation of switchgrass are addressed in Section 3, and feedstock costs are discussed in Section 3.1 below.

The composition of switchgrass is influenced by a variety of factors, including cultivar, soil type, harvest date, and agricultural inputs [23-25]. The wide ranges of composition values listed in Table 1 underscore the importance of accounting for such variability in analyses of biofuels processes employing cellulosic materials as feedstock.

Table 1. Selected properties of switchgrass. Composition values are moisture-free weight percent.

Feedstock Property	Low[a]	Baseline[b]	High[a]
HHV, MJ/kg[c]	17.9	18.1	18.4
Typical moisture content[d]	10%	15%	20%
Cellulose content	31%	34%	45%
Xylan content	20%	23%	26%
Other sugar polymer content	2%	4%	6%
Lignin content	17%	19%	22%
Ash content range	4.5%	7%	8.5%
Extractives & protein content	5%	13%	17%
Feedstock cost, $/dry metric ton	$60	$130	$180

[a] Composition ranges compiled from [26-30].
[b] Baseline values taken from [8, 26].
[c] Estimated from holocellulose and lignin content based on the relationship proposed by Demirbas [31].
[d] Compiled from [32, 33].

2.2 Fuels

Ethyl hexadecanoate (ethyl palmitate) - chemically similar to 1st generation biodiesel molecules derived from plant oils and animal fats - was selected as a representative water-immiscible fuel

molecule for comparison with ethanol. Steen and coworkers have demonstrated the production of C_{12}-C_{18} fatty acid ethyl esters (FAEE) including ethyl hexadecanoate from glucose and xylose in recombinant *Escherichia coli* (*E. coli*) strains [18]. The relevant properties of ethanol and ethyl hexadecanoate are listed in Table 2. Many of the conclusions derived from the current analysis will be more broadly applicable to other water-immiscible biofuels; however, the fact that FAEEs are included in the broader definition of biodiesel is an important advantage, as it obviates the need to undergo potentially lengthy fuel certification processes.

Table 2. Selected properties of ethanol and ethyl hexadecanoate (FAEE).

Property	Ethanol	Ethyl hexadecanoate
Chemical formula	C_2H_6O	$C_{18}H_{36}O_2$
Molecular weight, g/mol	46.07	284.48
HHV, MJ/kg	29.7[a]	39.8[b]
Density @ 20°C, kg/L	0.79[a]	0.86[a]
Water solubility in fuel @ 20°C, g/L	Miscible	1.3[c]

[a] Value taken from [34].
[b] Value estimated based on data from [35].
[c] Value estimated based on data from [36].

2.3 Process Description

The biochemical processes under consideration to produce liquid fuels from lignocellulosic biomass include four major operations: biomass pretreatment to disrupt the structure of the lignocellulosic material; hydrolysis of cellulose, xylan, and other sugar polymers via the action of enzymes to yield their respective monomeric sugars (saccharification); microbial fuel production; and fuel recovery and purification [3, 4, 37]. In addition, industrial processes will require operations to recover valuable residual streams, treat and dispose of waste, and generate process steam and electricity. Four biofuel production pathways were examined in the current analysis, based on acid and alkaline pretreatment technologies to produce ethanol and FAEE. The key process steps and their primary mass and energy inputs and outputs are depicted schematically in Figure 1.

The current analysis focuses on processes employing either the dilute acid pretreatment process developed by NREL [6] or the ammonia fiber expansion (AFEX) process developed at Michigan State University and described in a recent techno-economic analysis by Laser and coworkers [8]. The separate (or sequential) hydrolysis and fermentation (SHF) process configuration is assumed in all cases, with hydrolyzing enzymes purchased from an off-site vendor and co-fermentation of glucose and xylose occurring in a single microbe. Fermentation to ethanol proceeds anaerobically, whereas fermentation to FAEE is currently aerobic. Ethanol is recovered and purified via distillation followed by a vapor-phase molecular sieve adsorption operation, while the water-immiscible FAEE product is separated using a pair of centrifuges in series and a final vacuum drying step to remove residual moisture. The feedstock handling equipment, wastewater treatment facilities, steam and electricity generation plant, and auxiliary systems are identical for all pathways under consideration, with the process described by NREL [6] serving as the basis for analysis. A more detailed description of the process pathways under consideration is presented in the accompanying Supplementary Material.

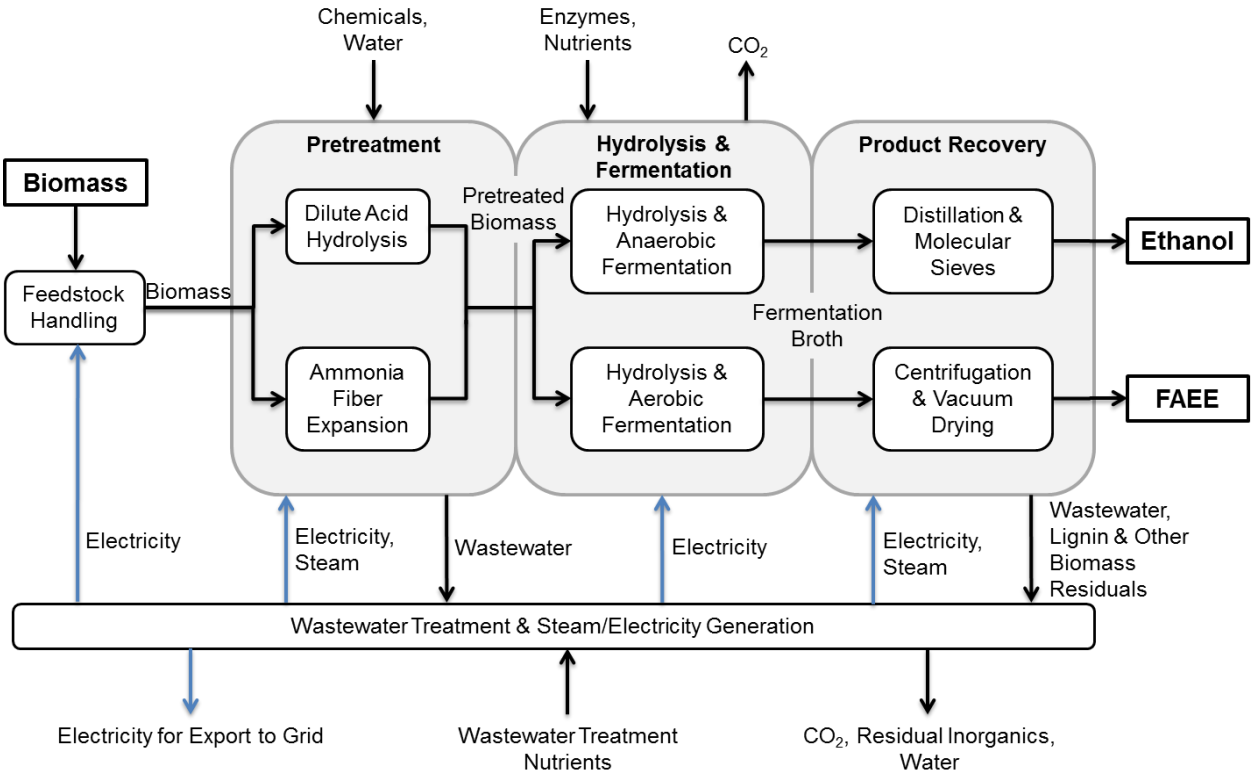

Figure 1. Process pathways evaluated in this study for the conversion of cellulosic feedstocks to ethanol and biodiesel (FAEE).

2.3.1 Pretreatment

The current analysis focuses on processes employing either the dilute acid pretreatment process developed by NREL [6] or the ammonia fiber expansion (AFEX) process developed at Michigan State University and described in a recent techno-economic analysis by Laser and coworkers [8]. Dilute acid pretreatment employs aqueous sulfuric acid at elevated temperature and pressure in order to cleave weak carbohydrate linkages, dissolve and hydrolyze hemicellulose, and de-wet, densify, and partially dissolve the lignin fraction of the biomass. The process increases the cellulose surface area accessible to enzymes and breaks the biomass into smaller particles. These effects are enhanced with the severity of the pretreatment process, in terms of increased residence time, temperature, and acid content; however, increased pretreatment severity also results in higher degradation rates of the desired sugar monomers to compounds such as furfural and hydroxymethyl furfural, which may also be detrimental to the fermentation process. After exiting the pretreatment reactor, the biomass slurry is conditioned via the addition of ammonia to a pH near 5, appropriate for the subsequent enzymatic hydrolysis step.

In the AFEX process, biomass is pressurized with ammonia at elevated temperature and then rapidly expanded to atmospheric pressure. The ammonia swells the crystalline cellulose and changes the crystal structure, introducing defects that increase the accessibility of the cellulose to enzymes. Lignin and hemicellulose are functionalized in the process, making them more water-soluble, and the rapid expansion serves to partially disrupt the structure of the biomass particles. Because both cellulose and hemicellulose remain largely intact, little degradation of sugars is

observed. The relatively high cost of ammonia necessitates steam stripping operations for recovery and recycling.

2.3.2 Hydrolysis and fermentation

Following pretreatment, cellulose and residual hemicellulose are hydrolyzed to yield sugar monomers via the hydrolytic action of enzymes. It is assumed that hydrolysis enzymes are purchased rather than produced on-site; enzyme cocktails developed specifically for lignocellulosic feedstocks are commercially available from several companies [38]. Microbial production of fuel molecules from sugars is carried out in batch mode across an array of parallel fermentation vessels. Fermentation to ethanol proceeds anaerobically, whereas fermentation to FAEE is currently aerobic. In practical terms, aerobic fermentation requires a continuous oxygen source, as well as a more sterile environment and more vigorous mixing than is necessary for anaerobic fermentation. For both fuels, co-fermentation of glucose and xylose is assumed within a single organism.

2.3.3 Product and waste solids recovery

Ethanol, a water-miscible molecule, is recovered via distillation followed by a vapor-phase molecular sieve adsorption operation to increase the product concentration from 92.5wt% to a final purity of 99.5wt%. The FAEE product is immiscible with water, and thus physical separation methods may be applied for product recovery operations. In an optimistic case, gravity settlers would be adequate to achieve separation of the FAEE from the fermentation broth; however, due to the complex nature of the starting mixture and the possible presence of free fatty acids, the potential for micelle formation may be an issue for these systems. In the absence of relevant experimental data, the separation process considered for the current analysis consists of a decanter centrifuge to remove solids followed by a disk stack separator to recover a FAEE-rich stream. Because the solubility of water in ethyl hexadecanoate (see Table 2 of the paper) is greater than the maximum water content of 0.050vol% specified in the ASTM standard for biodiesel [39], a final drying step is also necessary. We examine a vacuum drying system similar to that described by Haas and coworkers [20] for the recovery of vegetable oil-derived biodiesel to meet ASTM specifications.

3. MODELING AND ANALYSIS APPROACH

The primary objective of the current analysis is to compare the relative economic and environmental performance of biochemical processes to produce ethanol and FAEE from switchgrass. To this end, a deterministic model was constructed in Microsoft® Excel incorporating the four biomass-to-biofuels pathways of interest, consisting of equipment-level mass and energy balances as well as estimates of project investment costs, operating expenses, and revenues. A plant size capable of processing 2,000 dry metric tonss of switchgrass per day was selected for all pathways, as proposed by Aden and coworkers [40] for initial biorefineries utilizing cellulosic materials. The process model is primarily based on the techno-economic analysis by Humbird and coworkers at NREL [6], which examines the production of ethanol using dilute acid pretreatment. The process described by Laser and coworkers [8] served as the basis for an AFEX pretreatment module, and additional modules were constructed to represent aerobic fermentation and recovery of FAEE. The model yields an estimate of the minimum fuel selling price based on a 20-year discounted cash flow analysis, as well as overall mass and thermal conversion efficiency, electricity production or consumption, process water consumption, and net GHG emissions. Further details regarding the process model can be found in the Supplementary Material.

Greenhouse gas emissions attributed to the conversion process were estimated by tabulating the emissions associated with the main process inputs as well as the avoided emissions associated with the co-generation of electricity. Estimates of GHG emissions associated with switchgrass production and chemical inputs are from [41]. We adopt the estimate of Hsu and coworkers [42] for GHG emissions due to cellulase production and assume that it is also valid for xylanase production; however, as these researchers note, this value is uncertain due to the early-stage and proprietary nature of cellulase production technology. As no location is specified for the biofuels production facility, the emissions associated with electricity production are based on the average generation mix for the U.S. national grid [41]. Emissions associated with the biorefinery infrastructure and land-use changes are neglected.

3.1 Conversion Process Model Description

The Excel-based model developed for the current study incorporates many simplifications to the ASPEN-based process simulation model upon which it is based, yet retains the important physical relationships that govern the behavior of the system. Material and energy balances are calculated across all major equipment, with detailed accounting of 22 chemical components. A parameterization approach was employed in place of detailed kinetic and thermodynamic modeling of reaction systems (e.g., hydrolysis and fermentation), in which the reaction conditions, yield, and rate are input as independent parameters to the model (see Section 3.1 of paper). Mass balances for separation operations (e.g. distillation, flash separation, filtration, and centrifugation) are obtained by specifying separation efficiencies and/or outlet concentrations for key components over the relevant mixture composition ranges.

Heating and cooling requirements associated with heats of reaction, phase and temperature changes, and power dissipation are explicitly accounted for, and sensible heat effects are calculated using constant average heat capacity values estimated based on relationships introduced by Wooley and Putsche [43]. The only significant exception is the distillation system

for ethanol recovery, for which energy use was calculated based on previously published empirical relationships [44]. Power requirements for aerobic fermentation were estimated using published correlations [45], and centrifuge electricity use was based on vendor specifications. Electricity requirements for other major pieces of equipment were scaled linearly with an appropriate scaling quantity based on power consumption values from the NREL design report [6] and the analysis by Laser and coworkers [8].

Equipment costs for the ethanol processes were estimated according to the following exponential scaling expression, using parameters established by NREL [6] and Laser *et al.* [8] for each major piece of equipment:

Equation 1 ***New***

where *a* is a scaling exponent associated with a specific piece of equipment. Installation costs are accounted for using an equipment-specific installation factor that is applied to the uninstalled equipment cost obtained using Equation 1. Equipment costs for FAEE fermentation and recovery operations were estimated based on a combination of vendor quotes and the built-in cost models of the SuperPro Designer® process simulation software package. The cost-year for the current analysis was 2009, and all equipment costs were adjusted to this year using *Chemical Engineering Magazine*'s Plant Cost Index [46]. The total capital investment (TCI) for the project was estimated by applying factors to the total installed equipment costs to account for direct and indirect costs associated with the construction of the facility, as described in [6]. Fixed operating costs associated with various overhead items were also estimated in this manner.

Raw materials and waste handling charges and labor costs were taken from the NREL design report [6]. Raw materials and waste disposal costs were adjusted to the cost-year using the Industrial Chemicals Producer Price Index published by the U.S. Bureau of Labor Statistics [47], with annual costs calculated based on 8406 plant operating hours per year. Labor costs were adjusted to the cost-year using the Employment Cost Index for Wages and Salaries in Manufacturing published by the U.S. Bureau of Labor Statistics [48].

The project TCI, operating expenses and revenues were utilized in a discounted cash flow analysis in order to determine the minimum fuel selling price that would be required to obtain a net present value of zero for the overall project. Financial parameters - discount rate, debt/equity ratio, income tax rates, plant life, and construction start-up duration - and depreciation methodology were identical to those employed in the NREL design report [6], assumed to be appropriate for an "n^{th} plant" among a hypothetical fleet of similar biorefineries.

The conversion process model was validated against the results of NREL's technoeconomic analysis [6], after adjusting for the inclusion of on-site cellulase production in the NREL model. When input parameters identical to those employed in the NREL study were applied to the model, values of the minimum fuel selling price, ethanol yield per ton of biomass, total water consumption, and total electricity production were within 1% of the corresponding NREL result, and process electricity consumption was within 4% of the NREL value. The results of the single-point sensitivity analyses of MFSP and ethanol yield carried out by Humbird and coworkers [6] were also replicated to within 4% for each input parameter.

The use of a simplified spreadsheet-based model enabled a full Monte Carlo analysis based on input probability distributions for a subset of technical and economic model parameters, and reduced the time required for such an analysis by several orders of magnitude compared to those employing detailed models implemented in process simulation software packages. The ability to conduct rapid, credible Monte Carlo analyses is particularly valuable when evaluating pre-commercial processes and technologies for which performance at scale is uncertain. Additionally, the flexible and expandable nature of the model framework makes it possible to incorporate promising new process technologies as they are developed, such that the performance of all technology options is analyzed on a consistent basis.

3.2 Monte Carlo Analysis

Many of the technologies envisioned for biochemical conversion of biomass to biofuels are still under development, and their performance in commercial-scale facilities is unproven. Monte Carlo analysis techniques were employed in order to explicitly incorporate this uncertainty and variability in estimates of overall process performance. Probability distributions based on literature data were constructed for a subset of input parameters to the process model; where data were sparse or unavailable (e.g., FAEE fermentation performance), the authors employed engineering judgment based on prior research experience to construct input parameter distributions. The Crystal Ball add-in for Excel was utilized to perform 10,000 Monte Carlo trials for each combination of pretreatment technology and fuel, yielding stochastic distributions for each metric of interest. Input parameters were represented using the beta-PERT probability distribution, requiring only estimates of the minimum, maximum and most likely values [49].

The technical parameter distributions related to the pretreatment, enzymatic hydrolysis, and fermentation processing steps are given in Table 3. As hydrolysis performance is known to depend on the pretreatment method, independent hydrolysis parameter distributions were developed for pathways incorporating dilute acid and AFEX technologies. Pretreatment process condition ranges were compiled from previous studies utilizing switchgrass as feedstock [50-57], with the 'most likely' parameter values representing the optimized conditions reported by the most recent Biomass Refining Consortium for Applied Fundamentals and Innovation project (CAFI 3)[51]; the only exception was the 'most likely' value of the solids loading for dilute acid hydrolysis, which was selected to be midway between the CAFI 3 optimum of 10% and the value of 30% employed by NREL in their latest technoeconomic model [6]. Laser and coworkers [8] assume 99.5% recovery of ammonia following AFEX pretreatment; however, because this technology is unproven at commercial scale we also investigate the effect of higher ammonia losses.

Most investigations of biomass pretreatment techniques employ variations of NREL's Laboratory Analytical Procedure (LAP) for enzymatic saccharification [58] to determine their effectiveness, and the parameter ranges selected to represent hydrolysis conditions and performance for the current analysis are based on results from similar trials utilizing dilute acid- and AFEX-pretreated switchgrass [50-52, 54-57, 59], with a slight reduction in sugar yields for dilute acid pretreatment to account for fermentation inhibition due to the byproducts from that technology [60] (see discussion of fermentation parameters below). Despite significant efforts to optimize the conditions of dilute acid and AFEX pretreatments and the use of a consistent analytical method for hydrolysis trials, considerable variation exists in reported hydrolysis

performance of pretreated switchgrass; this variation is reflected in the relatively wide hydrolysis parameter ranges listed in Table 3.

Table 3. Pretreatment, hydrolysis, and fermentation parameter ranges and 'most likely' values used in Monte Carlo analysis (see text for references).

	Pretreatment and Hydrolysis	Dilute Acid			AFEX		
	Parameter	Low	High	Most Likely	Low	High	Most Likely
Pretreatment	Solids loading (catalyst-free basis), wt%	10%	30%	20%	30%	90%	33%
	Temperature, C	130	200	140	70	180	140
	Residence time, min	2	60	40	5	40	30
	Sulfuric acid loading, mg/g dry biomass	5	200	100	N/A	N/A	N/A
	Ammonia/biomass mass ratio	N/A	N/A	N/A	0.3	2.0	1.5
	Ammonia recovery for recycle	N/A	N/A	N/A	90%	99.5%	97%
Hydrolysis	Hemicellulose conversion[a]	60%	95%	85%	50%	98%	75%
	Cellulose conversion[a]	65%	90%	75%	70%	95%	80%
	(Maximum) solids loading, wt%[b]	10%	25%	20%	10%	25%	20%
	Residence time, hr	24	168	72	24	168	72
	Cellulase loading, mg enzyme/ g cellulose	5	40	20	5	40	15
	Hemicellulase loading, mg/mg cellulase	N/A	N/A	N/A	0	0.5	0.33
	Temperature, C	40	70	50	40	70	50
	Enzyme cost, $/kg	$7	$15	$10	$7	$15	$10
	Fermentation	**Ethanol**			**FAEE**		
	Parameter	**Low**	**High**	**Most Likely**	**Low**	**High**	**Most Likely**
	Yield on glucose, % of theoretical maximum[c]	85%	95%	90%	10%	50%	30%
	Yield on xylose, % of theoretical maximum[c]	70%	90%	80%	0%	40%	20%
	Residence time, hr	24	72	48	24	132	48

[a] Total conversion in pretreatment and hydrolysis stages
[b] Includes both soluble and insoluble solids; value was adjusted as necessary in the model if the effluent stream from the dilute acid pretreatment step was more dilute than the specified hydrolysis solids loading
[c] Theoretical maximum yield of ethanol and FAEE on glucose/xylose is 0.511 g/g sugar and 0.35 g/g sugar, respectively [61]

One factor contributing to uncertainty regarding the performance of commercial-scale hydrolysis operations on AFEX-pretreated biomass is the fact that the enzymes typically employed for laboratory-scale saccharification trials (Genencor Spezyme® CP) are not tailored for hydrolysis of hemicellulose. Because hemicellulose is not solubilized during AFEX pretreatment as it is during dilute acid pretreatment, the addition of xylanases is necessary to achieve high yield of

monomeric xylose and in turn increase the accessibility of cellulose to cellulases [62]; Gao and coworkers [63] have proposed an optimum xylanase to cellulase ratio of 1:3 for hydrolysis of AFEX pretreated switchgrass. The effectiveness of AFEX pretreatment on switchgrass has been also been shown to depend on harvest date [50, 64] and to a lesser extent on cultivar [51].

Another factor adding to uncertainty regarding the projected industrial hydrolysis performance of biomass pretreated via any technique is the relatively dilute (1wt% glucan) nature of the hydrolysis slurry specified in the NREL LAP. The dilute conditions minimize sugar inhibition, which has been shown to lower enzymatic hydrolysis sugar recovery efficiencies at higher (20wt%) solids concentration [65].

The fermentation yield parameter ranges for ethanol and FAEE production in Table 3 are given in terms of the theoretical maximum conversion based on the relevant metabolic pathways to produce each fuel molecule [61]. The parameter distributions for ethanol fermentation reflect the relatively mature state of industrial glucose fermentation; however, native strains of the two leading candidate hosts for microbial production of ethanol from switchgrass - *Saccharomyces cerevisiae* and *Zymomonas mobilis* - do not possess the ability to ferment the pentose sugars xylose and arabinose [66]. Progress has been made in developing pentose-fermenting organisms via metabolic engineering techniques [67-74], although yields and productivities still do not match those for glucose and performance at industrial scales has not been publicly demonstrated [75-77]. The performance of systems to produce FAEE is subject to even greater uncertainty; the best professional judgment of the authors based on experience with FAEE-producing *E. coli* was used to construct the parameter distributions listed in Table 3. Differences in the inhibitory effects of hydrolysates obtained using different pretreatment technologies are not explicitly accounted for in the fermentation parameter ranges, even though previous studies have indicated that AFEX pretreatment results in fewer inhibitory byproducts [60]; potential reductions in ethanol production from dilute acid-pretreated switchgrass are instead captured in lower hydrolysis conversion efficiencies.

Biomass and enzymes costs have long been acknowledged as major drivers of the cost of producing cellulosic biofuels, yet despite the attention these areas have received the costs of both are still highly uncertain. The biomass feedstock and enzyme cost distributions assumed in the current analysis are given in Tables 1 and 3, respectively. The delivered feedstock cost distribution spans the results of recent analyses of switchgrass costs in the U.S. Midwest [78], Great Plains [79], and Southeast [80], with transportation costs from the farm to the biorefinery assumed to be $14 per dry metric tons [81]; the 'most likely' feedstock cost corresponds to the average breakeven price in the low-cost scenario described by Jain et al. [78]. The enzyme cost distribution is based on the recent techno-economic analysis of Klein-Marchuschamer and coworkers [82].

Distributions were also assigned to the mass fractions of major chemical species in the dry switchgrass fed to the process, with the minimum and maximum values corresponding to the low and high values, respectively, listed in Table 1.

The performance of the biomass conversion processes was evaluated based on the following economic and environmental metrics: (1) fuel production per metric ton of dry biomass, (2)

minimum fuel selling price, (3) net electricity production, (4) process water consumption, and (5) process GHG emissions. Process water consumption does not include water associated with the production of feedstocks, other chemical inputs, or grid electricity used in the process.

4. RESULTS AND DISCUSSION

4.1 Near-Term Process Performance

Stochastic distributions of the chosen economic and environmental performance metrics are presented in Figures 2 and 3 for each of the four modeled pathways from switchgrass to fuel. As discussed in Section 3.2 the input parameter ranges employed to generate these stochastic distributions were selected to be representative of the current state of technology for the respective processes; it is assumed that the input parameter ranges are appropriate for an "n^{th} plant" among a hypothetical fleet of similar biorefineries as described in [6]. It is important to note that the resulting distributions capture only the variability and uncertainty in the feedstock compositions and process parameters discussed in Section 3.2, and do not represent the complete range of possible performance for a given process. For example, financial and operational parameters – which were fixed for the current analysis – can be expected to have a significant impact on estimated fuel production costs. The value of analyses such as presented here is in comparing similar processes and investigating the relative importance of input parameters to the process model, rather than providing absolute values of performance metrics.

4.1.1 Minimum fuel selling price (MFSP)

The break-even price per ethanol-equivalent liter for each of the four biomass conversion pathways under consideration are given in Figure 2a. The most striking feature of the results is the large disparity between the costs for ethanol and FAEE for both pretreatment technologies. These results are driven to a large degree by the respective fermentation parameters for each fuel (see Table 3). The fermentation yield of ethanol from glucose is assumed to be roughly three times that of FAEE, and an even greater advantage for ethanol is assumed for xylose fermentation; thus, for roughly the same cost in terms of feedstock, biorefinery infrastructure, and other raw materials, a significantly lower annual output of FAEE will be obtained compared to ethanol. It is recognized that the fermentation of FAEE is at a relatively early stage of development, and there is potential for significant improvements in the fermentation process that will narrow the gap in cost with ethanol. The impacts of such improvements are explored in Section 4.2.

Figure 4Figure 4. Contributions to the variance in minimum fuel selling price for process to produce (a) ethanol and (b) FAEE from switchgrass using dilute acid pretreatment. Variance in ethanol and FAEE selling price is $0.03 and $1.62, respectively. resolves the overall variance in fuel cost determined from the Monte Carlo analysis into the respective contributions from key input parameters for the pathways employing dilute acid pretreatment. It is important to note that the results depicted in Figure 4 are based on relative contributions, and that the total variance in ethanol MFSP ($0.03) is significantly lower than that for FAEE ($1.62). Not surprisingly, fermentation parameters dominate the variance in FAEE production costs, whereas for ethanol production, the pretreatment and hydrolysis parameters have the largest influence. This comparison highlights the relatively narrow distribution on the expected fermentation parameters for ethanol, a result of thousands of years of experience in producing this molecule.

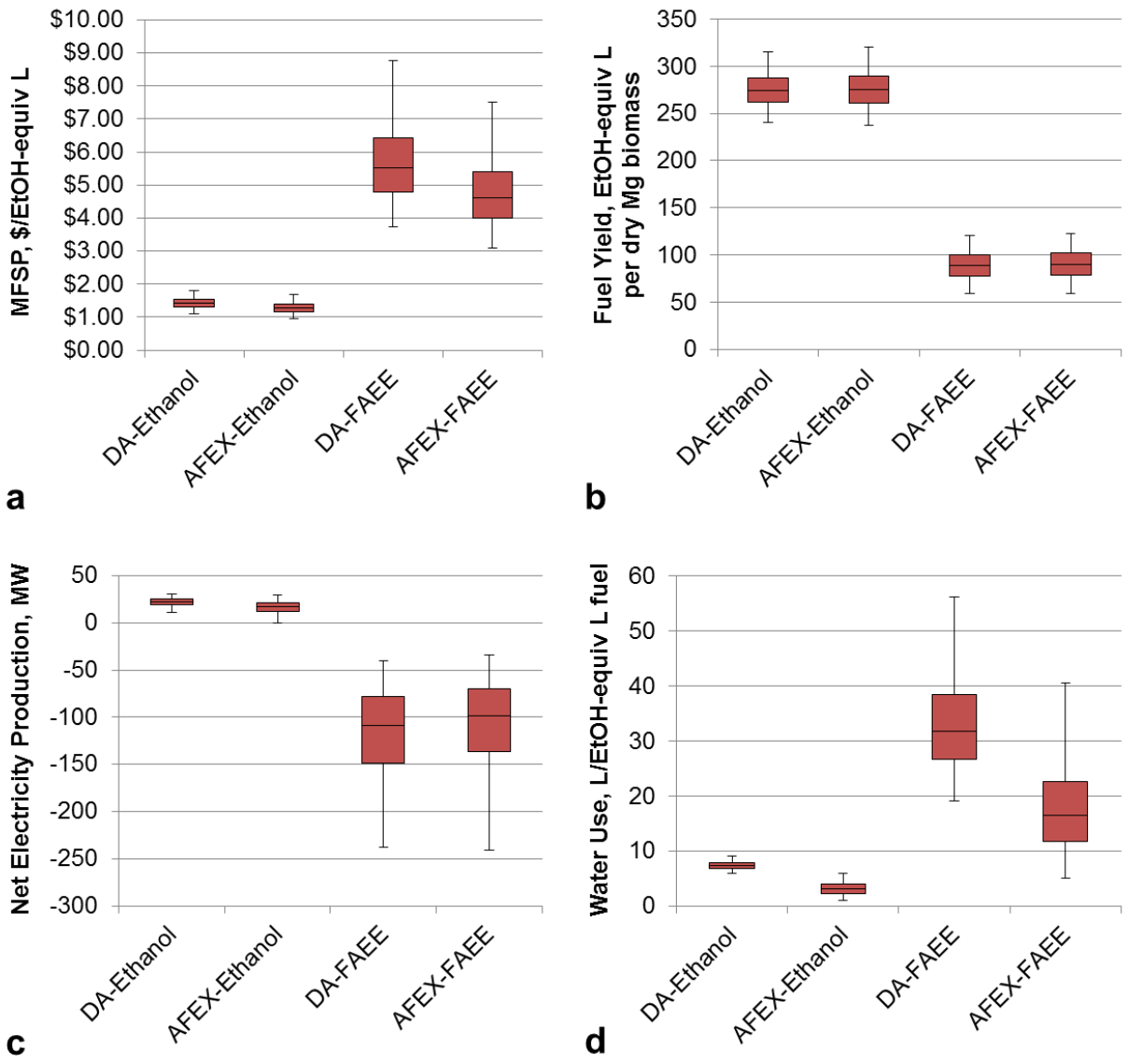

Figure 2. (a) Minimum fuel selling price ($ per ethanol-equivalent liter), (b) Fuel yield (ethanol-equivalent liters per metric ton of dry biomass), (c) Net electricity generation (MW) for a 2,000 metric ton/day conversion facility, and (d) process water consumption (liters of water per liter of ethanol-equivalent fuel produced) for all pathways to ethanol and FAEE. Stochastic distributions are represented as box plots. The top and bottom edges of each box represent the 75th and 25th percentiles, respectively, the middle line in each box represents the 50th percentile, and the top and bottom whiskers represent the 97.5th and 2.5th percentiles, respectively. Values of each metric at these percentiles are tabulated for all pathways in the Supplementary Material.

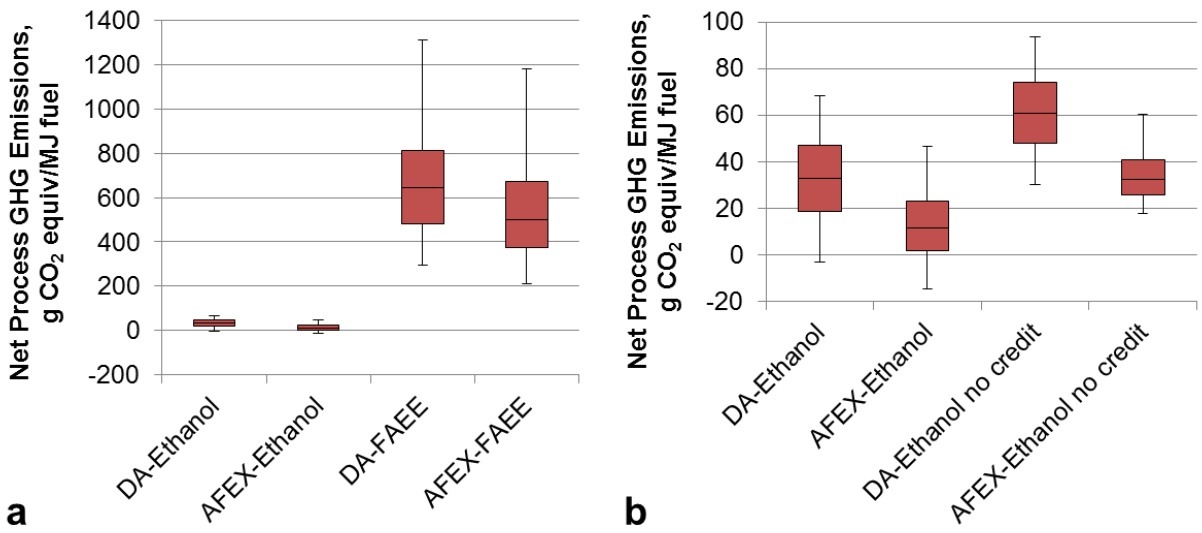

Figure 3. Net GHG emissions (g CO_2 equivalents per MJ of fuel produced) for all pathways to ethanol and FAEE. Results in (a) include credits due to co-production of electricity; results for ethanol pathways are presented in (b) both with and without electricity co-production credits. Stochastic distribution data represented by box plots are tabulated for all pathways in the Supplementary Material.

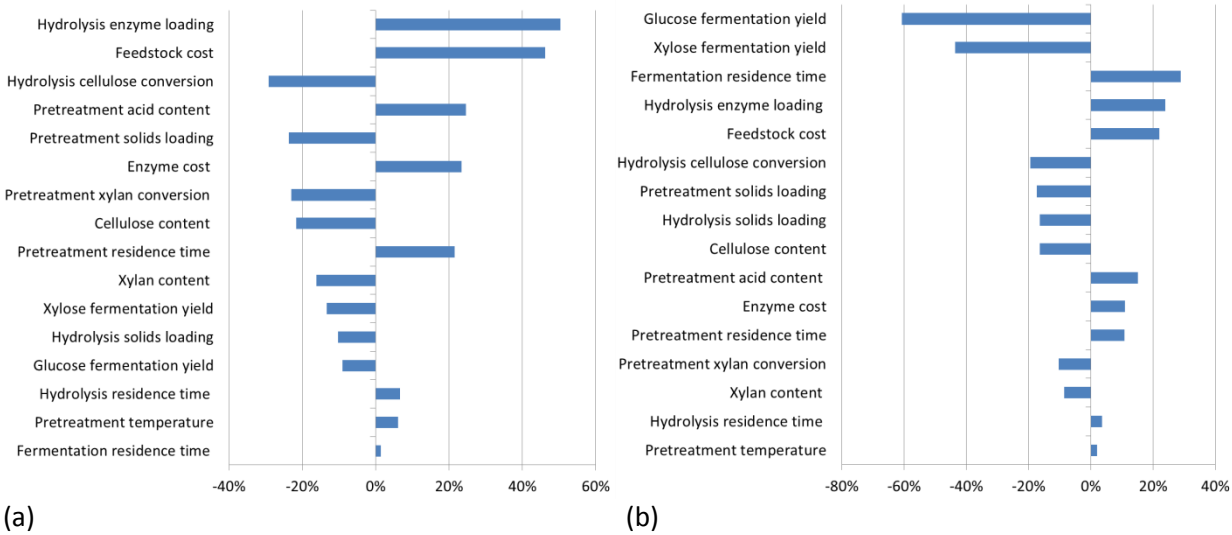

Figure 4. Contributions to the variance in minimum fuel selling price for process to produce (a) ethanol and (b) FAEE from switchgrass using dilute acid pretreatment. Variance in ethanol and FAEE selling price is $0.03 and $1.62, respectively.

A representative comparison of costs across different unit operations and raw materials streams for pathways employing dilute acid pretreatment is presented in Figure 5, for the scenario in which the 'most likely' values of each parameter is input to the conversion process model. The relative contributions are similar across both pathways, reflecting the fact that the increased cost for FAEE is primarily a result of lower fuel yield. There is also a significant increase in the relative cost of the fermentation unit operation for FAEE production, attributable to increased

capital costs associated with aerobic fermentation and longer fermentation times, as well as a dramatic swing from net electricity production to net consumption (discussed in Section 4.1.3). It is interesting to note that the product and solids recovery section represents only a minor contribution to the overall cost of fuel production in both cases.

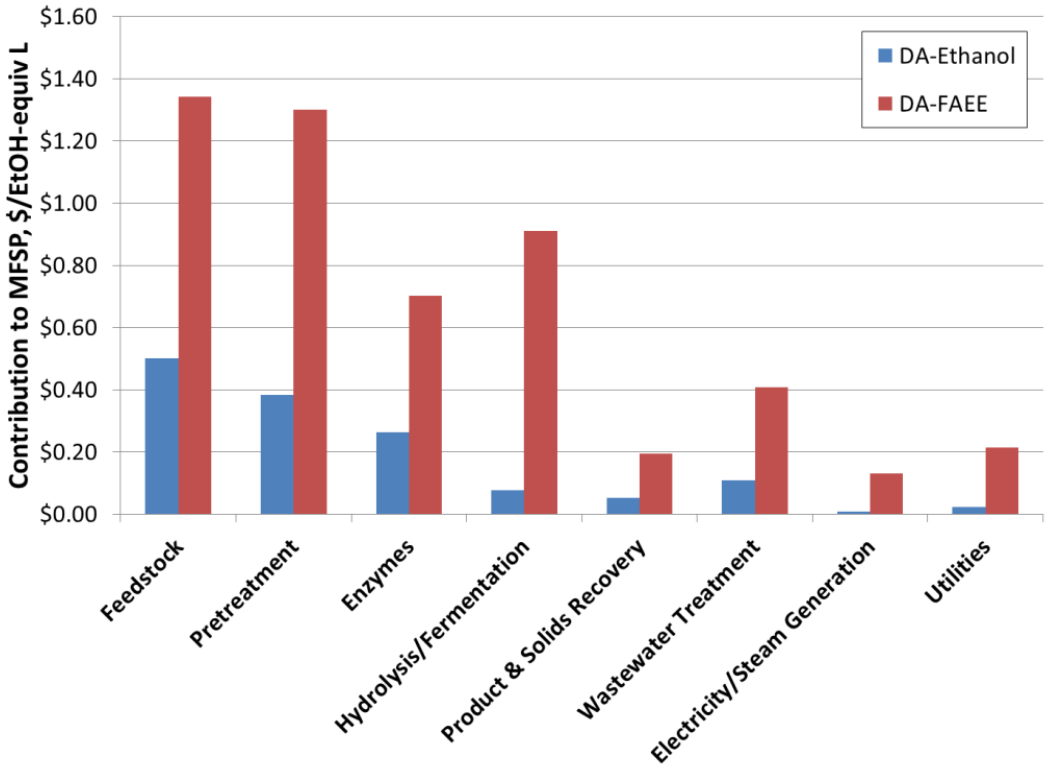

Figure 5. Comparison of costs for unit operations and major inputs for the 'most likely' input parameters for ethanol and FAEE production from switchgrass using dilute acid pretreatment. Unit operation costs include capital recovery charges, fixed costs, and raw materials and electricity costs (excluding biomass and enzymes).

The costs for pathways employing different pretreatment strategies to produce a given fuel are much more closely aligned, with significant overlap in the stochastic distributions in the case of both ethanol and FAEE production. This is consistent with the results of Tao and coworkers [83], who estimated similar costs for producing cellulosic ethanol via a range of pretreatment technologies. The cost of dilute acid pretreatment is slightly higher than that for AFEX pretreatment, a trend that will be observed regardless of the fuel being produced since the choice of pretreatment technology has no explicit influence on the fermentation step in the conversion process model. Ethanol costs shown in Figure 2a are higher than those reported in previously published studies due to the more conservative performance and raw materials (biomass and enzymes) cost assumptions in the current analysis; recent estimates of the cost of producing ethanol from herbaceous biomass using dilute acid or AFEX pretreatment range from $0.27/L to $1.21/L [7, 83-87], with Humbird and coworkers [6] reporting a value of $0.57/L (dilute acid pretreatment).

4.1.2 Fuel yield

Figure 2b presents fuel production per metric ton of dry biomass for the conversion process pathways of interest. Fuel production is given in terms of ethanol-equivalent liters on an energy basis, allowing direct comparison of the ethanol and FAEE processes. The estimated yield of ethanol via both pretreatment pathways is lower than those reported by Humbird *et al.* [6] (dilute acid, 330 L/Mg) and Laser *et al.* [8] (AFEX, 318 L/Mg) due to our selection of less aggressive conversion parameters. The production of FAEE is significantly lower than that of ethanol, due to the low fermentation yields assumed for the FAEE processes.

The maximum fuel production per metric ton of switchgrass is limited by the sugar oligomer content of the feedstock and by the maximum theoretical fermentation yield of fuel from sugar based on the relevant metabolic pathways. A key factor in the current analysis is the fact that the maximum theoretical fermentation yield of ethanol is over 10% higher than that of FAEE on an energy basis: the maximum yield is 97% for ethanol versus 88% for FAEE, based on a recent analysis of the relevant metabolic pathways [61]. Thus, assuming the baseline values of switchgrass composition from Table 1, the maximum yield of ethanol is 394 ethanol-equivalent liters per metric ton of biomass, whereas for FAEE the maximum yield is 358 ethanol-equivalent liters per metric ton of biomass.

4.1.3 Electricity production

In the cellulosic ethanol processes that serve as the basis for the model used in this work, electricity generated by the combustion of lignin and other residual organics is sufficient to meet the power needs of the process with some excess amount available for export to the grid. The only ethanol scenarios in which residual biomass may not be sufficient to provide excess power involve AFEX pretreatment with high water content and low reaction temperatures, necessitating large amounts of steam for ammonia recovery [87] and thus reducing the amount that is available for power generation. However, the production of FAEE from cellulosics as modeled here will likely require electricity inputs, as indicated by the net electricity generation results presented in Figure 2c. In this case, the reason for the poor performance of the FAEE process can be traced to the use of aerobic fermentation, which requires a considerable amount of power to aerate and agitate the fermentation vessels (2 HP per 100 gallons of fermentor volume). The result is an electricity demand that is expected to approach 12 kWh per liter of ethanol-equivalent fuel produced for fermentation alone. In addition, residual sugars not utilized for fuel production are converted primarily to CO_2 by the FAEE-producing microbes, and are thus unavailable for conversion to electricity.

To put this electricity demand in perspective, net consumption of 12 kWh for a single ethanol-equivalent liter of fuel produced would require 67 MJ of fuel at an electricity generation efficiency of 55%, which is more than three times the energy content (HHV) of a liter of ethanol. Clearly, a biofuel production process with a negative energy balance - even without considering energy inputs to produce and deliver biomass and other raw materials - is not likely to be a candidate for commercialization on a large scale.

4.1.4 Process water consumption

Detailed accounting of water use in each unit operation yields the total water consumption of the process, given in terms of liters of water consumed per liter of ethanol-equivalent fuel produced

in Figure 2d. Nearly 90% of the water present in the conversion process is recovered in the wastewater treatment section for recycle. The main source of water losses is cooling tower evaporation associated with cooling water use, with most of the remaining losses occurring via the combustor stack. As was the case for the minimum fuel selling price, the primary driver of high water consumption in the FAEE processes is low fuel yield; a secondary driver is the large cooling load of the fermentation system, attributable to power dissipation in compressors and agitators as well as heat generated by the oxidation of sugars that are not converted to fuel. The higher water consumption of dilute acid pathways reflects the higher pretreatment temperatures and lower solids loading - and thus the increased cooling requirements downstream – associated with that technology.

The estimates of water consumption for the dilute acid-ethanol pathways in Figure 2d are higher than that reported by Humbird and coworkers [6] (5.4 L water/L ethanol) due to the less aggressive conversion parameter and pretreatment solids loading ranges chosen for the current study. Only the AFEX-Ethanol pathway approaches the water consumption of 3.0 L/L reported for corn-derived ethanol production processes; however, irrigation of corn acreage results in total water consumption of between 14 and 236 L/L ethanol depending on the agricultural region [88], exceeding the total consumption of both FAEE processes (assuming no irrigation of switchgrass). Although irrigated switchgrass is not considered here, for cases in which irrigation is employed it is important to note that reduced biomass conversion efficiency will result in incrementally higher water consumption – both upstream and in the process – per unit of fuel. The production of gasoline is more water-efficient than all of the biofuels pathways under consideration, consuming between 1.9 and 2.5 L water/ethanol-equivalent L [88].

4.1.5 GHG emissions

The estimated GHG emissions associated with producing switchgrass-based ethanol are dominated by contributions from the production of biomass feedstock, ammonia, and enzymes. Lime and sodium hydroxide inputs are also significant sources of emissions for dilute acid pathways, resulting in higher estimated emissions relative to AFEX pathways. For the 'most likely' parameter values selected for the current analysis, GHG emissions due to the chemical and enzyme inputs exceed those due to the production of switchgrass; even at the lower catalyst and enzyme loadings assumed by MacLean and Spatari [89], the contribution of the chemical and enzyme inputs represents 30-35% of the total well-to-tank emissions. If the avoided emissions associated with co-production of electricity are allocated to switchgrass-based ethanol, the net process emissions become negative for at least some of the Monte Carlo trials, as shown in Figure 3. The lower fuel yields of the FAEE processes result in higher emissions per MJ of fuel produced based on the same raw materials. However, the primary driver of GHG emissions for the FAEE processes is the increased electricity demand, accounting for approximately 80% of the total in both cases.

The GHG emissions results for ethanol production are similar to those reported by Spatari and coworkers [9], who estimated emissions of 22.1-29.5 g CO_2 equiv/MJ for AFEX-based processes and 28.8-39.2 g CO_2 equiv/MJ for dilute acid-based processes without electricity credits. Lower values between 6.5 and 14.4 g CO_2 equiv/MJ (excluding credits for electricity generation) have been reported by other authors [41, 90, 91], due to the fact that emissions associated with process chemicals and enzymes were neglected. Spatari and MacLean [92] and Mullins et al. [93] have conducted stochastic studies which include emissions due to indirect land-use changes, resulting

in higher estimates of GHG emissions with wider distributions. The median GHG emissions presented here for the production of ethanol with no co-product credit represent a 31-63% reduction compared to gasoline (88 g CO_2 equiv/MJ [41]), whereas the median emissions for the FAEE pathways indicate an increase of 470-630%. Previous studies have estimated GHG emissions associated with the production of corn-based ethanol ranging from 34 to 111 g CO_2 equiv/MJ [90, 94-96].

4.2 Potential improvements to the FAEE process

Microbial production of FAEE was demonstrated at bench-scale only recently, and the fermentation performance can be expected to improve as resources are devoted to this goal. It is instructive to investigate the specific improvements that would be necessary to approach or exceed the performance of cellulosic ethanol processes. The obvious starting point for such an investigation is the fermentation step itself, as poor yields and the use of aerobic fermentation were shown to negatively affect the performance of the FAEE processes. There may also be possibilities for enhancing the separation of FAEE following fermentation, which was modeled as occurring via centrifugation. Use of a less capital- and energy-intensive unit operation such as a gravity settler may be possible, given the immiscibility of FAEE with water. The potential impacts of improvements in these areas are analyzed through comparisons of the following scenarios:

Ethanol baseline scenario: Production of ethanol from switchgrass employing dilute acid pretreatment, based on the parameter ranges described in Section 3.1.

FAEE baseline scenario: Production of FAEE from switchgrass employing dilute acid pretreatment, based on the parameter ranges described in Section 3.1.

FAEE high yield scenario: Identical to FAEE baseline scenario, but assuming ethanol fermentation parameter ranges for FAEE production (see Table 3).

FAEE anaerobic high yield scenario: Identical to the FAEE high yield scenario, but assuming anaerobic fermentation of sugars to FAEE.

FAEE best case scenario: Identical to the FAEE anaerobic high yield scenario, but assuming zero cost and zero energy use for FAEE recovery operations.

4.2.1 Minimum fuel selling price

Stochastic distributions of fuel cost for each of the five scenarios are compared in

Figure 6. An improvement in the FAEE fermentation parameters - yield and residence time - to match those of ethanol leads to a 65% reduction in the median fuel cost, whereas the switch to anaerobic fermentation and elimination of centrifugation costs yield more modest reductions. The improvement of fermentation yields is the main potential driver of cost reduction, as it would enable increased fuel production - and hence greater revenue - for essentially the same total production cost. Switching from aerobic to anaerobic fermentation reduces capital costs due to less stringent sterilization requirements and the elimination of aeration equipment, and also reduces electricity demand for agitation (see Section 4.2.2). Eliminating the costs of separating FAEE yields the smallest incremental cost reduction.

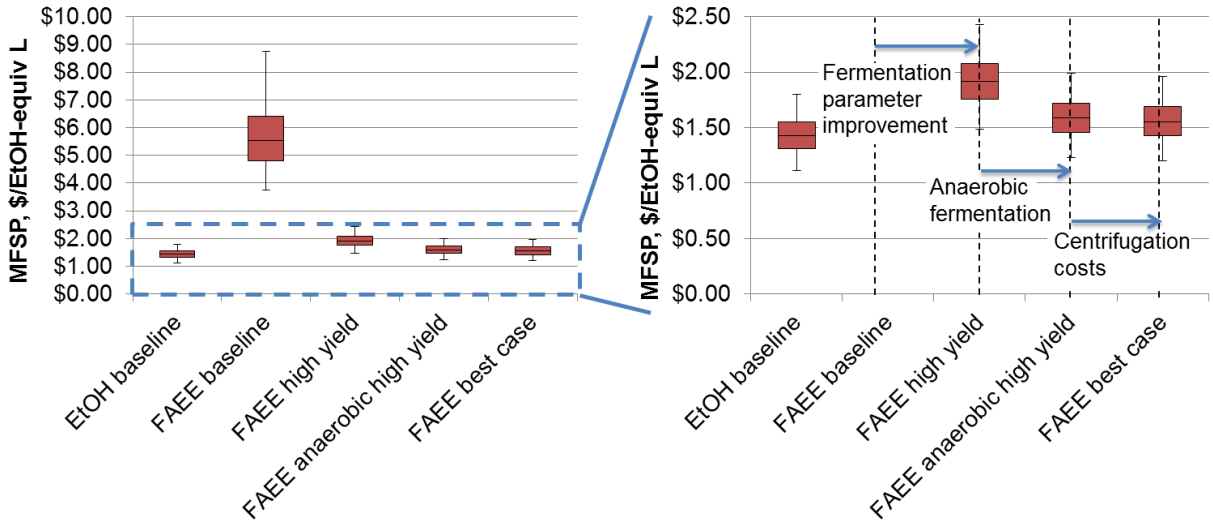

Figure 6. Minimum fuel selling price ($/ethanol-equiv liter) for the EtOH and FAEE scenarios. Stochastic distribution data are tabulated for all scenarios in Appendix A.

Although the advances that would be necessary to attain the FAEE best case scenario in practice present an enormous challenge, even the combination of these three changes does not result in a

median fuel cost that is lower than that for ethanol. Because the only difference between the ethanol baseline process and the FAEE best case scenario - other than the fuel being produced - is the lack of separation costs in the FAEE scenario, one might expect the FAEE costs to be lower; however, the cost reductions that accompany the "free" separation of FAEE are offset by reduced absolute sugar conversion efficiencies that are intrinsic to the metabolic pathways utilized by the microbes to produce FAEE. This conclusion is emphasized in Figure 7, showing a comparison of the costs associated with the ethanol baseline scenario and the FAEE best case scenario. A significant negative contribution due to reduced FAEE separation costs is offset by smaller increases across all other process areas and inputs due to the reduced fuel output. Thus, even in the most optimistic case of technology development for the FAEE production process, the best that can be expected is to match the performance of cellulosic ethanol technology. It is assumed that all improvements in feedstock production practices and pretreatment and hydrolysis technology will apply equally to the production of both fuels.

Despite this seemingly discouraging conclusion, it is important to note that other factors beyond the production cost will play an important role in determining the economic competitiveness of FAEE and other water-immiscible biofuels. Although the distribution and final use of fuels is beyond the scope of the current analysis, other researchers have documented the obstacles to expanding the use of ethanol significantly beyond current levels [97] due to fuel distribution infrastructure and vehicle incompatibilities; in contrast, the widespread use of FAEE or FAEE-diesel blends would be possible with little additional investment in these areas. Use in diesel engines will also enhance the overall efficiency of FAEEs as a fuel due to their higher energy conversion efficiency (translating to a ~20% advantage in fuel economy vs. gasoline engines [98]). Looking beyond road transportation, energy dense water-immiscible biofuels may also be developed for use as jet fuel, an application for which ethanol is unsuited. This last point highlights the fact that ethanol and water-immiscible biofuels are not competing with each other, but rather with petroleum-derived fuels. Given these considerations, it may not be necessary to match the production costs of ethanol in order to justify the large-scale commercialization of FAEE and other advanced biofuels.

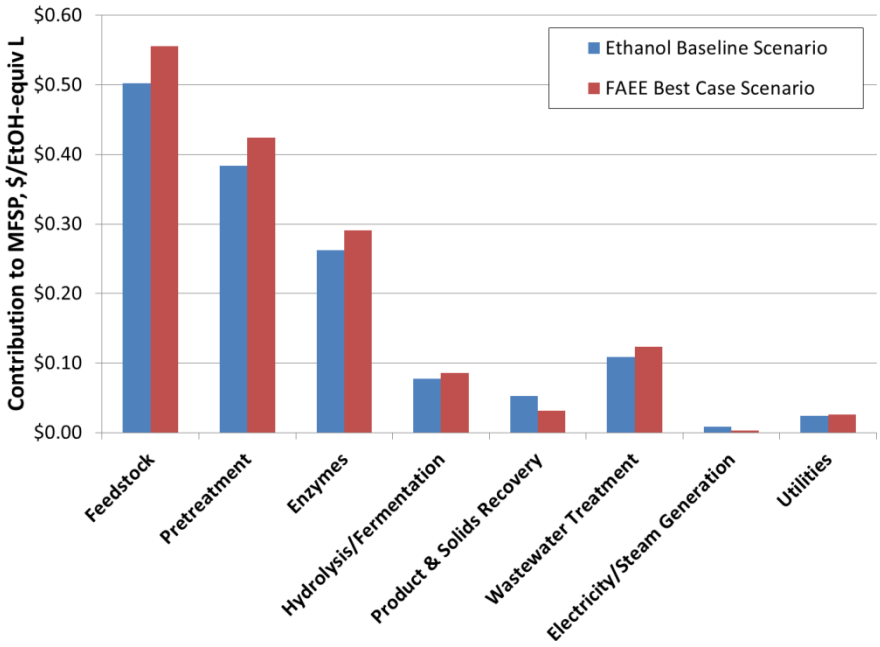

Figure 7. Comparison of costs for the 'most likely' parameter values of the ethanol baseline scenario and FAEE best case scenario by unit operation and major inputs.

4.2.2 Electricity production

The net electricity production for each of the scenarios under consideration is displayed in Figure 8. In contrast with the results for fuel cost, an enhancement in the fermentation performance (represented in the difference between the FAEE baseline scenario and the FAEE high yield scenario) does not result in a significant increase in electricity production, since fuel yield has little effect on the total electricity use. Some improvement is observed due to reduced fermentation residence times assumed in the FAEE high yield scenario; however, it is apparent from Figure 8 that the major driver of electricity consumption in the FAEE process is aerobic fermentation, and in particular the aeration and agitation requirements of the fermentation vessels. In comparison, the electricity consumption of the centrifuges is minor (also see Table 4), as reflected in the very slight rise in net electricity production in moving from the FAEE anaerobic high yield scenario to the FAEE best case scenario.

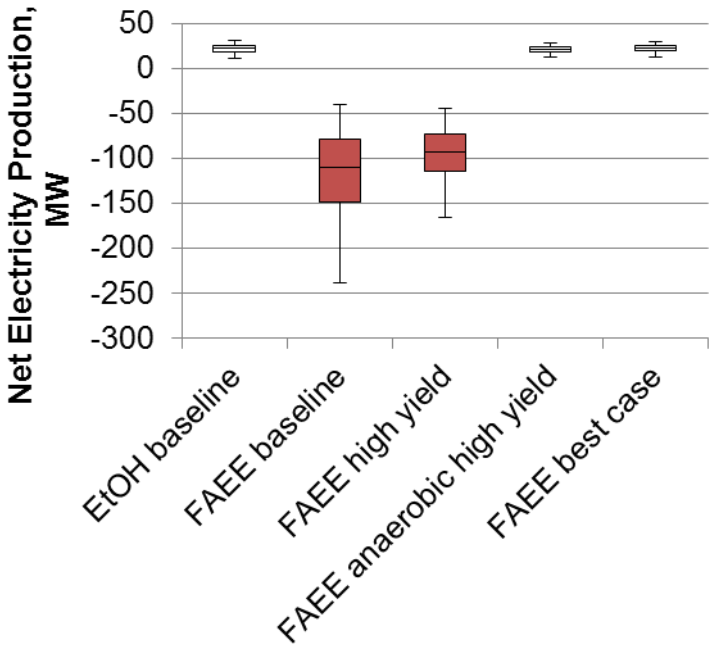

Figure 8. Net electricity production (MW) for the ethanol (EtOH) and FAEE scenarios. Based on a conversion facility receiving 2,000 dry metric tons of switchgrass per day. Stochastic distribution data are tabulated for all scenarios in Appendix A.

Although the elimination of distillation and ethanol drying operations has been offered as a potential justification for pursuing the development of water-immiscible biofuels, the estimated contribution of ethanol separation and purification to total biorefinery energy consumption (and fuel cost) is relatively minor, as seen in Table 4 for the 'most likely' ethanol baseline scenario. Thus, only modest energy and cost reductions for the overall biorefinery can be expected from changes to the product recovery step.

Table 4. Electricity and steam use and total capital costs for distillation and ethanol drying operations in the 'most likely' ethanol baseline scenario, and for centrifugation costs in the 'most likely' case of the FAEE anaerobic high yield scenario.

	Ethanol baseline scenario		**FAEE anaerobic high yield scenario**	
	% of plant total	% of feedstock HHV	% of plant total	% of feedstock HHV
Electricity use	3.1%	0.20%	4.1%	0.27%
Steam use	49.6%	8.5%	-	-
Capital costs	3.7%	-	4.2%	-

4.2.3 Process water consumption

Water losses in the processes under consideration occur primarily through cooling tower evaporation and loss through the flue stack with combustion gases. Since the composition of the materials sent to the combustor is similar across all pathways, the main source of variability in total water consumption is in the cooling load. Inspection of Figure 9 reveals a trend similar to

that of fuel cost in

Figure 6; the main driver of excessive water consumption on a per-fuel-liter basis is low fuel output. Modest reductions in water use accompany the switch from aerobic to anaerobic fermentation, as the cooling load of the fermentation vessels is significantly reduced, and the cooling of centrifuges accounts for the nearly imperceptible decrease in water use between the FAEE anaerobic high yield and best case scenarios.

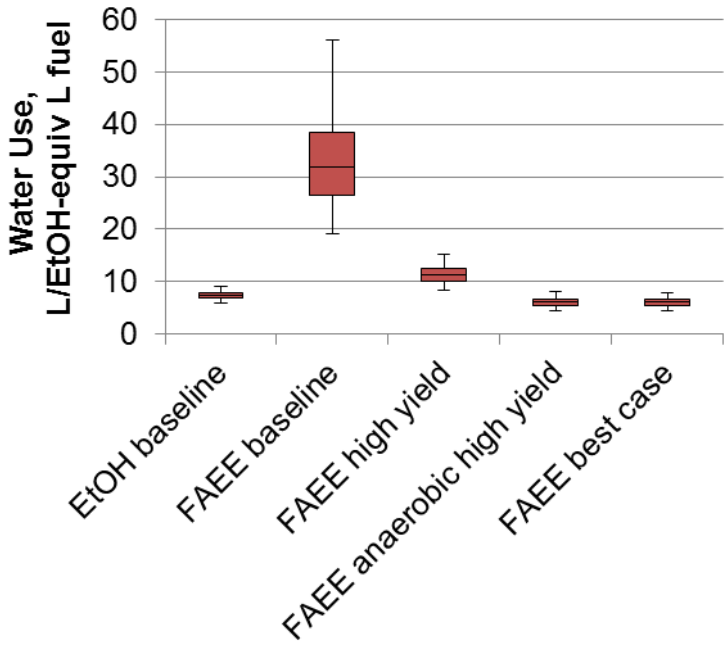

Figure 9. Process water use (liters per ethanol-equivalent liter of fuel) for the ethanol (EtOH) and FAEE scenarios. Stochastic distribution data are tabulated for all scenarios in Appendix A.

4.2.4 GHG emissions

The net GHG emissions associated with each of the scenarios under consideration are shown in Figure 10. As the fermentation yield increases in moving from the FAEE baseline scenario to the FAEE high yield scenario, more fuel is produced as the process inputs which drive GHG emissions - switchgrass, chemicals, and enzymes - remain fixed and process electricity demands are reduced by shorter fermentation residence times. The GHG intensity of the FAEE product is further reduced as the electricity requirements are slashed with the conversion to anaerobic fermentation. The GHG emissions associated with the FAEE anaerobic high yield and best case scenarios are both comparable to those for the ethanol baseline scenario, as the electricity demand of the centrifuges does not significantly impact the results.

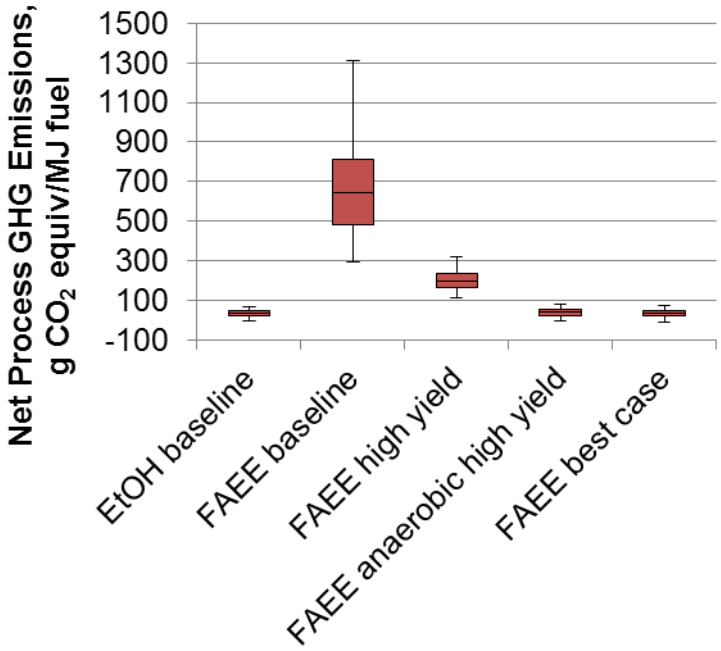

Figure 10. Net process GHG emissions (g CO_2 equivalents per MJ fuel produced) for the ethanol (EtOH) and FAEE scenarios. Stochastic distribution data are tabulated for all scenarios in Appendix A.

5. CONCLUSIONS

The results of the foregoing analysis indicate that biochemical processes to produce FAEE from switchgrass are uncompetitive with similar processes to produce ethanol under the current state of technology development, in terms of both economic and environmental metrics. This may be an unsurprising result, given the short development history of FAEE production technology. However, an investigation of potential improvements to the FAEE production processes highlighted the significant challenges that confront efforts to close the gap in performance with cellulosic ethanol processes.

The two most promising areas for potential improvement to the FAEE processes investigated are 1) an enhancement in fermentation parameters (yield on sugars and fermentation time) and 2) a switch from aerobic to anaerobic fermentation. The main path to process improvement is to increase the fermentation yield, and thus the production of fuel from a given amount of biomass. By improving the fermentation parameters to be on par with those for ethanol, the FAEE processes can make up most of the differences in cost, fuel production, GHG emissions, and water use relative to the ethanol pathways. The switch to anaerobic fermentation will offer modest gains in cost and water use, but will significantly decrease electricity consumption such that the processes become net electricity producers rather than net electricity consumers. Further improvements in FAEE separation efficiency offer only minor cost and energy reductions. Ultimately, FAEE production processes will approach intrinsic limitations in the metabolic pathways utilized by the host microorganisms, which place FAEE at a disadvantage versus ethanol in terms of the maximum potential fuel production from sugars (15.2 MJ of ethanol per kg of sugar vs. 13.8 MJ of FAEE per kg of sugar). This disadvantage in maximum energy conversion efficiency appears to offset any potential gains resulting from the elimination of distillation and dehydration steps in the cellulosic ethanol processes.

Parameters related to the feedstock, pretreatment, and hydrolysis unit operations did not affect fermentation in the model, and thus did not influence the relative performance of the processes used to produce different fuels. However, due to the relatively high yields achievable for ethanol fermentation, these parameters were observed to be major drivers of the performance of the ethanol pathways. Although the AFEX-based processes exhibited slightly lower median fuel costs, median GHG emissions, and water consumption than the dilute acid processes, there was significant overlap in the performance of processes utilizing different pretreatment strategies to produce the same fuel. Improvement in these areas will be crucial to reducing the cost of all cellulosic biofuels in relation to petroleum-derived fuels.

While the feedstock and processing technologies selected for analysis in the current study represent only a small subset of the many potential biochemical pathways from biomass to liquid transportation fuels, the conclusions that have been reached regarding the relative economic and environmental performance of the selected processes to produce ethanol and FAEE can be readily extended to any combination of feedstock and pretreatment method, provided they do not exhibit an influence on the fermentation step that would favor the production of one fuel over the other.

The authors acknowledge that the comparison between processes to produce ethanol and FAEE is an imperfect one, as ethanol is a gasoline additive/replacement and FAEE is appropriate for

diesel engines. However, the results of our analysis are broadly applicable to other water-immiscible biofuels, most if not all of which suffer from similarly low maximum theoretical fermentation yields (see [61] for a discussion and examples). This point also underscores the need to extend the scope of such comparisons beyond the biorefinery to the distribution of the fuel to end users and ultimately to combustion in engines. Further study is needed to explore the question of whether potential advantages in infrastructure compatibility and combustion efficiency will be sufficient to overcome the apparent process limitations of producing FAEE for fuel via biochemical pathways.

6. REFERENCES

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APPENDIX A: TABULATION OF STOCHASTIC DISTRIBUTIONS

Stochastic distributions presented graphically in Figures 2, 3, 6, and 8-10 of the report are tabulated in the following tables.

Table A-1. Minimum fuel selling price ($ per ethanol-equivalent liter) for all pathways to ethanol and FAEE. Data are presented in Figure 2a.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Dilute Acid-Ethanol	$1.11	$1.31	$1.43	$1.55	$1.80
AFEX-Ethanol	$0.96	$1.17	$1.28	$1.40	$1.70
Dilute Acid-FAEE	$3.74	$4.79	$5.53	$6.42	$8.76
AFEX-FAEE	$3.09	$3.99	$4.62	$5.41	$7.50

Table A-2. Fuel yield (ethanol-equivalent liters per dry metric ton of dry biomass) for all pathways to ethanol and FAEE. Data are presented in Figure 2b.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Dilute Acid-Ethanol	240.0	261.9	274.3	287.5	315.2
AFEX-Ethanol	237.0	261.0	275.1	289.9	319.8
Dilute Acid-FAEE	59.3	77.6	88.4	99.6	120.1
AFEX-FAEE	59.3	78.5	89.8	101.5	122.9

Table A-3. Net electricity generation (MW) for all pathways to ethanol and FAEE, assuming a biomass feed rate of 2000 dry metric tons per day. Data are presented in Figure 2c.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Dilute Acid-Ethanol	11	19	23	26	31
AFEX-Ethanol	0	12	17	21	29
Dilute Acid-FAEE	-238	-149	-109	-78	-40
AFEX-FAEE	-241	-137	-99	-70	-34

Table A-4. Process water consumption (liters of water per liter of ethanol-equivalent fuel produced) for all pathways to ethanol and FAEE. Data are presented in Figure 2d.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Dilute Acid-Ethanol	5.87	6.80	7.33	7.89	9.09
AFEX-Ethanol	1.06	2.25	3.08	3.99	5.91
Dilute Acid-FAEE	19.12	26.55	31.79	38.40	56.05
AFEX-FAEE	4.99	11.63	16.46	22.56	40.56

Table A-5. Net GHG emissions (g CO_2 equivalents per MJ fuel produced) for all pathways to ethanol and FAEE. Values in parentheses do not include credits due to co-production of electricity. Data are presented in Figure 3.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Dilute Acid-Ethanol	-3 (30)	19 (48)	33 (61)	47 (74)	68 (94)
AFEX-Ethanol	-15 (18)	2 (26)	12 (33)	23 (41)	47 (60)
Dilute Acid-FAEE	295	482	645	811	1312
AFEX-FAEE	212	373	502	674	1180

Table A-6. Minimum fuel selling price ($ per ethanol-equivalent liter) for ethanol and FAEE scenarios. Data are presented in Figure 6.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Ethanol Baseline	$1.11	$1.31	$1.43	$1.55	$1.80
FAEE Baseline	$3.74	$4.79	$5.53	$6.42	$8.76
FAEE High Yield	$1.48	$1.76	$1.91	$2.08	$2.43
FAEE Anaer. High Yield	$1.23	$1.46	$1.59	$1.72	$1.99
FAEE Best Case	$1.20	$1.42	$1.55	$1.69	$1.96

Table A-7. Net electricity generation (MW) for ethanol and FAEE scenarios, assuming a biomass feed rate of 2000 dry metric tons per day. Data are presented in Figure 8.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Ethanol Baseline	11	19	23	26	31
FAEE Baseline	-238	-149	-109	-78	-40
FAEE High Yield	-166	-114	-92	-73	-44
FAEE Anaer. High Yield	12	18	21	24	29
FAEE Best Case	13	20	23	25	30

Table A-8. Process water consumption (liters of water per liter of ethanol-equivalent fuel produced) for ethanol and FAEE scenarios. Data are presented in Figure 9.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Ethanol Baseline	5.87	6.80	7.33	7.89	9.09
FAEE Baseline	19.12	26.55	31.79	38.40	56.05
FAEE High Yield	8.28	10.13	11.29	12.57	15.23
FAEE Anaer. High Yield	4.50	5.52	6.12	6.74	8.04
FAEE Best Case	4.40	5.45	6.05	6.68	8.00

Table A-9. Net GHG emissions (g CO_2 equivalents per MJ fuel produced) for ethanol and FAEE scenarios. Values include credits due to co-production of electricity. Data are presented in Figure 10.

Pathway	2.5th percentile	25th percentile	50th percentile	75th percentile	97.5th percentile
Ethanol Baseline	-3	19	33	47	68
FAEE Baseline	295	482	645	811	1312
FAEE High Yield	110	165	196	235	322
FAEE Anaer. High Yield	-2	23	38	54	81
FAEE Best Case	-8	19	34	49	73

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