



Biorefinery upgrading of herbaceous biomass to renewable hydrocarbon fuels, Part 1: Process modeling and mass balance analysis

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ABSTRACT

Process simulation has long been a well-established tool to track key operational, design, and mass and energy balance metrics for pre-commercial technologies such as advanced lignocellulosic biofuels. While tools such as this are well-documented in the public literature around 2nd-generation cellulosic ethanol technologies (which have been scaled up to commercial deployment to some degree over the past decade), such models and analysis information remain more sparse for more complex biorefinery pathways focused on producing drop-in hydrocarbon fuels and blend-stocks, particularly regarding information required to support air emissions or other environmental analysis. In this work, we summarize key details for an established “design case” modeling the conversion of herbaceous lignocellulosic biomass into a renewable diesel hydrocarbon blend-stock based on a representative lipid pathway from oleaginous yeast. The process is based on a biochemical deconstruction and upgrading approach utilizing deacetylation and dilute acid pretreatment, followed by enzymatic hydrolysis, fermentation, and catalytic upgrading of hydrolysate sugars to fuels. We provide key mass and energy balance outputs from the process models, with accompanying stream tables and component-level flowrates. A total of 12 model scenarios are presented spanning two feedstocks, three biorefinery scales, and two processing approaches for the lignin/residual solids waste streams. This “Part 1” manuscript presents the resulting impacts across the 12 cases on fuel yields and key output streams, focused here on direct biorefinery air emissions for selected components including CO₂ as well as sulfur (SO_x) and nitrogen oxides (NO_x). In the context of cleaner production, the latter focus on selected biorefinery air emission outputs establishes an initial baseline estimate and accompanying framework of the model cases, upon which an accompanying “Part 2” study will build to refine the values for these and other air pollutants across these scenarios, also considering mitigation options to comply with applicable regulatory standards. We also highlight further optimization opportunities based on potential tradeoffs identified here between air emissions versus life-cycle greenhouse gas profiles attributed to the disposition of lignin/residual solids.

1. Introduction

For many years, process modeling has been used to guide energy technology research and development efforts (Kumar et al., 1993), as a key tool to prioritize research directions as well as to envision an integrated process to highlight important considerations for technology commercialization and scale-up (Sukumara et al., 2015). In the case of

biofuels, numerous such analyses based on rigorous process design models have been published, focused initially on 2nd-generation (2G) lignocellulosic ethanol. Laser et al. (2009) performed process modeling using Aspen Plus framework and techno-economic analysis (TEA) for seven process design scenarios for conversion of switchgrass to ethanol. Gregg et al. (1998) evaluated the effects of increased cellulose yield and enzyme recycling on the economics of a wood-to-ethanol conversion

Abbreviations: AD, anaerobic digestion; BC, bubble column; CO₂, carbon dioxide; DDA, deacetylation and dilute acid; FGD, flue gas desulfurization; FFA, free fatty acid; GGE, gallon gasoline equivalent; INL, Idaho National Laboratory; LCA, life-cycle analysis; MM, million; MSW, municipal solid waste; MVR, mechanical vapor recompression; NO_x, nitrogen oxides; NREL, National Renewable Energy Laboratory; NRTL, non-random two-liquid; OFA, over-fire air; OTR, oxygen transfer rate; RDB, renewable diesel blend-stock; SNCR, selective non-catalytic reduction; SO_x, sulfur oxides; STR, stirred-tank reactor; TEA, techno-economic analysis; TPD, tonne per day; UFB, uniform format blend; WWT, wastewater treatment.

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process utilizing a detailed process model. Similarly, Franko et al. (2016) performed TEA for a cellulosic ethanol biorefinery using forest residues as a feedstock from a process model simulated in Aspen Plus. While more room for technology development and scale-up exists for 2G ethanol, in order to further expand the market volume potential for biofuels to contribute to national and global fuel energy supply in support of today's fuel infrastructure, process modeling and analysis efforts have shifted focus over more recent years towards fungible hydrocarbon fuel pathways. For example, Michailos et al. (2017) performed a techno-economic comparison between Fischer-Tropsch and fast pyrolysis pathways, while Baral et al. (2019) focused on decarbonizing the air transportation sector by investigating five bio-jet conversion technologies. Also, Sorunmu et al. (2020) focused their analysis on modeling for upgrading fast pyrolysis bio-oil to drop-in fuels and co-products for decarbonizing chemical markets. For any such pathway, TEA and life-cycle analysis (LCA) are complementary tools which together alongside process modeling can provide a comprehensive picture of the economic and environmental sustainability implications for the pathway (Sorunmu et al., 2020). Such tools allow for examination of cost (TEA), greenhouse gas or other emissions (LCA), and feedback loops connecting those metrics together (e.g., costs of emissions mitigation) (Baral et al., 2019).

Similar trends have been reflected at the National Renewable Energy Laboratory (NREL), following a shift in focus in TEA modeling from demonstration of 2G ethanol process and cost targets in 2011–2012 to newer pathways for production of hydrocarbon fuels or fuel blendstocks over 2013–2018. For instance, Humbird et al. (2011) and Dutta et al. (2011) in 2011 documented models focused on process design and economics for conversion of lignocellulosic biomass to ethanol through biochemical and thermochemical pathways, respectively. Tao et al. (2014) incorporated updates to the biochemical conversion process areas to benchmark the economic performance reflective of demonstrated bench- and pilot-scale data. In 2012, Dutta et al. (2012) further investigated the production and economics of ethanol production from woody biomass via indirect gasification. Following achievement of economic targets based on demonstrated experimental performance for ethanol production, the focus was shifted to production of fungible hydrocarbon fuels and blendstocks (Davis et al., 2013) as well as bio-derived chemicals (Davis et al., 2018). For example, Dutta et al. (2015) shifted their focus to production of gasoline and diesel blendstock via *in situ* and *ex situ* upgrading of fast pyrolysis vapors while Tan et al. (2015) focused on designing technologies to convert lignocellulosic biomass to high-octane gasoline blendstock through methanol/dimethyl ether intermediates. For technologies focused on biochemical processing via herbaceous biomass deconstruction and subsequent fermentation of cellulosic sugars, this was initiated through a “design report” published in 2013 documenting future technical targets that were envisioned to translate to a modeled minimum fuel selling price (MFSP) projection of approximately \$5 per gallon gasoline equivalent (GGE) (Davis et al., 2013). The underlying process model for that pathway reflected a design broadly focused on deacetylation and dilute acid (DDA) pretreatment of herbaceous lignocellulosic biomass, followed by enzymatic saccharification and fermentation of pretreated hydrolysate to fatty acids and subsequent catalytic upgrading of the fatty acid intermediates to paraffinic hydrocarbons constituting a “renewable diesel blend-stock” (RDB). The RDB term is used throughout this paper to acknowledge that the final hydrocarbon product produced from this particular pathway (hydrotreated lipids) may not constitute a neat fuel meeting all applicable specifications on its own (for example, this product may not meet cloud point and other cold-flow property specifications for diesel fuel without an added isomerization step), but still may be blended with petroleum fuels. This may provide an important first step to decarbonize transportation fuels while leveraging existing hydrocarbon fuel infrastructure and engine technologies.

The NREL 2013 design case established a benchmark process for a hypothetical biorefinery geared towards RDB production, presenting

design and economic details for such a process based on rigorous mass and energy balance simulations in Aspen Plus (2019). While numerous variations in each step of the modeled biorefinery are possible based on different technologies for pretreatment, hydrolysis, and fermentation/upgrading, this design case presents a representative example for one “typical” selection of such operations as are the subject of considerable research (recognizing that it is impossible to reflect a “typical” biorefinery for advanced cellulosic hydrocarbon biofuels as no such biorefinery yet exists at commercial scale). Based on the details presented in such an analysis, other factors may also begin to be considered such as environmental implications for constructing and operating a biorefinery for biochemical RDB production, e.g., ramifications on air quality based on criteria air pollutant emissions and needs for mitigation controls. However, the focus on the reports cited above was primarily on the relevant processing operations for in-scope technology performance and resulting production costs; while supporting operations were also accounted for in the process models, including a residual solids boiler, power generation, wastewater treatment, and other utilities, the Aspen Plus models were not focused on tracking air emissions or criteria air pollutant components (particulates, sulfur dioxide, nitrogen oxides, etc.) in great detail, and further analysis of such details is warranted. More generally, very few detailed process models have been published as may support a comprehensive sustainability or life-cycle assessment around the influence on environmental metrics attributed to variances in biorefinery scale, feedstock, or product choices. This work addresses this gap by providing critically needed information to allow for sustainability analysis across a comprehensive range of inputs, namely an analysis of air pollutant emissions which are commonly overlooked in prior studies of advanced cellulosic biofuels.

Accordingly, here in this “Part 1” work we provide a summary of the modeled 2013 design case and further details around mass balances reflected in the models after making updates to the base case, to serve as an initial basis for subsequent work to focus on air emissions, controls, and applicable regulations for such a process. Additionally, we expand the models in Aspen Plus to include additional scenarios for feedstock scale and delivered feedstock type/composition, evaluating impacts on resulting mass balances and fuel yields/emissions outputs. Finally, in light of the lignin solids boiler representing the primary source of air pollutant emissions for the integrated biorefinery (Davis et al., 2013), we also consider an alternative disposition of the lignin through pelletizing and sale of lignin pellets for use off-site. The focus of this work is *not* on TEA modeling and production costs, nor optimization therein, but strictly on the process design scenarios and associated mass balance/yield details generated from the Aspen Plus models. The outputs of this study will be leveraged in our accompanying “Part 2” study for more in-depth air emissions considerations attributed to the modeled scenarios. The two-part format of this work allows for presentation of the framework and process simulation outputs across all scenarios in greater detail than would be afforded by a single combined paper. Taken together, these two accompanying papers present a comprehensive analysis for one exemplary biorefinery configuration for advanced hydrocarbon biofuel production across a range of feedstock and lignin usage scenarios, highlighting carbon, mass, and energy balances and associated air emissions implications in detail. This may allow for subsequent process optimization opportunities when considering permitting and deployment of such scenarios, particularly if considered alongside TEA and LCA impacts.

2. Methodology

2.1. Aspen model framework

The biorefinery process configurations as considered here are depicted in Fig. 1. The base case schematic is documented in detail in Davis et al. (2013). In summary, the base case configuration processes 2000 dry metric tonne per day of herbaceous biomass feedstock,

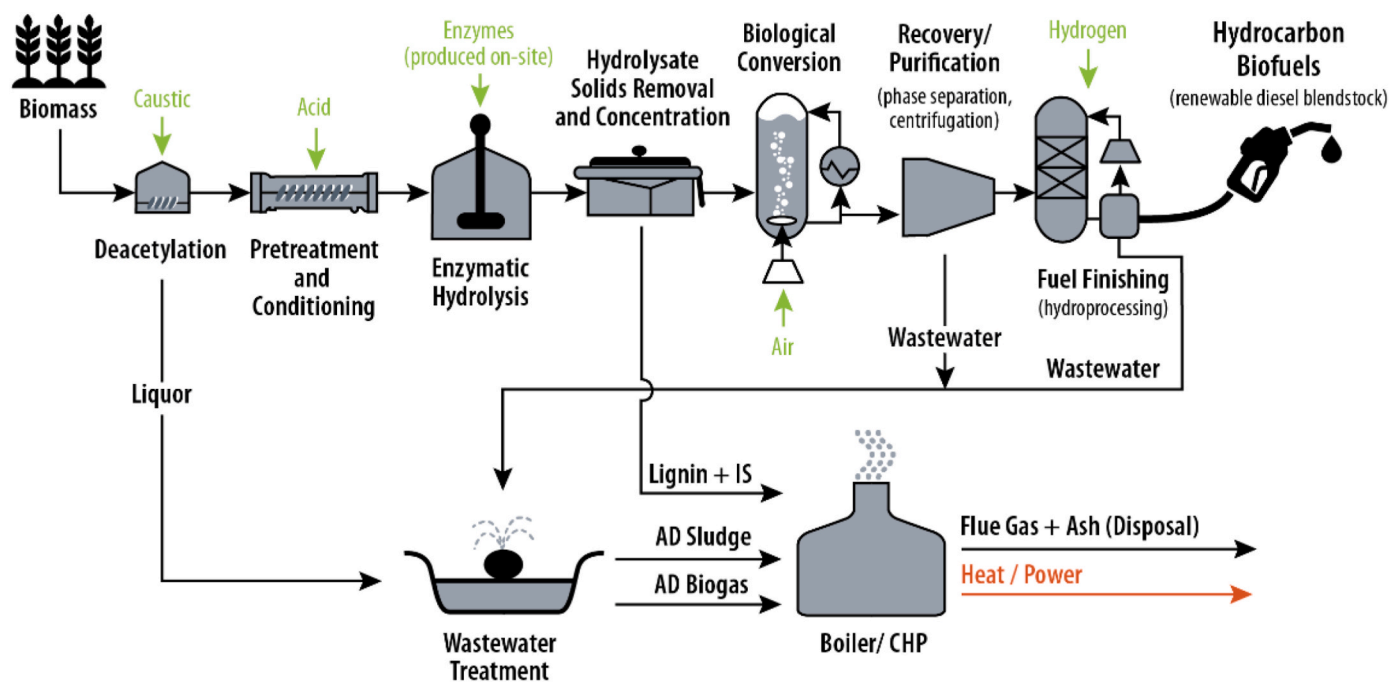


Fig. 1. Schematic diagram of biorefinery process for biochemical production of RDB fuel blend-stock.

delivered to the DDA pretreatment operation. In this step, the biomass is subjected to a mild alkaline deacetylation reaction, utilizing 17 kg NaOH/tonne dry biomass in a stirred tank at 80 °C for 1 h, after which point solubilized black liquor is drained from the tank, removing with it a majority (88%) of the acetate in the incoming biomass feedstock (known to be a typical fermentation inhibitor [Aghazadeh et al., 2016]), as well as 75% of the biomass ash, 20% of the lignin, and 100% of water-soluble extractives; see Supporting Information (SI) Table S1. Additionally, some loss (2%) of xylan is incurred into the black liquor phase. The black liquor is routed to on-site wastewater treatment (WWT), consisting of anaerobic and aerobic digestion, clarification, sludge dewatering, and reverse osmosis, to maximize water recovery and reuse in the process. The deacetylation solids are subjected to dilute acid pretreatment, utilizing sulfuric acid at a loading of 9 kg/tonne dry biomass as present in the pretreatment reactor. This step takes place at 160 °C for 5 min at 30 wt% total solids loading, with temperature and solids content controlled by high-pressure steam injection. The operation is targeted to achieve 90% conversion of hemicellulose components (namely xylan and arabinan) to monomeric sugars, as well as 9.9% conversion of glucan to glucose. Further details for all key biorefinery unit operations are provided in the Supporting Information. The Aspen Plus model cases make use of the non-random two-liquid (NRTL) property package as the default thermodynamic property method given the widespread presence of oxygenated/polar molecules across most of the unit operations generally operating under mild temperature and pressure conditions. Aspen native properties are utilized along with custom component specifications as necessary to specify non-native components (e.g. organism cell mass, hemicellulose components, enzymes and other protein components) – further details on custom component specifications may be found in Appendix D of the Davis et al. (2013) report.

The pretreated material is cooled, flashed, and neutralized with ammonium hydroxide, then routed to enzymatic hydrolysis. This step is targeted to achieve 90% of glucan to glucose utilizing cellulase enzymes produced on-site, at a loading of 10 mg enzyme protein per g of cellulose with a total solids loading of 20 wt% (SI Table S2). Saccharification is initiated in a 24-h continuous liquefaction vessel, followed by 2.5 days of additional time in batch stirred tank reactors. The hydrolysate is then clarified through a two-stage vacuum belt filter press to remove lignin

and residual solids, and partially concentrated via mechanical vapor recompression (MVR) evaporation (increasing the sugar concentration from 14 to 46 wt%). The hydrolysate is then routed to fermentation, splitting 10% of the stream to initiate biomass organism propagation in a seed train and 90% to primary bioconversion (SI Table S3). Bioconversion takes place via aerobic fed-batch fermentation, targeting 95% conversion of glucose and 85% of arabinose and xylose to fatty acids (represented in the model as palmitic acid, though recognizing in reality a mixture of fatty acid components would typically be produced [Patel et al., 2017]), for a total fatty acid process yield of 0.28 g/g sugars at a fermentation productivity of 1.3 g/L-hr. The process assumes the use of a bacterial organism capable of secreting the fatty acid product (Westfall and Gardner, 2011), given high energy and costs associated with intracellular extraction (Huang and Zhang, 2011). Thus, secreted fatty acids are targeted to be recovered via simple phase separation (decantation/centrifugation).

Finally, the recovered fatty acids are upgraded in a hydrotreating facility, following process design and costing guidance from commercial vendors in consultation with an engineering subcontractor (Davis et al., 2011) and published literature (Marker, 2005). The upgrading process consists of relatively mild hydrotreating conditions at 350 °C and 35 atm but high hydrogen feed ratio of 6000 standard cubic ft/bbl and 1.2 hr⁻¹ liquid hourly space velocity (SI Table S4), achieving complete conversion of the model palmitic acid component to an equimolar mixture of pentadecane and hexadecane, representing a simplistic reaction mechanism for deoxygenation to both water and CO₂. The reactor product stream is cooled via feed/effluent cross-exchange and trim cooling, and flashed to recycle hydrogen after removing CO₂ and other off-gases in a pressure swing adsorption unit.

The biorefinery also includes supporting operations for on-site WWT, boiler combustion of solids and other residual byproduct streams, steam turbine co-generation to produce power, and utility units such as cooling water and chiller systems. The WWT system is configured to maximize water reuse and minimize discharge, based on design guidance provided by a WWT technology consultant (Steinwinder et al., 2011). In this process, anaerobic digestion (AD) provides primary destruction of organics, with further treatment completed by aerobic digestion. The solids from AD and aerobic digestion are dewatered, and the clarified effluent is routed to reverse osmosis for removal of salts (primarily those

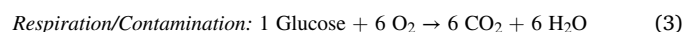
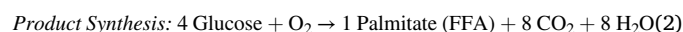
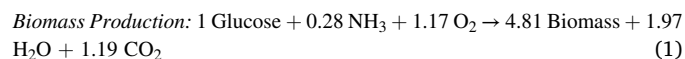
formed from upstream addition of acid and base during pretreatment processing), with additional water recovered from evaporation of the brine stream.

The boiler is a key unit operation in the present work scope, representing the majority of the biorefinery air emissions, which will be the subject of our accompanying “Part 2” manuscript expanding from this work. The design, operational, and cost details for the boiler were based on guidance from a vendor, as documented in previously published work (Humbird et al., 2011). In summary, the unit is specified as a bubbling fluidized bed boiler designed to accommodate high-moisture feedstocks, in this case the lignin solids cake from upstream hydrolysate clarification and the WWT sludge stream, also combined with all biorefinery off-gas streams. The boiler package quotation utilized in the TEA includes emission controls for SO_x via flue gas desulfurization (FGD) and NO_x via selective non-catalytic reduction (SNCR) and over-fire air (OFA). After accounting for a 6.6% thermal efficiency loss, the heat raised in the boiler is used to generate superheated steam at approximately 450 °C and 60 atm, which is routed through a multi-stage steam turbine to generate power, with intermediate extraction points to supply steam for biorefinery process/utility needs. The generated electricity is used to support biorefinery power demands, with a net excess surplus sold to the grid as a coproduct (for the base case burning lignin and residual solids; in the present study, alternative scenarios routing lignin to a pelletizer reduces power generation and requires a net power input). The boiler process conditions are summarized in SI Table S5.

2.2. Modifications to base case model

For this study, a number of updates were made to the base case Aspen model framework relative to the details documented in the design report (Davis et al., 2013), reflecting more recent improvements in the TEA modeling fidelity for key units, namely fermentation and boiler operations. For the former, the fermentor design was updated from a stirred tank reactor (STR) to a bubble column (BC), given the BC design as the more standard commercial approach to aerobic fermentation as confirmed in consultation with industry (Crater et al., 2017) and given advantages in more economical delivery of oxygen to the culture (Humbird et al., 2017). Additionally, the organism biomass composition was updated consistent with models described in Biddy et al. (2016). Numerous organisms are being investigated for production of fatty acids, but the present model assumes the use of *Lipomyces starkeyi*, a

frequently researched oleaginous yeast with a modeled composition $C_1H_{1.85}O_{0.83}N_{0.06}$ for the lipid-free portion of the cell mass (Anschau and Franco, 2015). The BC operational logic was also updated as described in Humbird et al. (2017) and reflected in Fig. 2, employing a continuous pump-around loop to circulate the broth through a chiller for removal of heat generated from the exothermic reaction, and to better synchronize the aeration requirements to the oxygen transfer rate (OTR) (following oxygen mass transfer equations developed by Van't Riet and Tramper et al., [1991] and expanded upon by Doran [1995]), as necessary to satisfy the targeted fermentation productivity rate and stoichiometric oxygen demands according to the example equations for glucose:



Additional updates were made to the boiler operation, relative to the original basis documented in the design report. Primarily, the fermentor vent stream was routed to the boiler for combustion of volatile organic compounds present in this stream, following previously identified recommendations to meet regulatory requirements (Eberle et al., 2017). Additionally, the boiler was specified to generate combustion reactions, relative to previously published models that manually specified individual stoichiometric combustion equations (Humbird et al., 2011). This allows for more robust automation of this operation and more accurate calculation of resulting heat generation. Finally, the modeling sequence was modified to explicitly reflect inclusion of the SNCR unit for NO_x control, which had implicitly been part of the overall boiler design package but not previously included in the Aspen model framework. The model maintains assumptions for NO_x and CO generation from the boiler of 0.2 l b/MM BTU heat input based on previously documented work (Humbird et al., 2011), with NO_x subsequently reduced by 55% through the combination of SNCR and over-fire air, utilizing ammonia for SNCR in stoichiometric quantities. SO_x generation (reflected as SO₂ in the models) is calculated via the automated combustion reaction specifications in the model, subsequently reduced by 92% in the FGD operation by reaction with lime (calcium hydroxide). We stress that these are preliminary estimates in keeping with previously published work (Davis et al., 2013); as such air emissions metrics have not historically been a focus for such prior modeling work, these details will be

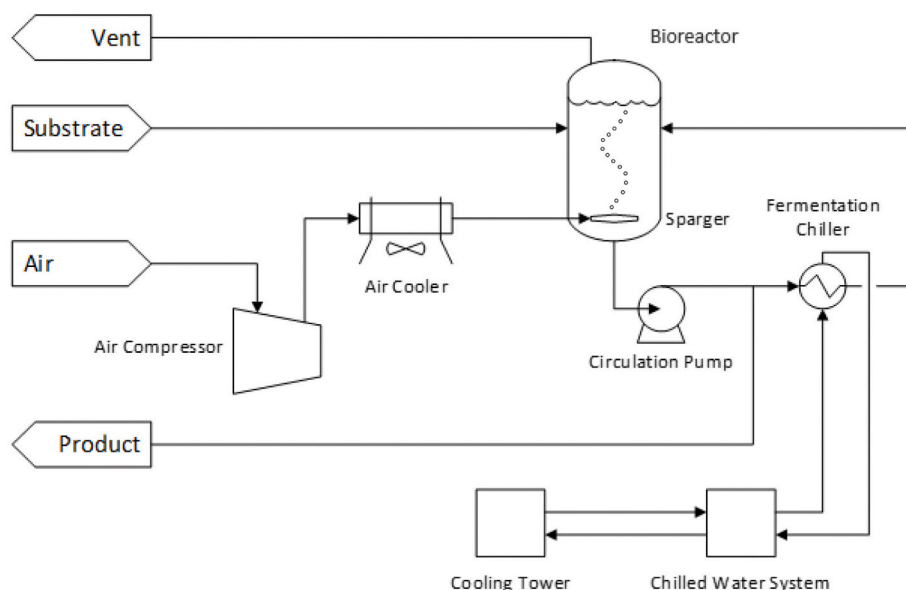


Fig. 2. Updated bioreactor modeling logic. Modified from Humbird et al. (2017).

further investigated and refined in our “Part 2” study focused on this subject.

2.3. Model scenario studies

A total of 12 model scenarios are considered here, spanning three biomass feed rate scales, two feedstock types, and two approaches for lignin/residual solids handling, summarized in Table 1. We stress that the scope of this manuscript is not intended to select a single condition as a “winner” based on a process optimization method, but rather to present the mass and energy output details of all modeled scenarios as well as initial estimates for selected air emissions components upon which the accompanying “Part 2” study builds (including optimization to mitigate emissions in light of applicable permitting guidelines). However, each individual scenario has itself undergone process optimization, e.g. considering process recycles and heat integration to minimize wasted energy and maximize yields. Additionally, this study focuses on a single biomass deconstruction technology approach via DDA pretreatment and enzymatic hydrolysis to saccharify carbohydrates to sugars, followed by a single upgrading technology approach to convert sugars to hydrocarbon fuels. Numerous other technology options exist for both deconstruction and conversion approaches, with distinct advantages and challenges. For example, Tao et al. (2011) presented a comprehensive analysis of process and economic comparisons spanning six pretreatment technologies for conversion of switchgrass to ethanol, finding substantial differences in monomeric sugar yields ranging from 52 to 79% corresponding to similarly dramatic ranges in minimum ethanol selling price between \$2.74–\$4.09 per gallon. Such a multi-technology comparison is beyond the scope of this study, focusing instead on a single design case framework evaluated across the variations summarized in Table 1.

First, the biomass feed rate is varied across a range from 2000 to 9100 dry tonne/day to track resulting yield outputs and emission rates across such a range in scale. The 2000 tonne/day base case is consistent with previously published reports, representing a *n*-th-plant scale envisioned for a commercial facility as an optimum between biorefinery economies of scale versus economical feedstock delivery costs (Aden et al., 2002). The upper range was selected strictly for hypothetical analysis to estimate air emission rate outputs for a scale more comparable to a small petroleum refinery (approximately 150 MM gal/year diesel fuel output) (U.S. Energy Information Administration, 2020). However, it is recognized that such a scale may exceed practical constraints imposed by reverse economy of scale trends (Kenney et al., 2013) given that larger biorefinery scales require an increasingly larger biomass collection radius and transportation distance to supply such a feed rate resulting in higher delivered feedstock costs (Argo et al., 2013) (though economics are not part of the present analysis). The intermediate scale is selected as an approximate mid-point between the two

Table 1
Scenario cases evaluated in this study.

Parameter	Cases Evaluated	Notes
Feed rate (dry tonne/day)	2000/5200/9100	Hypothetical evaluation between commercial scale envisioned for a biorefinery versus that for a small petroleum refinery ^a
Feedstock type	Uniform format blend/corn stover	Evaluate potential impacts on target fuel yields and emissions outputs based on differing feedstock compositions
Lignin/solids handling	Boiler/Pelletized coproduct	Establish base models to evaluate implications for emissions rates from boiler based on combusting all solids versus gas-only (pelletize solids)

^a 2000 dry tonne/day lower bound corresponds to published base-case (Davis et al., 2013), while 9100 dry tonne/day upper bound corresponds more closely to a small-scale petroleum refinery (150 MM gal/year output) as a reference for emissions estimates.

bounds.

Two feedstock materials are considered, with details presented in Table 2. The first, termed the “uniform format blend” (UFB), constitutes the basis as reflected in the 2013 design report (Davis et al., 2013), in turn based on feedstock logistics goals established at that time from Idaho National Laboratory (INL) reflecting a blend of herbaceous feedstocks projected to achieve cost and compositional specifications (Jacobson et al., 2014). Based on INL’s analysis considering feedstock availability, composition, processing logistics, and delivery costs, the resulting blend consisted of 60% corn stover (35% single-pass, 25% multi-pass), 35% switchgrass, and 5% municipal solid waste (MSW). Single-pass versus multi-pass stover refers to the number of passes taken through the field during stover collection, where a multiple-pass harvesting system collects more introduced ash (dirt and other inorganics) than a single-pass harvesting method which may utilize a single piece of equipment to collect the stover. The resulting compositional specifications for the UFB material are provided in Table 2, in turn utilized as the base case in the biorefinery design report. Alternatively, a feedstock reflective exclusively of corn stover alone is also considered here. For this case, the INL 2019 “State of Technology” basis was utilized, reflecting a mix of 33% three-pass and 67% two-pass corn stover (Roni et al., 2020b). The resulting corn stover blend is similar in composition to the UFB case, with comparable overall carbohydrate content and more lignin and ash, offset by lower acetate and extractives contents. The resulting compositions for either feedstock case were input to the Aspen conversion models to evaluate resulting impacts on output yields and emissions rates.

Finally, two options for lignin/solids disposition are considered. The base case maintains routing all solids to the boiler, primarily lignin/residual solids cake from hydrolysate clarification and WWT sludge streams, alongside biorefinery off-gas waste streams (AD biogas, fermentor vent, hydrotreating off-gas, and lignin filter press vent streams) as summarized previously. Recognizing this represents the largest single source of air emissions in the biorefinery (Eberle et al., 2017), an alternative case removes the lignin and WWT sludge streams from the boiler, resulting in a gas boiler combusting only the remaining gas streams. In this case, the lignin solids material is routed to a pelletizer to sell lignin pellets for use off-site, while the WWT sludge is assumed to be sent for further treatment in off-site wastewater processing. The boiler details are maintained consistently with the solids boiler case, except that the emissions estimates for NO_x and CO are reduced to 0.16 and 0.017 l b/MM BTU, respectively (prior to SNCR

Table 2
Feedstock types/compositions evaluated through biorefinery process models.

Component (dry wt%)	INL 2014 Uniform Format Blend ^b	3-Pass Stover	2-Pass Stover	Corn Stover Blend ^c
Glucan	35.1	35.4	37.1	36.5
Xylan	19.5	17.4	18.4	18.1
Lignin	15.8	15.8	16.6	16.4
Ash	4.9	12.2	7.6	9.2
Acetate ^a	1.8	0.1	0.2	0.2
Protein	3.1	2.9	3.1	3.0
Extractives	14.7	11.5	12.2	12.0
Arabinan	2.4	2.1	2.2	2.2
Galactan	1.4	1.1	1.2	1.2
Mannan	0.6	0.5	0.5	0.5
Sucrose	0.8	0.8	0.9	0.8
Total carbs (excl. sucrose)	59.0	56.5	59.4	58.5
Moisture (bulk wt %)	20.0	11.5	11.5	11.5

^a Represents acetyl groups present in the hemicellulose polymer; converted to acetic acid in pretreatment.

^b Blend consists of 35% single-pass corn stover, 25% multi-pass corn stover, 35% switchgrass, 5% MSW (Jacobson et al., 2014).

^c Corn stover consists of 33% three-pass, 67% two-pass corn stover (Roni et al., 2020b).

controls for NOx), based on published emission factor guidelines for biogas-fired combustion (U.S. Environmental Protection Agency, 2000). Further information on boiler sizes based on feed heat input rate across the various scenarios is provided in SI Table S6. Details for the lignin pelletizer were based on published reports for whole corn stover pelletizing, namely dewatering (utilizing a lignin pressure filter) and drying to 18 wt% moisture utilizing a drum dryer, with further moisture losses across the pelletizer due to self-heating (Roni et al., 2020a). The resulting combined vent stream from lignin drying, pelletizing, and pellet cooling represents an additional emissions source for the biorefinery under this scenario. In contrast to the burn lignin scenario, the lignin pelletizing scenario generates less heat and power, leaving a net power import demand rather than an exported coproduct after considering biorefinery power requirements (i.e., additional electricity is purchased from the grid). While alternative uses of the lignin e.g. for higher-value coproducts are also possible, many such approaches are in nascent stages of experimental development (Davis et al., 2018), and this work considers lignin pelletization as a more near-term deployment opportunity.

3. Results and discussion

The resulting yields and key emission outputs as reflected in the Aspen models are presented in Fig. 3, with further mass and energy balance details provided in Table 3. A more complete stream table with component-level mass flows is provided in the Supporting Information. Over all feed rates and lignin uses, RDB fuel yield remains constant at 45.4 GGE/ton between either feedstock material, increasing proportionately from roughly 100,000 to 455,000 GGE/day as a function of feed scale increasing between the 2000 and 9100 TPD range. Fuel yield outputs are independent of the choice of lignin disposition, and are comparable between the two feedstock cases (minimally lower for the stover case compared to the UF blend feedstock, although the difference is trivial), owing to a general tradeoff between cellulose versus hemicellulose content translating to a near-equivalent net carbohydrate content between either feedstock for subsequent conversion through fermentation (though recognizing that in reality, many fermentation organisms prefer glucose over hemicellulose sugars [Eiteman et al., 2008]).

As expected, air emission outputs reduce substantially when diverting solids away from the boiler to pelletize lignin and send WWT sludge

for off-site treatment. Namely, CO₂ and SOx (both calculated by Aspen combustion reactions) reduce by 40% and 98%, respectively, with CO₂ tied to lower boiler heat input and SOx reflective of sulfur content in the boiler feed, the large majority of which is present with the solids as sulfate salt. NOx is reduced by roughly 55% based on emission factor estimates as a function of boiler feed heat input discussed in the “Methods” section. CO₂ emissions (100% biogenic) increase from roughly 2700 to 12,000 ton/day between the 2000 TPD and 9100 TPD feed scale for burning lignin, or from 1600 to 7500 ton/day for pelletizing lignin. SOx emissions increase from roughly 600 to 2800 ton/day over the range of feed scales considered for burning lignin, reducing substantially to between 10 and 50 ton/day for pelletizing lignin. NOx emissions range from 1700 to 7900 ton/day for burning lignin, and from 800 to 3500 ton/day for pelletizing lignin. The rates reported here for SOx and NOx are after the included mitigation controls utilizing FGD and SNCR technologies, respectively. Still, we reiterate that these values are reflective of estimates attributed to the current granularity of the Aspen models (reflecting the framework of the models from their published design report basis) and will be further refined in our accompanying “Part 2” study explicitly focused on biorefinery air emissions.

Comparing between feedstocks, emissions outputs are slightly lower for the corn stover feedstock compared to the UF blend material. This is driven primarily by a lower heat input rate to the boiler in the stover case, in turn a function of the feedstock compositional differences. Namely, stover has a slightly higher lignin content (and accordingly a higher solids feed rate to the boiler), but also higher ash and less non-carbohydrate/lignin organics (i.e., extractives and acetate) which report to the WWT section and ultimately get converted to AD biogas, thus a lower gas feed rate to the boiler versus the UF blend case. Together this translates to a net 6% reduction in boiler feed heat content and a similar reduction in CO₂ and NOx emissions. SOx emissions are more comparable, reflecting similar upstream chemical loadings and resulting sulfate salts. The lower boiler feed heat input is further magnified in the stover case by a higher boiler efficiency penalty due to more water in the feed, resulting in 8% lower heat/steam generation. This leads to less power generation and a lower net power export in the lignin combustion cases or greater net power import in the pelletizing cases. Comparing between biorefinery sizes, all biorefinery inputs, fuel yields, and emissions outputs scale linearly as feedstock rate increases for a given biomass feed type/lignin use, translating to consistent values for those metrics on a per-ton biomass input basis (summarized in SI

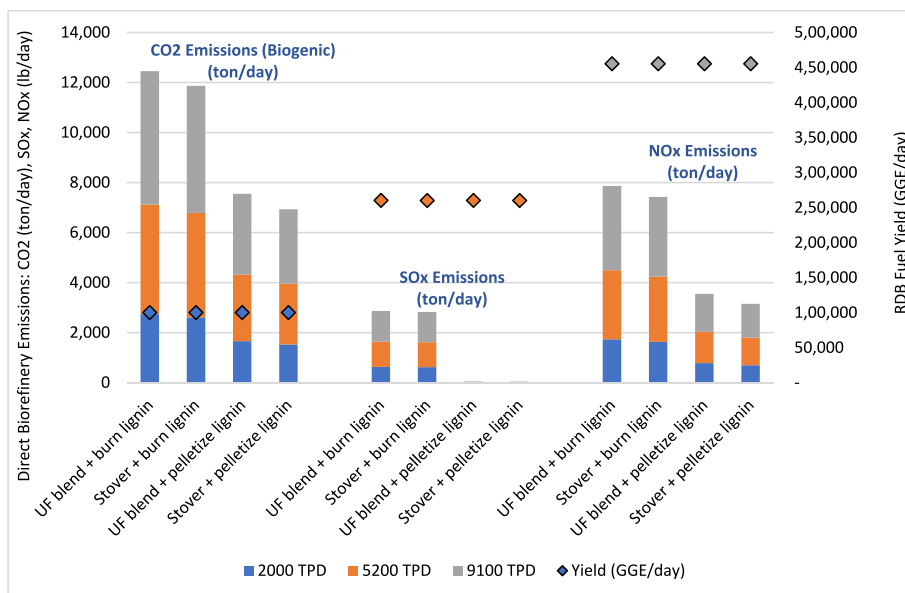


Fig. 3. Key yield/emission output estimates from biorefinery model scenarios.

Table 3

Summary of key mass/energy balances for modeled biorefinery cases (results per-ton biomass feed rate are provided in SI Table S7; more comprehensive stream/component flows are also provided in SI Fig. S1).

	2000 TPD				5200 TPD				9100 TPD			
	UF blend + burn	Stover + burn	UF blend + pelletize	Stover + pelletize	UF blend + burn	Stover + burn	UF blend + pelletize	Stover + pelletize	UF blend + burn	Stover + burn	UF blend + pelletize	Stover + pelletize
Feed rate (dry ton/day)	2205	2205	2205	2205	5733	5733	5733	5733	10,033	10,033	10,033	10,033
Cellulose	773	805	773	805	2009	2093	2009	2093	3516	3663	3516	3663
Xylan	431	398	431	398	1120	1036	1120	1036	1959	1813	1959	1813
Lignin	347	361	347	361	903	937	903	937	1581	1640	1581	1640
Other	654	641	654	641	1701	1667	1701	1667	2977	2917	2977	2917
RDB fuel yields (GGE/day)	100,117	100,101	100,117	100,101	260,338	260,259	260,338	260,259	455,571	455,456	455,571	455,456
Boiler feed heat content (MM BTU/day)	18,849	17,792	8608	7469	49,004	46,255	22,378	19,415	85,755	80,956	39,160	33,986
Biorefinery net power export (KW) ^a	10,086	6985	(14,075)	(17,348)	29,646	20,929	(33,322)	(42,225)	52,994	37,751	(56,993)	(72,906)
Direct CO ₂ emissions (ton/day)	2737	2609	1660	1523	7116	6783	4315	3960	12,453	11,870	7551	6930
Boiler	2610	2492	1531	1404	6786	6478	3980	3651	11,874	11,337	6964	6388
Other	127	117	129	119	331	305	335	310	579	534	587	542
Direct SO _x emissions (lb/day)	628	620	10	10	1633	1614	27	26	2867	2824	47	46
Boiler	626	618	0.1	0.1	1627	1608	0.2	0.2	2856	2814	0.3	0.3
Other	2	2	10	10	6	6	27	26	11	11	46	45
Direct NO _x emissions (lb/day)	1729	1632	779	692	4494	4244	2027	1800	7864	7427	3548	3150
Boiler	1696	1601	620	538	4410	4163	1611	1398	7718	7286	2819	2447
Other	32	31	159	154	83	81	416	402	146	141	729	703

^a Positive value = net power export to grid (coproduct), negative value = net power import.

Table S7).

Across all cases, the boiler constitutes the large majority of air emissions evaluated here. Accordingly, substantial reductions in CO₂ and controlled NO_x/SO_x emissions are observed when diverting lignin and WWT sludge away from the boiler. However, emissions outputs increase from non-boiler sources in the lignin pellet cases, primarily for NO_x and SO_x. While a new source of air emissions is introduced from the pelletizer vent in the lignin pelletizing scenarios, this stream does not contain appreciable amounts of criteria air pollutants as tracked in this study (although it does represent an additional source of VOCs and likely particulates). Instead, the increase in NO_x and SO_x is due to routing an additional aqueous stream to WWT from the lignin press utilized as the first dewatering step prior to the pelletizer, and resultant air emissions from the aerobic digestion lagoon.

While the scope of this study does not include a life-cycle analysis (LCA) to quantify overall greenhouse gas emissions of the modeled biorefineries, it is noted that all CO₂ emissions reflected here are biogenic originating from carbon contained in the biomass feedstock, and there is no fossil CO₂ directly emitted from the biorefinery (i.e., natural gas supplementation or other fossil fuels are not required in normal biorefinery operations in any of the modeled scenarios here). However, given a reduction in boiler heat input ranging from 55 to 60% for the lignin pelletizing cases, the overall power balance switches from a net power export coproduct to a net import purchase from the grid, which may carry important tradeoffs in LCA performance relative to the lignin combustion cases. This represents an additional area planned for future study of the model scenarios established herein.

4. Conclusions

This work provides a summary overview of process modeling and design conducted for an example design case pathway reflecting the production of hydrocarbon biofuels under *n*th-plant, commercial-scale projections. Beyond the established base case, additional scenarios were investigated for their impacts on key mass/energy balances, yields, and estimated air emission outputs across a range of feedstock scales, herbaceous feedstock types, and disposition of lignin/residual solids. This work showed minimal impacts on fuel yield potential based on maintaining consistent fractional conversions across the unit operations, given overall similar carbohydrate content between the UF blend and corn stover compositions (trading for higher cellulose versus lower hemicellulose content in the stover case), translating to annual fuel yields increasing proportionately with higher feed scales across either feedstock independent of lignin use. However, the stover feedstock leads to slightly lower emissions of three key components tracked in this analysis, namely CO₂, SO_x, and NO_x, owing to lower energy content of the combined feed to the boiler system, reflecting feedstock compositional tradeoffs and the fate of residual/unconverted organics to the boiler versus wastewater treatment.

Alternatively, diverting all solids away from the boiler by pelletizing lignin and routing wastewater sludge to off-site treatment leads to more substantial reductions in modeled emissions outputs, roughly cutting CO₂ and NO_x in half (owing to a similar reduction in boiler feed heat input) and reducing SO_x by over 90% (given a large reduction in sulfur-containing species when only leaving the gas feed streams to be combusted on-site). However, the lower heat generation also leads to switching from a net power coproduct export to a net import after

accounting for biorefinery heat and power demands, implying potential tradeoffs between savings in air pollutant emissions versus penalties in life-cycle greenhouse gas profiles when moving from solids plus gas to gas-only combustion. This is outside the scope of the present work but may be investigated in the future. Additional opportunities for future work could also consider alternative uses of lignin, such as valorization for higher-value chemical coproducts. The accompanying "Part 2" study to this work will expand from the framework cases and mass balance information presented here, to focus further on updating the estimates for these and other criteria air pollutant emissions and implications on governing regulations and mitigation measures.

CRedit authorship contribution statement

Ryan Davis: Conceptualization, Methodology, Writing – original draft, Writing – review & editing. **Arpit H. Bhatt:** Methodology, Writing – original draft, Writing – review & editing. **Yimin Zhang:** Methodology, Writing – original draft, Writing – review & editing. **Eric C.D. Tan:** Conceptualization, Writing – original draft, Writing – review & editing. **Vikram Ravi:** Visualization. **Garvin Heath:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2022.132439>.

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