This item is the archived peer-reviewed author-version of:

Life-cycle assessment of alternative pyrolysis-based transport fuels : implications of upgrading technology, scale, and hydrogen requirement

Reference:

Sorunmu Yetunde, Billen Pieter, Elangovan S. Elango, Santosa Daniel, Spatari Sabrina.- Life-cycle assessment of alternative pyrolysis-based transport fuels : implications of upgrading technology, scale, and hydrogen requirement

ACS Sustainable Chemistry and Engineering - ISSN 2168-0485 - 6:8(2018), p. 10001-10010

Full text (Publisher's DOI): <https://doi.org/10.1021/ACSSUSCHEMENG.8B01266>

To cite this reference: <https://hdl.handle.net/10067/1532290151162165141>

Life cycle assessment of alternative pyrolysis-based transport fuels: implications of upgrading technology, scale and hydrogen requirement

Yetunde Sorunmu¹, Pieter Billen^{1, 2}, S (Elango) Elangovan³, Daniel Santosa⁴, Sabrina Spatari^{1}*

¹Drexel University, Department of Civil, Architectural and Environmental Engineering, 3141 Chestnut Street, PA 19104, United States

²University of Antwerp, BioGEM, Salesianenlaan 90, 2660 Hoboken, Belgium

³Ceramatec, Inc., 2425 South 900 West, Salt Lake City, UT, 84119

⁴Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA, 99354

*Corresponding author, ss3226@drexel.edu, 215-571-3557

Keywords

Fast Pyrolysis, Biomass, Biofuel, Life cycle assessment, Hydrodeoxygenation, Electrochemical Deoxygenation

Abstract

Bio-oil produced from fast pyrolysis of biomass is a promising substitute for crude oil that can meet climate change mitigation goals, but, due to its high oxygen content it requires upgrading to remove oxygen in order to be used as a transportation fuel. Hydrodeoxygenation (HDO) is one means of upgrading fast pyrolysis oil, however, its main limitation is its large hydrogen requirement. We evaluate an alternative electrochemical deoxygenation (EDOx) method that uses catalytic electrode membranes on a ceramic, oxygen-permeable support, to generate hydrogen in-situ for deoxygenation at the cathode and oxygen removal at the anode. We analyze the life cycle greenhouse gas (GHG) emissions and scale effects of gas-phase upgrading of pyrolysis oil (300 metric tons per day (MTPD)) using different configurations of EDOx and compare it with the large scale HDO process (2000 MTPD). We observe that the EDOx configurations have lower total GHG emissions of 5–8.4 g CO₂ eq. and 7.4–11 g CO₂ eq. per MJ of a vehicle operated with diesel and gasoline, respectively compared to HDO (39 gCO₂ eq. per MJ). Furthermore, the EDOx processes offers potentially 10 times more small-scale pyrolysis upgrading facilities in the U.S. compared to HDO, suggesting that small-scale on-site EDOx processes can reach more inaccessible forest biomass resources.

Introduction

The U.S. renewable fuels standard (RFS2) requires blending 136 billion liters of renewable fuel annually with transportation fuel by 2022 ¹. Along with policies that incentivize high fuel economy, increased domestic oil production, and expanded use of renewable fuels, biofuels have been projected to help reduce U.S dependence on imported fuels thereby, stimulating the economy and increasing domestic employment ². In recent years, studies have shown that biomass is a promising alternative for conversion to fuels due to being renewable, ³ locally sourced, ⁴ and cost effective ⁵ relative to petroleum-based fuels ⁶⁻¹³.

Fast pyrolysis converts biomass to bio-oil, non-condensable gas and char at moderately high temperatures (e.g. 500 °C), in the absence of oxygen ¹⁴. The short residence times applied maximize the fraction of bio-oil, improving the potential yield of renewable liquid fuels. However, fast pyrolysis bio-oil is not suitable for direct blending with petroleum-based transportation fuels, due to the presence of oxygen. The oxygenated structure makes bio-oil thermally unstable, viscous, low in heating value and corrosive ¹⁵. Hence, upgrading is required to render the bio-oil useable as a transportation fuel ⁶. Catalytic cracking ¹⁶, catalytic hydrodeoxygenation (HDO) ¹⁷, catalytic steam reforming and catalytic esterification ¹⁸ and emulsification ¹⁹⁻²⁰ were recently studied as upgrading technologies, but to date none of these have been successfully commercialized, and some bio-oils have only been used in the food flavoring industry on a commercial scale ²¹⁻²². Among the upgrading technologies described above, HDO has been described as the most promising alternative ²³, because other alternatives are associated with high coking (8-25%), formation of light ends and low final fuel product quality ²⁴.

Despite the advantages of HDO compared to its current alternatives, it faces many challenges ²⁵, including large hydrogen consumption, polymerization, minor coke formation ²⁶ and biomass availability at economic supply scales of 2000 metric tons per day (MTPD) ²⁷⁻²⁹. However, the

biomass supply available at 2000 MTPD within an economically feasible distance (within a 80 km radius) is limited in the U.S., and thus requires long feedstock transportation distances (> 80 km), which raises feedstock delivery costs and renders it a limiting factor in the size of a biomass processing plant³⁰.

Electrochemical deoxygenation (EDOx)³¹ uses membrane cells that are integrated directly into the vapor tract of the pyrolysis unit before the condenser to deoxygenate the pyrolysis vapor²⁴. In the EDOx process, an electric potential is applied across an oxygen ion conducting ceramic membrane at high temperatures (400°C – 1000°C). At the nickel-catalyst cathode, oxygen from the hydrocarbon reactant and the electrolysis of water ionizes, permeates through the ceramic membrane and oxidizes at the anode, where it is released in the gaseous state. Hydrogen produced from the electrolysis of water reacts with the remaining hydrocarbon radical, giving deoxygenated hydrocarbon or water. The reduction extent depends on the catalytic properties of the cathode, characteristics of oxygenated bio-oil, applied electric potential and temperature.

Although EDOx reactions are similar to HDO reactions, the configuration of the EDOx mechanism, which requires electricity rather than hydrogen, makes it different from the HDO mechanism. Furthermore, EDOx has some advantages over HDO, including minimal external hydrogen supply needs and the electrical input allows for small-scale operation, which in turn allows integration with the pyrolyzer. Hence, upgrading of the pyrolysis oil occurs in the gas phase, obviating a cooling/heating cycle, which is necessary with the larger scaled HDO process. Theoretically, the EDOx unit can fully deoxygenate bio-oil but at its current state of technological development, it would need additional external hydrogen to fully deoxygenate and experimentally the EDOx unit has only been demonstrated to deoxygenate bio-oil to a stable oil with an oxygen content of 30 wt %. Therefore, we evaluate a concept whereby the bio-oil is deoxygenated to the

full extent of the EDOx deoxygenating potential at which point the oil is assumed stable for transportation to a refinery for complete deoxygenation via hydrodeoxygenation. The proposed concept, referred to as partial electrochemical deoxygenation (partial EDOx), integrates the EDOx and HDO processes by deoxygenating the bio-oil using both processes sequentially to produce a deoxygenated fuel. In addition, the partial EDOx process addresses the possibility previously proposed by Jones et al.³⁰ that small distributed pyrolysis plants can take advantage of lower feedstock cost and improved access to isolated biomass supply to produce a stable and transportable product that can be further upgraded in an existing petroleum refinery³⁰.

This paper uses life cycle assessment (LCA) to compare EDOx, a small scale (300 MTPD) bio-fuel upgrading process, with HDO, a large scale (2000 MTPD) biofuel upgrading process, and partial EDOx, a small scale (300 MTPD) integrated process that merges the EDOx and HDO processes. The comparison quantifies the GHG emissions from biomass collection to vehicle operation of the three processes.

Life cycle GHG emissions of woody biomass-based biofuels from upgraded fast pyrolysis bio-oil have been documented in literature (Table 1). However, because these studies have all focused on HDO upgrading, which requires a large feedstock supply (2000 MTPD) and external hydrogen, we compare their life cycle environmental performance results to EDOx and partial EDOx processes based on their differences such as unit operations, operating condition and process scale.

Table 1. Review of life cycle GHG emissions of upgraded fast pyrolysis bio-oil from HDO technology

Hsu et al.	Hsu et al.	Snowden-Swan et al.	Snowden-Swan et al.
6, 30	6, 30	10	10

Feedstock	Forest Residue	Forest Residue	Forest Residue	Poplar (plantation)
Electric Source	Electricity grid	Biomass based	Electricity grid	Electricity grid
Products	Gasoline and Diesel			
GHG emissions gCO ₂ -e/MJ	38.9	25	36.8	35.8

Methods

Process Configurations

We modeled the EDOx and partial EDOx processes and compared them to the parameters from the HDO process previously studied³⁰. Since neither of the investigated processes have been commercialized to date, the process data was based on laboratory experimental work in combination with computer simulation³¹.

Fast Pyrolysis

The laboratory scale fast pyrolysis reactor at Pacific Northwest National Laboratory (PNNL) was fed Ponderosa pine from American Wood Fiber (AWF) at a rate of 0.9 kg/hr. The feed had been sieved for removal of fine fractions >100 mesh. The main fast pyrolysis design allowed for a gas residence time of less than two seconds at full operating temperature (480-500°C) to achieve maximum liquid yield from pine wood. In addition, the fast pyrolysis unit contained newly designed dust cyclones with reduced internal friction in the inlet and two-stage cyclones designed to collect smaller sized particles, with cyclone 1 having a larger volume than cyclone 2. Hot gas filtration (25-micron sintered metal filter) was used to capture fine particles prior to entering the slip-stream to the EDOx and a slip-stream metering valve helps to ensure proper control of the flowrate. The slip-stream metering valve was also used to make manual adjustments during the

run for constant flowrate with potential changes to back-pressure in the system. The slip stream was used experimentally for testing the bio-oil but was not modeled in the simulation. An electrostatic precipitator (ESP) operating at 15 kV and 0.05 mA was used to ensure coalescing of the vapors without the added back-pressure typically encountered when using a filter unit, as this is crucial in a good leak-free performance of the stack-cell.

The fast pyrolysis unit achieved isothermal operating temperature conditions throughout the bed (480 °C). The gas flow rate was consistent with approximately $1.2\text{e-}3 \text{ m}^3 \cdot \text{s}^{-1}$ to ensure a low gas residence time (<2s). Cyclone 1 and Cyclone 2 was able to collect the majority of the char products (>99%), and the remaining fine solids were collected by the hot gas filtration. The ESP unit was operated during the test and was found to effectively work to coalesce aerosols at 15 kV. During the operations with the ESP, most of the vapor flow was measured at about $3.3\text{e-}5 \text{ m}^3 \cdot \text{s}^{-1}$ (~3 wt. % of the overall pyrolysis vapor) condensed. Product oil and aqueous samples were collected in both the ESP and from the dry-ice trap to be weighted and accounted for mass balance. Non-condensable gases were analyzed with a gas chromatograph (GC) and their flow rate was measured by a wet test meter.

The fast pyrolysis unit was operated at 480 °C and the EDOx stack was operated at 550°C and 600 °C. At the higher temperature, initially the stack had an effective total current of ~ 2A, however with subsequent runs, amperage increased up to 25 A. A schematic diagram of the fast pyrolysis unit is found in Figure S.1.a and S.1.b in the SI.

Electrochemical deoxygenation (EDOx):

Prior to upgrading, the upstream feedstock supply, pretreatment and pyrolysis³² are similar to the HDO process. Three main differences between the two processes are the scale (300MTPD of

biomass in EDOx), the integration of EDOx into the pyrolyzer owing to its size, the electricity used for deoxygenation and the absence of condensing, cooling and reheating units in the EDOx process. The pyrolysis vapor fed to the EDOx unit deoxygenates vapor using electrons provided via electrical current that passes through an oxygen ion transporting dense ceramic membrane reactor to produce a deoxygenated pyrolysis vapor and coproducing oxygen. The deoxygenated pyrolysis vapor condenses to deoxygenated pyrolysis oil. After separation, the final main products are renewable gasoline range compounds while oxygen is produced as a coproduct.

We used Aspen Plus³³ software to model the EDOx upgrading process by adding heat exchangers, separators, a water splitting reactor and an EDOx reactor operation. Some operating conditions and parameters of the EDOx process model were based on previous fast pyrolysis modeling from Ringer et al³⁴. More detailed analysis of the modeling is shown in figure S.1.a in the supporting information (SI).

Partial Electrochemical-deoxygenation (partial EDOx):

The partial EDOx (Figure 1b) process combines HDO and EDOx processes such that the first hydrotreater in the HDO process is replaced by an EDOx unit. The EDOx unit is integrated with the pyrolyzer; hence, the pyrolysis vapor produced by the pyrolyzer proceeds to the EDOx unit in its gaseous phase. The pyrolysis product in its gaseous phase contains 39 wt. % oxygen which goes into the EDOx unit operating at a temperature of 550°C. The EDOx reactor deoxygenates the vapor by removing 33% of the oxygen by mass; this vapor is condensed to a liquid phase and at this deoxygenation level, the oil is stable enough to be trucked to a refinery for further deoxygenation by HDO and subsequent hydroprocessing and product separation producing renewable gasoline and oxygen as a co-product. Similar to the EDOx process, we model the partial EDOx process using Aspen Plus³³. We add the EDOx and HDO units as well as other operating units to the

existing Ringer et al ³⁴ fast pyrolysis model. A more detailed description of the modeling is shown in figure S6 in the SI.

Hydrodeoxygenation (HDO):

The HDO process studied was modeled by PNNL using data from literature ³⁵⁻³⁷, experimental results ³⁰ and Chemcad [®] modeling software. The HDO plant is designed to process 2000 MTPD of biomass. This biomass is pre-processed by drying to 7 wt. % water from its as received moisture level of 50 wt. % and size reduced to 2mm to 6mm before conversion to bio-oil via fast pyrolysis. Pyrolysis is generally performed using a range of temperatures and residence times in order to optimize the desired product. In this case (Figure 1c), the biomass is heated to approximately 520°C in less than 1 second, and then rapidly cooled to stop the reaction. The char and a portion of the gas are burned to heat the circulating sand while the bio-gas produced in the pyrolysis process is condensed to bio-oil, which is oxygenated. The oxygenated bio-oil is pressurized and heated before dual stage catalytic hydrodeoxygenation in two hydrotreaters. External hydrogen is fed to a fixed bed hydrotreater reactor and interacts with the oxygenated bio-oil under pressures of about 170 atm and 137 atm and temperatures of 240°C and 370°C respectively in the two hydrotreaters converting it to a stable hydrocarbon oil ³⁰. The stable oil requires further processing before it can be used in an existing refinery; hence, hydrocracking and product separation are carried out on the oil before producing the gasoline and diesel range products.

Figure 1. Process flow diagram for: a) electrochemical deoxygenation, b) partial electrochemical deoxygenation, and c) hydrodeoxygenation processes

Biomass supply logistics

A major difference between the EDOx and HDO processes is the scale. While the HDO process requires scales of 2000 MTPD of biomass to be economical, EDOx may be economical at a scale of 300 MTPD similar to other fast pyrolysis-based processes^{11, 38-39}. The plant size of 2000 metric tons per day (MTPD) was chosen in order to be consistent with biorefinery sizes considered in previous research^{29-30, 40-44}, which are consistent with feasible agricultural residue supply. In addition, some studies^{11, 39, 45} have looked at the economic feasibility of smaller scales for bio-oil production. Likewise, we also tackle the need to access stranded resources at smaller scales

addressed by studies ⁴⁶⁻⁴⁷ that show that it is worthwhile to produce a densified commodity at depots. Herein, the densified commodity is the stable bio-oil. Biomass resources are not densely available for conversion to energy commodities consistently across forest and agricultural landscapes ⁴⁷⁻⁵². Thus, to gather 2000 MTPD of biomass within a cost-effective radius of less than 80.5 km (50 miles) supplying HDO facilities may be limited to those locations with high density and access to transportation infrastructure. At smaller scales proposed for the EDOx and partial EDOx processes, there is potential for cost savings and reduced environmental burden due to shorter biomass transportation distances and access to a greater number of feedstock supply areas compared to higher production scales ⁴⁷.

We focus on all the forest biomass regions in the continental USA and used ArcGIS and LCA to determine which region will be most feasible for an EDOx/partial EDOx unit. The feasibility of the site is assessed by biomass supply and environmental sustainability based on the electricity grid used by the region. In order to determine the locations for the partial EDOx process, we used ArcGIS ⁵³ to create a map that shows the possible siting for HDO and EDOx locations. To determine the maximum radius of biomass transportation, we used literature values to estimate a distance of 80.5 km (50 mile), beyond which the environmental impact and cost of transportation of biomass has been said to be disproportionately large ³⁵. Shape files extracted from the data layers in the NREL Biofuels Atlas ⁵⁴ on the quantity of forest residue measured in bone dry ton per year (BDTPY) statewide were merged onto a US map. In the merged GIS map, we apply the 80.5 km radius cutoff for supply to create a feature class containing a net of rectangular cells called fishnets. Each fishnet defines an acceptable or “go” supply boundary outside of which is a “no-go” supply area within ArcGIS ⁵⁵. We determined the amount of forest residue available within the 80.5 km radius fishnet. If the amount of forest residue in the fishnet is within an 80.5 km radius,

below 2000 MTPD and above 300 MTPD, an EDOx unit can be placed in that area. If the amount of forest residue is greater than 2000 MTPD, both EDOx and HDO units can be sited in that area. To evaluate the environmental sustainability, we calculated the amount of power needed for deoxygenation in the EDOx unit. We used Simapro v.8.4 software⁵⁶ and Ecoinvent data⁵⁷ to estimate GHG emissions based on the power calculated in all the electricity grids in the continental USA and used graduated colors to illustrate spatial differences in GHG emissions across the U.S.

Furthermore, we extracted the shape files for petroleum refineries⁵⁸ and crude oil pipelines⁵⁹ from petroleum data layers in the NREL biofuel atlas and merged them with the current forest residue map. If the petroleum refineries were within the maximum allowable distance (80.5 km radius) to the HDO locations, we overlaid the map section to indicate that the oil produced at the HDO locations could be completely stabilized and separated at a refinery within a close distance.

Finally, to test the sensitivity of biomass availability and its effect on GHG emissions at small (300 MTPD) biorefinery scales, we reduce the transportation radius from 80.5 km to 32.2 km to determine access to biomass within a smaller transportation radius. The 32.2 km radius corresponds with a feasible radius ranging from 5 miles (8.05 km) to 50 miles (80.5 km) described by Brechbill et al⁶⁰ and a radius ranging between 25 and 50 km described to be economical by Zafar et al⁶¹.

Life Cycle Assessment Model

The LCA modeling follows the guidelines of the International Organization for Standardization⁶². Simapro v.8.4⁵⁶ LCA modeling software is used to develop and link the unit processes for biomass production and transportation, bio-oil production, bio-oil upgrading, product distribution and vehicle operation. The specific Ecoinvent v.3.4⁵⁷ inventory data used are summarized in Tables S3, S4, S5, S6 and S7 in the supporting information.

The system boundary (Figure 2) illustrates the processes from the harvest of forest residue to vehicle operation. Similar to other studies ^{6, 63}, we do not consider indirect effects such as land use change. We use the IPCC 2013 GWP 100a ⁶⁴ metric to identify the environmental impact of the processes with functional units per 1 MJ of fuel produced and per 1 km of distance driven by a light-duty passenger vehicle. This study uses system expansion to handle all co-products. The feedstock is harvested, pre-processed, and transported to a pyrolysis conversion site. There, the biomass undergoes pyrolysis, the vapor of which is available for deoxygenation via EDOx and partial EDOx. In the HDO process, the pyrolysis vapor is condensed before upgrading in two hydrotreaters (Fig. 2). After upgrading and product fractionation, the renewable diesel and gasoline products are distributed and used to operate an automobile with a fuel economy of 10.8 km l⁻¹ and 13 km l⁻¹ of gasoline and diesel type vehicles respectively. Although the upstream operations in the three processes (EDOx, partial EDOx and HDO) consist of the same operations, they supply feedstock at two different scales (EDOx and partial EDOx operate at 300 MTPD while HDO operates at 2000MTPD). In the EDOx process, since we assume full deoxygenation by the EDOx unit, after complete deoxygenation, the fuel produced is transported to the refinery for product separation followed by distribution to the market and consumer use in a vehicle. In the partial EDOx process, the delivered feedstock is pyrolyzed and partially deoxygenated to a stable bio-oil via the EDOx process, and then transported to a petroleum refinery for HDO processing in a second hydrotreater to fully deoxygenate the partial EDOx oil. In this case, we assume the EDOx site is in the same location or in very close proximity to the HDO unit at the refinery; hence, transportation distance is negligible. After HDO deoxygenation, the pyrolysis oil is separated, distributed to the consumer and used for vehicle operations. Electricity needed for the EDOx and HDO unit is assumed to be generated from the average US electricity grid. Although a sensitivity

analysis described later, examines the effect of location on the GHG emissions by varying regional electricity grids.

For the HDO process, we used the results of the LCA published by the National Renewable Energy Laboratory (NREL) ⁶ without any modifications.

We assumed that the CO₂ uptake during tree growth for forest residue is the same as that of pine studied in Hsu et al ⁶, which was 300g CO₂ eq. and 350g CO₂ eq. per 1 Km of distance driven with diesel and gasoline respectively ⁶.

For product transportation and distribution, we use the boundary settings from a pyrolysis study ⁶³ that assumes product transportation by barge (8%), pipeline (63%) and rail (29%), respectively for gasoline and barge (8%), rail (29%) and truck (63%) for diesel ⁶⁵. We assume distances of 520 km, 400km, 800km and 50km for barge, pipeline, rail and truck, respectively. All other inventory data for the LCA appear in Tables S3, S4, S5, S6 and S7 in the supporting information.

277

278

279

280

281

282

283

Figure 2. System boundary diagrams for (a) electrochemical deoxygenation, (b) partial electrochemical deoxygenation and (c) hydrodeoxygenation. In the partial EDOx process, the insertion point (the point where the oil goes to the refinery) is a stable oil produced by the EDOx process that can be easily transported to a refinery for further upgrading/processing. In the full EDOx process, the insertion point is a near finished fuel/blend stock that requires minimal processing in a refinery.

Sensitivity analysis of net differences in electricity and hydrogen consumption

To compare the differences among the three conversion processes, we conduct a sensitivity analysis based on electricity use and hydrogen consumption, two inputs that distinguish EDOx from HDO.

The electricity input needed to run the EDOx unit was parameterized according to experimental measurement. Since electricity and only a small fraction of hydrogen are required in the EDOx and partial EDOx processes, we calculated hydrogen requirements and electricity input based on mass balance. Specifically, we calculated the amount of electricity needed to remove one oxygen molecule. Based on these calculations, the GHG intensities were quantified for the 9 electricity grids (NPCC, RFC, SERC, FRCC, TRE, SPP, MRO, WECC and ASCC) ⁶⁶ using Simapro ⁵⁶.

We also calculated the external hydrogen needed for the three processes based on a mass balance of hydrogen. In the EDOx process, hydrogen is produced by the splitting of the water molecules present in the bio-oil. The bio-oil contains ~ 50 wt. % moisture; hence, it has enough water to produce hydrogen required for the EDOx process and thus needs a small amount of external hydrogen. However, since the HDO process utilizes a different mechanism that does not split the water, the HDO requires a large amount of external hydrogen. We used LCI data for hydrogen production from methane steam reforming in GREET ⁶⁵ to evaluate the GHG intensity of the HDO and partial EDOx processes.

Hydrogen Consumption

From stoichiometry, one hydrogen molecule is needed to break a carbonyl bond and another to remove an oxygen atom in oxygenated bio-oil compounds. We used this information to calculate the quantity of hydrogen that will be consumed in each of the hydrotreaters reported by PNNL ³⁰. In the hydrotreaters, two main reactions occur that require hydrogen; hydrodeoxygenation (the use

of hydrogen to remove oxygen) and non-deoxygenation (the saturation of double bonds). Stoichiometric calculations (Table S1) suggest that less hydrogen is consumed in the non-deoxygenation reactions in the 1st hydrotreater (H1) than is needed for the non-deoxygenation reactions in the 2nd hydrotreater (H2). This is consistent with the findings of Jones et al.³⁰ that mild hydrotreating takes place in the 1st hydrotreater and severe hydrotreating in the 2nd hydrotreater. In addition, based on stoichiometric calculations, we use the chart illustrated in Figure S6 in the SI to show that hydrogen is consumed at a slower rate in the 1st hydrotreater and at a much faster rate in the 2nd hydrotreater further confirming mild followed by severe hydrotreating.

Results and Discussion

Biomass Supply

Availability of forest residues across the United States can supply 216 locations with feedstock at 300 MTPD for EDOx facilities and 18 locations can supply feedstock at 2000 MTPD for HDO facilities (Figure 3a). The map also shows GHG intensity (kg CO₂ eq. per metric ton) of the relevant grid with the darker colors indicating a higher environmental impact. The Northeast region, which utilizes the Northeast Power Coordinating Council (NPCC) grid, has low GHG emissions while also fulfilling the biomass supply needed for the siting of an EDOx pyrolysis facility; however, the most feasible location would be in the south, specifically in Arkansas and Louisiana where biomass availability could supply numerous EDOx facilities and provide access to petroleum refineries. To fulfil the partial-EDOx process mechanism, we used red dots and green lines on the map to represent petroleum refineries and crude oil pipelines, respectively. The presence of a petroleum refinery in close proximity to EDOx sites will enable efficient transport of the bio-oil produced from the EDOx pyrolysis sites to a petroleum refinery for further deoxygenation and separation. If the EDOx process can fully deoxygenate the bio-oil, then the

330 deoxygenated bio-oil will be infrastructure compatible and can be directly added to the crude oil
331 pipeline. The map also shows that when the feedstock transportation radius declines from 80.5 km
332 to 32.2 km (Fig 3b), there will not be any HDO sites to accommodate feedstock supply within this
333 smaller radius but there will still be over 300 EDOx sites (represented in yellow borders in figure
334 3b) to accommodate this smaller supply radius.

335 (a)

336

337 (b)

338

Figure 3(a) U.S. map showing EDOx and HDO locations as well as the GHG intensity in CO₂ eq. per metric ton varying by the different electricity grids, forest residue availability in bone dry ton per year (BDTPY), petroleum refineries and pipeline locations. The lighter green indicates a lower GHG intensity and the darker green indicates a higher GHG intensity. The black grid represents the potential EDOx sites while the red grid represents the potential HDO sites. The purple highlights represents HDO locations near refineries **(b)** U.S. map showing the EDOx and HDO sites with the yellow borders representing a feedstock transportation radius of 32.2km (20 miles).

Greenhouse Gas Emissions

Life Cycle GHG emissions of the three processes

Figures 4a and 4b show that GHG emissions from the EDOx process is lower than the HDO process. In all the results, diesel produced from the EDOx and partial EDOx processes (8.36 g CO₂ eq. and 4.95 g CO₂ eq. per MJ) have lower GHG emissions than gasoline produced from the same processes (10.9 g CO₂ eq. and 7.43 g CO₂ eq.) per MJ of vehicle operation due to the higher fuel efficiency of diesel engines compared to gasoline engines ⁶. The partial EDOx upgrading process produces the least amount of GHG emissions due to a lower demand for external hydrogen and electricity than the HDO process and EDOx, respectively. Vehicle operation contributes the largest emissions in the partial EDOx process; however, those emissions are biogenic and offset by CO₂ uptake during biomass growth ⁶⁵. Oxygen is co-produced in the full EDOx and partial EDOx processes and credited, assuming it displaces oxygen produced via cryogenic processing. The GHG emissions in the pyrolysis and upgrading process are highest for the EDOx system mainly due to the electricity and additional hydrogen required for deoxygenation owing to the limited amount of water in the bio-oil for hydrogen production (shown in SI Table S.4). Although GHG emissions for the full EDOx process are high, the credit from co-produced oxygen is

considerable towards reducing net GHG emissions. Overall, the net GHG emissions for the partial and full EDOx processes are lower than the net GHG emissions from the HDO process. When considering the sensitivity of the feedstock collection radius, with lower and upper bounds set to 32.2 km and 950km (the maximum refinery distance), GHG emissions from the full EDOx and partial EDOx processes remain lower than those of HDO process (Figure 4a).

In comparison to conventional fuels, on a per MJ basis GHG emissions for the pyrolysis fuels produced through the partial EDOx and full EDOx processes are 88% to 95% lower than conventional gasoline and diesel GHG emissions (91 g CO₂-eq. and 94 g CO₂-eq. per MJ) based on GREET data ⁶⁷. This reduction exceeds the RFS-2 requirement, which obliges advanced biofuels to meet a 50% life cycle GHG emission reduction threshold relative to conventional gasoline or diesel ⁶⁸. While all upgraded pyrolysis biofuels, whether EDOx or HDO, would meet RFS2, the EDOx and partial EDOx upgraded biofuels are 68% to 72% and 78% to 84% lower than HDO upgraded biofuels.

Figure 4. (a) GHG emissions for a U.S passenger car operated over a distance of 1km using alternative upgraded pyrolysis biofuels. The figure estimates life cycle GHG emissions from feedstock collection to fuel product transportation and distribution including oxygen as a co-product. **(b)** Net GHG emissions for a U.S passenger car operated over a distance of 1km using alternative upgraded pyrolysis biofuels. Error bars show lower and upper bounds. The EDOx lower bound represents the GHG reduction limit for a smaller feedstock supply radius of 32.2 km from 80.5 while the upper bound represents the maximum refinery distance from the upgrade units. The

HDO lower bound represents the GHG emissions from the use of biomass-derived electricity as feedstock while the baseline represents GHG emissions from grid electricity.

Spatial variability in biomass accessibility

The influence of spatial variables in biomass supply, hydrogen generation and electricity grid input was evaluated for the full EDOx, partial EDOx and HDO upgrading processes. The effect of different hydrogen generation methods on life cycle GHG intensity is evident. Due to excess demand for hydrogen by the HDO process, hydrogen is externally supplied; therefore, there are limited locations in which HDO can be sited for proximity to hydrogen supply. On the other hand, with hydrogen supplied in-situ via electrical means and little external hydrogen need, in regions with a large share of coal based electricity, the GHG intensity of EDOx is significantly higher than in regions with a large share of electricity from renewables and natural gas.

Influence of hydrogen generation on the three processes

To investigate the effect of hydrogen generation method on life cycle GHG emissions (Figure 5a), we study the GHG intensity of hydrogen supplied by four processes and feedstocks: (1) natural gas from shale, (2) coal without CO₂ sequestration, (3) electricity (Distributed U.S. mix) and (4) nuclear from high temperature gas reactor plant from uranium fuel. The means of hydrogen generation determines the GHG intensity and can affect the total environmental impact of the process. In comparing the means of hydrogen generation, we observe that irrespective of the type of hydrogen generation used, the GWP for partial EDOx is lower than HDO due to low hydrogen requirements for both EDOx processes compared to HDO as a result of the extent of deoxygenation from the electrolysis-supplied H₂. Therefore, there is a tradeoff between electricity and hydrogen (supplied by different sources) when using different combinations of full and partial EDOx whereby electricity input is small compared to the hydrogen required. Considering the

aforementioned assumptions, full EDOx results in much lower GHG emissions compared to HDO and partial EDOx; due to its minimal external hydrogen needs.

Influence of electricity grid on the three processes

When analyzing the GHG emissions from the three processes across nine electricity grids in the United States (Figure 5b), as the HDO upgrade process does not require a significant amount of electricity, there is only a difference in the GHG emissions from EDOx and partial EDOx units. The results indicate that the EDOx and partial EDOx processes emit fewer GHGs than the HDO process irrespective of supplying electricity grids. In particular we examine two grid locations that supply forest residue – NPCC and Southwest power pool (SPP). An EDOx unit located in the NPCC region would have the lowest GHG emissions compared to one located in regions using the SPP electricity grid, which would have the highest out of the eight grids. This is due to the breakdown of the NPCC distribution mix, which consists of 30.85% nuclear and 2.38% coal, while the SPP mix consist of 4% nuclear and 47.65% coal ⁶⁹; hence, the SPP grid is the most carbon intensive due to the contribution of coal. Overall the partial EDOx process will have fewer emissions than the other two processes.

423

424

425

426

427

428

Figure 5. (a) Hourly GHG emissions of hydrogen consumed in EDOx, partial EDOx, and HDO processes through hydrogen generated by natural gas, coal, electricity and nuclear. **(b)** Greenhouse Gas Emissions per CO₂ equivalent for production of pyrolysis fuel per km of vehicle operated for the 9 electrical grids and U.S. Average. Note: Figure b evaluates the GHG emissions from feedstock collection to pyrolysis and upgrading only.

As several studies have demonstrated that pyrolysis can act as a densification depot⁷⁰⁻⁷², the EDOx process uses a relatively small and distributed scale to overcome feedstock logistics and distribution of densified and stabilized fuel challenges compared to HDO to make infrastructure compatible fuels. While all pyrolysis oil upgrading technologies studied herein would meet RFS2 advanced fuel standards; compared to petroleum-based fuels, the partial EDOx process has the lowest net life cycle GHG intensity (a reduction of 92% to 95%), compared to the HDO process's more modest GHG reduction of 53% to 57%. In regulatory frameworks that reward incremental reductions in GHG intensity, such as California's low carbon fuel standard, partial or full EDOx technology would be more economically competitive than HDO due to its significant marginal⁷³ GHG reduction. Although this study demonstrates that partial EDOx has the lowest life cycle GHG emissions among the three processes examined, it has potential for further process improvement if optimized for deoxygenation above 30%, which would reduce external hydrogen input need and cost.

Acknowledgments

This work is sponsored by the U.S. Department of Energy, DOE-EERE Award Number DE-EE0006288 under the Carbon, Hydrogen and Separation Efficiencies in Bio-Oil Conversion Pathways (CHASE Bio-Oil Pathways) program.

Associated Content:

Funding Sources: Supported by the U.S. Department of Energy, DOE-EERE Award Number DE-EE0006288 under the Carbon, Hydrogen and Separation Efficiencies in Bio-Oil Conversion Pathways (CHASE Bio-Oil Pathways) program.

Corresponding Author:

S. Spatari, Tel.: +1-215-571-3557. E-mail: ss3226@drexel.edu

ORCID:

Yetunde E. Sorunmu: 0000-0003-2074-6371

Pieter Billen [0000-0003-3546-0157](https://orcid.org/0000-0003-3546-0157)

Sabrina Spatari: [0000-0001-7243-9993](https://orcid.org/0000-0001-7243-9993)

Supporting Information:

Supporting deoxygenation reactions, life cycle inventory data and GHG reduction results are summarized; process flow diagrams from Aspen Plus simulations show details of feedstock conversion and upgrade to bio-fuels (PFD).

References

1. United States Environmental Protection Agency *RFS2 provisions and attest requirements*; 2010, <https://www.epa.gov/renewable-fuel-standard-program/renewable-fuel-standard-rfs2-final-rule#rule-summary>
2. United States Department Of Energy *Replacing the Whole Barrel To Reduce U.S. Dependence on Oil*; DOE/EE-0920; July 2013, 2013; p 24, http://www.energy.gov/sites/prod/files/2014/04/f14/replacing_barrel_overview.pdf
3. Zhu, J. Y.; Pan, X.; Zalesny, R. S., Pretreatment of woody biomass for biofuel production: energy efficiency, technologies, and recalcitrance. *Appl. Microbiol. Biotechnol.* **2010**, 87 (3), 847-857. DOI: 10.1007/s00253-010-2654-8
4. Dale, B. E.; Holtzapple, M., The Need for Biofuels. *Chem. Eng. Prog.* **2015**, 111 (3), 36-40.
5. Hammer, N. L.; Boateng, A. A.; Mullen, C. A.; Wheeler, M. C., Aspen Plus® and economic modeling of equine waste utilization for localized hot water heating via fast pyrolysis. *J. Environ. Manage.* **2013**, 128, 594-601. DOI: <http://dx.doi.org/10.1016/j.jenvman.2013.06.008>
6. Hsu, D. D., Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing. *Biomass Bioenergy* **2012**, 45, 41-47. DOI: <http://dx.doi.org/10.1016/j.biombioe.2012.05.019>

7. Hsu, D. D.; Inman, D.; Heath, G. A.; Wolfrum, E. J.; Mann, M. K.; Aden, A., Life cycle environmental impacts of selected U.S. Ethanol production and use pathways in 2022. *Environ. Sci. Technol.* **2010**, *44* (13), 5289-5297. DOI: 10.1021/es100186h
8. Li, X.; Mupondwa, E., Life cycle assessment of camelina oil derived biodiesel and jet fuel in the Canadian Prairies. *Sci. Total Environ.* **2014**, *481*. DOI: 10.1016/j.scitotenv.2014.02.003
9. Murphy, C. W.; Kendall, A., Life cycle analysis of biochemical cellulosic ethanol under multiple scenarios. *GCB Bioenergy* **2015**, *7* (5), 1019-1033. DOI: 10.1111/gcbb.12204
10. Snowden-Swan, L.; Male, J. *Summary of Fast Pyrolysis and Upgrading GHG Analyses*; Pacific Northwest National Laboratory: Richland, Washington, 2012; p 28,
11. Sorunmu, Y. E.; Billen, P.; Elkasabi, Y.; Mullen, C. A.; Macken, N.; Boateng, A. A.; Spatari, S., Fuels and chemicals from equine waste derived tail gas reactive pyrolysis oil: techno-economic analysis, environmental and exergetic life cycle assessment. *ACS Sustainable Chemistry & Engineering* **2017**, 10.1021/acssuschemeng.7b01609. DOI: 10.1021/acssuschemeng.7b01609
12. Spatari, S.; Bagley, D. M.; MacLean, H. L., Life cycle evaluation of emerging lignocellulosic ethanol conversion technologies. *Bioresour. Technol.* **2010**, *101* (2), 654-667. DOI: 10.1016/j.biortech.2009.08.067
13. Spatari, S.; Zhang, Y.; MacLean, H. L., Life Cycle Assessment of Switchgrass- and Corn Stover-Derived Ethanol-Fueled Automobiles. *Environ. Sci. Technol.* **2005**, *39* (24), 9750-9758. DOI: 10.1021/es048293+
14. Zhang, Y.; Brown, T. R.; Hu, G.; Brown, R. C., Techno-economic analysis of two bio-oil upgrading pathways. *Chem. Eng. J.* **2013**, *225*, 895-904. DOI: <http://dx.doi.org/10.1016/j.cej.2013.01.030>
15. Oasmaa, A.; Kuoppala, E.; Solantausta, Y., Fast pyrolysis of forestry residue. 2. Physicochemical composition of product liquid. *Energy Fuels* **2003**, *17* (2), 433-443. DOI: <http://dx.doi.org/10.1021/ef020206g>
16. Hangtao, L.; Xiaoning, Y.; Qiang, L.; Changqing, D., Overview of Bio-oil Upgrading Via Catalytic Cracking. *Advanced Materials Research* **2014**, *827*, 25-9. DOI: <http://dx.doi.org/10.4028/www.scientific.net/AMR.827.25>
17. Tran, N.; Uemura, Y.; Chowdhury, S.; Ramli, A., A Review of Bio-Oil Upgrading by Catalytic Hydrodeoxygenation. *Applied Mechanics and Materials* **2014**, *625*, 255-8. DOI: <http://dx.doi.org/10.4028/www.scientific.net/AMM.625.255>
18. Wang, J.-J.; Chang, J.; Fan, J., Upgrading of Bio-oil by Catalytic Esterification and Determination of Acid Number for Evaluating Esterification Degree. *Energy & Fuels* **2010**, *24* (5), 3251-3255. DOI: 10.1021/ef1000634
19. Yin, Q.; Wang, S.; Li, X.; Guo, Z.; Gu, Y. In *Review of bio-oil upgrading technologies and experimental study on emulsification of bio-oil and diesel*, 2010 International Conference on Optoelectronics and Image Processing, ICOIP 2010, November 11, 2010 - November 12, 2010, Haiko, China, IEEE Computer Society: Haiko, China, 2010; pp 343-347. <http://dx.doi.org/10.1109/ICOIP.2010.112>.
20. Sang, X.; Li, H.; Li, M.; Li, D., The properties and upgrading of bio-oil. *Shiyou Xuebao, Shiyou Jiagong/Acta Petrolei Sinica (Petroleum Processing Section)* **2015**, *31* (1), 178-187. DOI: <http://dx.doi.org/10.3969/j.issn.1001-8719.2015.01.028>
21. Ackom, E.; Gan, J.; Clark, J. H.; Patton-Mallory, M.; Kraus, G. A.; Skog, K.; Dale, V.; Kelley, S. S.; Wegner, T.; Illman, B., *Integrated Forest Biorefineries: Challenges and Opportunities*. Royal Society of Chemistry: 2012,

22. Gary Underwood, R. G. G. Method of Using Fast Pyrolysis Liquids as Liquid Smoke. 4,994,297, February 19, 1991, 1991, <http://www.google.com/patents/US4994297>
23. Xu, X.; Zhang, C.; Liu, Y.; Zhai, Y.; Zhang, R., Two-step catalytic hydrodeoxygenation of fast pyrolysis oil to hydrocarbon liquid fuels. *Chemosphere* **2013**, 93 (4), 652-660. DOI: <http://dx.doi.org/10.1016/j.chemosphere.2013.06.060>
24. Elangovan, S.; Larsen, D.; Hartvigsen, J.; Mosby, J.; Staley, J.; Elwell, J.; Karanjikar, M. In *Electrochemical upgrading of bio-oil*, Symposium on Electrosynthesis of Fuels 3 - 227th ECS Meeting, May 24, 2015 - May 28, 2015, Chicago, IL, United states, Electrochemical Society Inc.: Chicago, IL, United states, 2015; pp 1-9. <http://dx.doi.org/10.1149/06603.0001ecst>.
25. De, S.; Saha, B.; Luque, R., Hydrodeoxygenation processes: Advances on catalytic transformations of biomass-derived platform chemicals into hydrocarbon fuels. *Bioresour. Technol.* **2015**, 178, 108-118. DOI: <http://dx.doi.org/10.1016/j.biortech.2014.09.065>
26. Furimsky, E., Catalytic hydrodeoxygenation. *Applied Catalysis A: General* **2000**, 199 (2), 147-190. DOI: [http://dx.doi.org/10.1016/S0926-860X\(99\)00555-4](http://dx.doi.org/10.1016/S0926-860X(99)00555-4)
27. Brown, T. R., A techno-economic review of thermochemical cellulosic biofuel pathways. *Bioresour. Technol.* **2015**, 178 (Supplement C), 166-176. DOI: <https://doi.org/10.1016/j.biortech.2014.09.053>
28. Brown, T. R.; Hu, G., Technoeconomic Sensitivity of Biobased Hydrocarbon Production via Fast Pyrolysis to Government Incentive Programs. *Journal of Energy Engineering* **2012**, 138 (2), 54-62. DOI: 10.1061/(ASCE)EY.1943-7897.0000061
29. Brown, T. R.; Thilakaratne, R.; Brown, R. C.; Hu, G., Techno-economic analysis of biomass to transportation fuels and electricity via fast pyrolysis and hydroprocessing. *Fuel* **2013**, 106 (Supplement C), 463-469. DOI: <https://doi.org/10.1016/j.fuel.2012.11.029>
30. Jones, S. B.; Holladay, J.; Valkenburg, C.; Stevens, D.; Walton, C.; Kinchin, C.; Elliott, D.; Czernik, S. *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case* PNNL-18284; 2009; p 76, http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-18284.pdf
31. Elangovan, S.; Karanjikar, M. Hydrogen Utilization and Carbon Recovery. US20150060296 A1, 2015, <https://www.google.com/patents/US20150060296>
32. Ringer, M.; Putsche, V.; Scahill, J. *Large-scale pyrolysis oil production: a technology assessment and economic analysis*; National Renewable Energy Laboratory (NREL), Golden, CO.: 2006,
33. Aspen Technology *Aspen Plus*, 9.0; Aspen Technology, Inc: Bedford, Massachusetts, 2016,
34. Ringer, M.; Putsche, V.; Scahil, J. *Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis*. Golden (CO): National Renewable Energy Laboratory; 2006 Nov. Report No; NREL/TP-510-37779. Contract No.: DE-AC36-99-GO10337: 2006, <https://www.nrel.gov/docs/fy07osti/37779.pdf>
35. Aden, A., Ruth, M., Ibsen, K., Jechura, J., Neeves, K., Sheehan, J., Wallace, B. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*; NREL/TP-510-32438; National Renewable Energy Laboratory Golden, Colorado, 2002; p 154, <https://www.nrel.gov/docs/fy02osti/32438.pdf>
36. Phillips S, A. A., and J Jechura, D Dayton, and T Eggman *Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass.*; National Renewable Energy Laboratory: Golden, Colorado, 2007,

<http://www.nrel.gov/docs/fy07osti/41168.pdf>

37. Spath, P.; Aden, A.; Eggeman, T.; Ringer, M.; Wallace, B.; Jechura, J. *Biomass to hydrogen production detailed design and economics utilizing the Battelle Columbus laboratory indirectly-heated gasifier*; National Renewable Energy Lab., Golden, CO (US): 2005, <https://www.nrel.gov/docs/fy05osti/37408.pdf>

38. Fan, J.; Shonnard, D.; Kalnes, T.; Streff, M.; Hopkins, G., Emission Reduction Using RTP Green Fuel in Industry Facilities: A Life Cycle Study. *Energy & Fuels* **2013**, 27 (9), 5260-5267. DOI: 10.1021/ef400926x

39. Pourhashem, G.; Spatari, S.; Boateng, A. A.; McAloon, A. J.; Mullen, C. A., Life Cycle Environmental and Economic Tradeoffs of Using Fast Pyrolysis Products for Power Generation. *Energy & Fuels* **2013**, 27 (5), 2578-2587. DOI: 10.1021/ef3016206

40. Swanson, R. M.; Platon, A.; Satrio, J. A.; Brown, R. C., Techno-economic analysis of biomass-to-liquids production based on gasification. *Fuel* **2010**, 89, S11-S19. DOI: <https://doi.org/10.1016/j.fuel.2010.07.027>

41. Tan, E. C.; Marker, T. L.; Roberts, M. J., Direct production of gasoline and diesel fuels from biomass via integrated hydrolysis and hydroconversion process—A techno-economic analysis. *Environmental Progress & Sustainable Energy* **2014**, 33 (2), 609-617.

42. Thilakaratne, R.; Brown, T.; Li, Y.; Hu, G.; Brown, R., Mild catalytic pyrolysis of biomass for production of transportation fuels: a techno-economic analysis. *Green Chemistry* **2014**, 16 (2), 627-636. DOI: 10.1039/C3GC41314D

43. Wright, M. M.; Daugaard, D. E.; Satrio, J. A.; Brown, R. C., Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *Fuel* **2010**, 89, Supplement 1, S2-S10. DOI: <http://dx.doi.org/10.1016/j.fuel.2010.07.029>

44. Jones, S. B.; Meyer, P. A.; Snowden-Swan, L. J.; Padmaperuma, A. B.; Tan, E.; Dutta, A.; Jacobson, J.; Cafferty, K. *Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and hydrotreating bio-oil pathway*; Pacific Northwest National Laboratory (PNNL), Richland, WA (US): 2013,

45. Shonnard, D. R.; Williams, L.; Kalnes, T. N., Camelina-derived jet fuel and diesel: sustainable advanced biofuels. *Environ Prog Sustain Energy*. **2010**, 29. DOI: 10.1002/ep.10461

46. Kim, S.; Dale, B. E., Comparing alternative cellulosic biomass biorefining systems: Centralized versus distributed processing systems. *Biomass Bioenergy* **2015**, 74, 135-147. DOI: <http://dx.doi.org/10.1016/j.biombioe.2015.01.018>

47. Nguyen, L.; Cafferty, K.; Searcy, E.; Spatari, S., Uncertainties in Life Cycle Greenhouse Gas Emissions from Advanced Biomass Feedstock Logistics Supply Chains in Kansas. *Energies* **2014**, 7 (11), 7125. <http://www.mdpi.com/1996-1073/7/11/7125>

48. Argo, A. M.; Tan, E. C. D.; Inman, D.; Langholtz, M. H.; Eaton, L. M.; Jacobson, J. J.; Wright, C. T.; Muth, D. J.; Wu, M. M.; Chiu, Y.-W.; Graham, R. L., Investigation of biochemical biorefinery sizing and environmental sustainability impacts for conventional bale system and advanced uniform biomass logistics designs. *Biofuels, Bioproducts and Biorefining* **2013**, 7 (3), 282-302. DOI: 10.1002/bbb.1391

49. Ray, A. E.; Hoover, A. N.; Nagle, N.; Chen, X.; Gresham, G. L., Effect of pelleting on the recalcitrance and bioconversion of dilute-acid pretreated corn stover under low- and high-solids conditions. *Biofuels* **2013**, 4 (3), 271-284. DOI: 10.4155/bfs.13.14

50. Richard, T. L., Challenges in Scaling Up Biofuels Infrastructure. *Science* **2010**, 329 (5993), 793-796. DOI: 10.1126/science.1189139

51. Rijal, B.; Igathinathane, C.; Karki, B.; Yu, M.; Pryor, S. W., Combined effect of pelleting and pretreatment on enzymatic hydrolysis of switchgrass. *Bioresour. Technol.* **2012**, *116*, 36-41. DOI: <https://doi.org/10.1016/j.biortech.2012.04.054>

52. Theerarattananoon, K.; Xu, F.; Wilson, J.; Staggenborg, S.; McKinney, L.; Vadlani, P.; Pei, Z.; Wang, D., Effects of the pelleting conditions on chemical composition and sugar yield of corn stover, big bluestem, wheat straw, and sorghum stalk pellets. *Bioprocess Biosystems Eng.* **2012**, *35* (4), 615-623. DOI: 10.1007/s00449-011-0642-8

53. ESRI, ArcGIS desktop: release 10. *Environmental Systems Research Institute, CA* **2011**.

54. United States Department of Agriculture, Forest Service's Timber Product Output database. National Renewable Energy Laboratory: 2012, <https://maps.nrel.gov/biofuels-atlas/#/?aL=0gBHTu%255Bv%255D%3Dt&bL=groad&cE=0&lR=0&mC=40.17887331434696%2C-91.58203125&zL=4>.

55. Gorr, W. L.; Kurland, K. S., *GIS tutorial: workbook for ArcGIS 10.1*. ESRI, Inc.: 2013, p 447

56. PRé SimaPro V. 8.5.2.0, 8.5.2.0; PRé Consultants: The Netherlands, 2018,

57. Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., and Weidema, B., The ecoinvent database version 3 (part I): overview and methodology. *The International Journal of Life Cycle Assessment* **2016**, <http://link.springer.com/10.1007/s11367-016-1087-8>, 13.

58. Energy Information Administration, Petroleum Refineries. National Renewable Energy Laboratory: 2016, <https://maps.nrel.gov/biofuels-atlas/#/?aL=6JpW2v%255Bv%255D%3Dt&bL=groad&cE=0&lR=0&mC=40.17887331434696%2C-91.58203125&zL=4>.

59. Energy Information Administration, Crude Oil Pipelines. National Renewable Energy Laboratory: 2016, <https://maps.nrel.gov/biofuels-atlas/#/?aL=rZVVfY%255Bv%255D%3Dt%260gBHTu%255Bv%255D%3Dt%260gBHTu%255Bd%255D%3D1&bL=groad&cE=0&lR=0&mC=40.17887331434696%2C-91.58203125&zL=4>.

60. Brechbill, S. C.; Tyner, W. E.; Ileleji, K. E., The economics of biomass collection and transportation and its supply to Indiana cellulosic and electric utility facilities. *BioEnergy Research* **2011**, *4* (2), 141-152.

61. Zafar, S. How is Biomass Transported. <https://www.bioenergyconsult.com/biomass-transportation/> (accessed May 9), <https://www.bioenergyconsult.com/biomass-transportation/>

62. International Organization for Standardization, ISO 14041: Environmental Management: Life Cycle Assessment- Goal and Scope Definition and Inventory Analysis. Geneva, 2006, <https://www.iso.org/standard/23152.html>.

63. Zhang, Y.; Hu, G.; Brown, R. C., Life cycle assessment of the production of hydrogen and transportation fuels from corn stover via fast pyrolysis. *Environmental Research Letters* **2013**, *8* (2), 025001. DOI: 10.1088/1748-9326/8/2/025001

64. Myhre, G.; D. Shindell; F.-M. Bréon; W. Collins; J. Fuglestedt; J. Huang; D. Koch; J.-F. Lamarque; D. Lee; B. Mendoza; T. Nakajima; A. Robock, G. S.; Takemura, T.; Zhang, H. *Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science Basis*; Cambridge, United Kingdom

New York, NY, USA, 2013; p 104, https://www.ipcc.ch/pdf/assessment-report/ar5/wg1/WG1AR5_Chapter08_FINAL.pdf

65. Han, J.; A.Elgowainy; I. Palou-Rivera; J.B. Dunn; Wang, M. Q., Well-to-Wheels Analysis of Fast Pyrolysis Pathways with GREET. Argonne National Laboratory: Oak Ridge, Tennessee, 2011, http://greet.es.anl.gov/publication-wtw_fast_pyrolysis 76.
66. Ecoinvent, 05-19-2015 ed.; <http://www.ecoinvent.org/>, 2016, <https://ecoquery.ecoinvent.org/Details/UPR/84ADD57A-F3E5-4AA6-98BF-30C047A31CE5/DD7F13F5-0658-489C-A19C-F2FF8A00BDD9>.
67. Wang M, Huo H. Fuel-cycle assessment of selected bioethanol production pathways in the United States; 2006. pp. 1–65. <https://greet.es.anl.gov/files/2lli584z>.
68. United States Department of Energy - Office of Energy efficiency and Renewable energy, Biomass Feedstock and Composition Database. 2006, : http://www1.eere.energy.gov/biomass/printable_versions/feedstock_databases.html
69. U.S. Energy Information Administration *Annual Energy Outlook 2017 with projections to 2050*; p 64, [https://www.eia.gov/outlooks/aeo/pdf/0383\(2017\).pdf](https://www.eia.gov/outlooks/aeo/pdf/0383(2017).pdf)
70. Bals, B. D.; Dale, B. E., Developing a model for assessing biomass processing technologies within a local biomass processing depot. *Bioresour. Technol.* **2012**, *106*, 161-169. DOI: <https://doi.org/10.1016/j.biortech.2011.12.024>
71. Sundaram, V.; Muthukumarappan, K.; Gent, S., Understanding the Impacts of AFEX™ Pretreatment and Densification on the Fast Pyrolysis of Corn Stover, Prairie Cord Grass, and Switchgrass. *Appl. Biochem. Biotechnol.* **2017**, *181* (3), 1060-1079. DOI: 10.1007/s12010-016-2269-3
72. Wang, H.; Zhang, B.; Xiu, S.; Li, R.; Shi, J., Densification and Pyrolysis of lignocellulosic biomass for renewable energy. *Curr. Org. Chem.* **2016**, *20* (23), 2480-2488.
73. Gao, S., Gurian, P.L., Adler, P.R., Spatari, S., Gurung, R., Ogle, S.M., Parton, W.J., Del Grosso, S.J., Framework for improved confidence in modeled nitrous oxide estimates for biofuel regulatory standards, Mitigation and Adaptation Strategies for Global Change. **2017**, DOI: 10.1007/s11027-018-9784-1

For Table of Contents Use Only

Table of Contents Graphic:

Life cycle assessment is used to evaluate transportation fuels produced via fast pyrolysis and subsequent electrochemical deoxygenation upgrade.