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Arna Ganguly  
*iowa State University*, aganguly@iastate.edu

Irene M. Martin  
*iowa State University*, iremas@iastate.edu

Robert C. Brown  
*iowa State University*, rcbrown3@iastate.edu

Mark M. Wright  
*iowa State University*, markmw@iastate.edu

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Application of Hydroprocessing, Fermentation, and Anaerobic Digestion in a Carbon-Negative Pyrolysis Refinery

Abstract
This study investigates the economic and environmental benefits of integrating hydroprocessing, fermentation, and anaerobic digestion into a pyrolysis refinery. Two scenarios were developed for upgrading and/or utilizing the primary products of pyrolysis (bio-oil, gas, and char). The first (hydroprocessing) scenario hydroprocesses whole bio-oil into gasoline and diesel. The second (fractionation) scenario fractionates bio-oil into sugars for fermentation to cellulosic ethanol and residual phenolic oil as the primary product. Both scenarios use the gaseous product of pyrolysis for process heat in the plant and employ biochar to enhance anaerobic digestion of manure for power generation. The fast pyrolysis plant processes 2000 ton/day of corn stover while the anaerobic digester employs 430 ton/day of manure to generate power. The hydroprocessing scenario produces gasoline at a minimum fuel-selling price (MFSP) of $2.77 per gallons of gasoline while the fractionation scenario produces ethanol and phenolic oils (diesel) as a transportation fuel for $1.2 per gallon ($1.41 per GGE). Sensitivity analysis indicates that the MFSP for both scenarios is highly sensitive to the fixed capital cost. Fixed capital costs for the hydroprocessing and fractionation scenarios were estimated to be $643 and $288 million, respectively. Fuel production rates for the hydroprocessing and fractionation scenarios were estimated to be 60.5 and 16 million GGE per year, respectively. Life cycle greenhouse gas emissions were calculated as −9.6 and −16.6 g CO2,eq per MJ for the hydroprocessing and fractionation scenarios, respectively. LCA emissions are sensitive to byproduct credits derived from biochar sequestration and power generation. This study shows that both systems produce transportation fuels at competitive market prices with an additional reduction in atmospheric CO2 levels compared to fossil fuel sources.

Keywords
Fast pyrolysis, hydroprocessing, anaerobic digestion, fermentation, techno-economic analysis, life cycle analysis

Disciplines
Bioresource and Agricultural Engineering | Energy Systems | Other Economics | Process Control and Systems | Sustainability

Comments
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Application of hydroprocessing, fermentation and anaerobic digestion in a carbon-negative pyrolysis refinery

*Arna Ganguly¹, Irene M. Martin¹, Robert C. Brown¹, ², Mark M. Wright¹, ²*

¹Department of Mechanical Engineering, Iowa State University, Ames, IA 50014, United States
²Bioeconomy Institute, Iowa State University, Ames, IA 50015 United States
*Corresponding author: markmw@iastate.edu

ABSTRACT. This study investigates the economic and environmental benefits of integrating hydroprocessing, fermentation and anaerobic digestion into a pyrolysis refinery. Two scenarios were developed for upgrading and/or utilizing the primary products of pyrolysis (bio-oil, gas and char). The first (hydroprocessing) scenario hydroprocesses whole bio-oil into gasoline and diesel. The second (fractionation) scenario fractionates the bio-oil into sugars for fermentation to cellulosic ethanol and residual phenolic oil as primary product. Both scenarios use the gaseous product of pyrolysis for process heat in the plant and employ biochar to enhance anaerobic digestion of manure for power generation.

The fast pyrolysis plant processes 2000 ton/day of corn stover while the anaerobic digester employs 430 ton/day of manure to generate power. The hydroprocessing scenario produces gasoline at a minimum fuel-selling price (MFSP) of $2.77 per gallons of gasoline while the fractionation scenario produces ethanol and phenolic oils (diesel) as transportation fuel for $1.2 per gallon ($1.41 per GGE). Sensitivity analysis indicates that the MFSP for both scenarios is highly sensitive to the fixed capital cost. Fixed capital costs for the hydroprocessing and fractionation scenarios were estimated to be $643 million and $288 million, respectively. Fuel production rates for the hydroprocessing and fractionation scenarios are 60.5 and 16 million GGE per year, respectively. Life cycle greenhouse gas emissions were calculated as -9.6 and –16.6 gm CO₂eq per MJ for the hydroprocessing and fractionation scenarios, respectively. LCA emissions are sensitive to by-product credits derived from biochar sequestration and power generation. This study shows that both systems produce transportation fuels at competitive market prices with an additional reduction in atmospheric CO₂ levels compared to fossil fuel sources.

KEYWORDS. Fast pyrolysis, hydroprocessing, anaerobic digestion, fermentation, techno-economic analysis, life cycle analysis
INTRODUCTION

Limited fossil fuel reserve and its detrimental effects to the environment has led to climate change which has become a global issue (1). Atmospheric carbon dioxide (CO$_2$) levels have recently exceeded 400 parts per million (2). According to the Intergovernmental Panel on Climate Change (IPCC), these levels will likely increase global average temperatures by 2 °C (3). Thus, we need renewable energy-based technologies to meet society’s growing demand for energy while reducing atmospheric carbon levels. Several carbon negative energy technologies have been proposed (4), but a detailed economic and environmental impact assessments remain limited (5,6).

Biofuels and electricity can be produced from crop residues like corn stover and wastes such as animal manure (7,8). Fast pyrolysis, anaerobic digestion (AD) and fermentation can produce bioenergy with much lower environmental impacts than fossil-based alternatives, but their economic costs are often higher than industrial technologies (9,10). Recent studies have shown that process integration and product portfolios could lower the market risk of bio-renewable technologies (11). For example, fast pyrolysis provides a flexible platform to produce biofuels and bioproducts because of its ability to decompose biomass to organic fractions with distinct characteristics (12). Previous studies have shown that these fractions can be upgraded into gasoline, ethanol, sugars (13–15), biocement (16), bioasphalt (17), lignocoal (18), aromatics(19), and other commodity and specialty chemicals. Bio-oil is the primary product from fast pyrolysis, and it contains hundreds of organic compounds(20). Bio-oil can be upgraded to gasoline and other hydrocarbon fuels through hydroprocessing(14). Bio-oil also contains sugars that can be separated and fermented to produce ethanol (21). Bio-oil includes a large number of specialty chemicals that could be recovered with further technology development (22). Finally, biochar, the solid co-product of biomass fast pyrolysis, is a carbon-rich resource that could displace coal for combustion
applications (23) or serve as a carbon sequestration agent in agricultural applications (24). There is a growing interest in studying the use of biochar in anaerobic digesters (25–28). Recent studies have shown that biochar can enhance microbial productivity, improve biogas quality, and enrich nutrient content in the solid digestate of anaerobic digesters (29). A study by Luo et.al. (2015) showed that biochar increased methane production content by 86.6% under biochar incubation conditions with glucose being used as a substrate (30). According to Junting Pan et al., addition of biochar at the ratio of 5% to chicken manure (dry weight) in anaerobic digester lead to an increase in methane yield by 69% compared to the control (31). These novel strategies improve bio-renewable resource utilization by enhancing productivity and system efficiency.

Techno-economic analysis (TEA) of a fast pyrolysis system using corn stover as feedstock showed potential in producing naphtha and diesel range fuel products at a minimum-selling price of $2.00-3.00 per gallon (32–35). Life cycle analysis (LCA) of fast pyrolysis system using corn stover as input shows a reduction in GHG emission by 67% when compared to petroleum gasoline (35–37). Similarly, TEA and LCA of AD system had produced bio-electricity worth $0.44/kWH_e along with an average reduction of 88% in GHG emissions (4). Combined systems of anaerobic digestion and pyrolysis processes have been investigated to identify energy recovery strategies for processing agricultural residues. These strategies employ excess heat from the AD process for drying biomass before pyrolysis to improve process energy efficiency (38). Further integration with fermentation or hydroprocessing could yield transportation fuels, electricity and high-value chemicals while improving resource use and energy efficiency.

Carbon-negative bioenergy is achieved when the process of producing the former encounters lesser GHG emissions than what it withdraws from the environment (39). To our knowledge, there have not been studies evaluating the prospects of carbon negative energy from pyrolysis refineries.
by integrating them with anaerobic digestion of manure. This paper evaluates the prospects for producing carbon-negative transportation fuels and electricity from pyrolysis refineries. Two scenarios were developed for upgrading and/or utilizing the primary products of pyrolysis (bio-oil, gas and char). The first (hydroprocessing) scenario hydroprocesses the whole bio-oil into gasoline and diesel. The second (fractionation) scenario fractionates the heavy ends of the bio-oil into sugars for fermentation to cellulosic ethanol and phenolic oil for transportation fuel applications. Both scenarios use the gaseous product of pyrolysis for process heat and employ biochar to enhance anaerobic digestion of manure for power generation.

METHODOLOGY

This study conducts both life cycle analysis (LCA) and techno-economic analysis (TEA) of two integrated systems consisting of four primary processes as shown in Figure 1. Corn stover is first processed through a fast pyrolysis unit to produce bio-oil. In the hydroprocessing scenario, the bio-oil is hydroprocessed to gasoline. In the fractionation scenario, the bio-oil is first split into a sugar stream for fermentation to ethanol and the remaining fraction left is phenolic oil, both of which is further utilized as transportation fuel. In both scenarios, fast pyrolysis biochar mixes with cow manure for anaerobic digestion to generate power.
Figure 1. Integrated corn stover fast pyrolysis and bio-oil hydroprocessing to gasoline (green) or fermented and fractioned to ethanol and phenolic oils (blue) with biochar-enhanced manure anaerobic digestion to power. Units and products shaded in grey are common to both scenarios.

The system analysis for both scenarios follows three steps: 1) process modeling, 2) TEA, and 3) LCA. Process modeling employs Aspen Plus™ to calculate mass and energy balances across processing units. TEA involves estimating the capital and operating costs of the commercial scale biorefinery eventually quantifying the minimum fuel selling prices produced in the two scenarios. The LCA is based on the well-to-wheel methodology employed by GREET.net (40).

PROCESS MODELLING

Two process models were developed to simulate commercial scale biorefineries processing 2000 metric tonnes per day (MTPD) of corn stover to either gasoline or ethanol and 430 dry (MTPD) of cow manure and biochar to power. The fast pyrolysis process model for both scenarios is built upon recent work by Li et al. (33) as well as hydroprocessing to gasoline. The sugar fractionation model is based on the National Renewable Energy Laboratory design report by Humbird et al. (41). The anaerobic digestion design is based on a study by Aui et al. (5). Figures S1 and S2 in the supporting information show simplified diagrams for each scenario.

Biomass fast pyrolysis, hydroprocessing, and anaerobic digestion for gasoline and power production: This study uses similar assumptions to those of Li et al. (33). The biorefinery receives corn stover with 25% moisture content and 10 mm average particle diameter. The feedstock is initially dried and ground to less than 10 wt. % moisture and 3 mm particle size before feeding into the pyrolysis reactor. The reactor operates at 500 °C and yields pyrolysis vapors and biochar. The pyrolysis vapors are upgraded through a condensation system into heavy ends, light ends, and
non-condensable gases (NCG)(33,34). For the hydroprocessing scenario, the heavy ends are further hydroprocessed to produce gasoline; the light ends are steam reformed with natural gas to produce hydrogen; and the NCG are combusted to generate process heat. The biochar is collected and mixed with manure at a 15:1 manure to biochar ratio(26). The manure and biochar mixture feed into the anaerobic digester operating at mesophilic temperatures of about 35 °C while producing biogas, and biochar-rich solid and liquid digestate. The biogas is combusted for power production, and the biochar-rich digestate streams are used to replace soil fertilizer. The biochar becomes sequestered through the soil application of the solid digestate.

Biomass pyrolysis, fractionation and anaerobic digestion for ethanol, phenolic oil and power production: This scenario shares similar fast pyrolysis and anaerobic digestion structures with the hydroprocessing scenario. In this particular scenario, the pyrolytic sugars are recovered as a syrup from the heavy ends through water extraction(21), and before being sent to the fermentation system, they pass through a cleaning block to eliminate toxic compounds which might inhibit the fermentation process(42). After the cleaning process, the syrup goes to the fermentation system where it mixes with conditioning chemicals like DPA, ammonia, glucose, and sulfuric acid. The heavy end oil fractions from pyrolysis of corn stover primarily consists of G- and H-phenols(43). Pyrolyzed bio-oil consists of around 21% of phenolic compounds, and it can be upgraded to fuels for marine markets(44,45). In this study, we assume that phenolic oils would be considered as transportation (diesel) fuel along with ethanol. The anaerobic digestion system is the same as in the hydroprocessing scenario.

The ethanol production model is based on the study by NREL on Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover (41). The pyrolytic syrup contains a mixture of C₅ and C₆ sugars that would ferment into ethanol with similar yields to sugars from the enzymatic hydrolysis
of corn stover. Thus, all other assumptions in the ethanol model are the same as described by Humbird et al. The NREL model contains 9 sections with over 250-unit operations and describing it in detail would significantly extend the scope of the paper.

LIFE CYCLE ANALYSIS (LCA)

Life Cycle Analysis is a common method for evaluating the environmental impacts of a product over the course of its lifetime. ISO 14040 is an international standard for LCA, and it defines the principles and framework for evaluating the environmental management of a process or product (46). Several databases and software packages have been developed to implement common LCA methods. We employ Argonne National Laboratory’s Greenhouse gases, Regulated Emissions, and Energy use in Transportation GREET.net (40) software to evaluate the emissions of gasoline and ethanol production from the integrated biorefineries modeled in this study. Table 1 shows the inventory table for all resources considered in the LCA analysis. To compare both scenarios, GHG emissions were normalized to a functional unit of 1 MJ of liquid fuel output. The displacement method was employed to allocate emissions to by-products.

**Table 1.** Life cycle analysis emission factor inventory table

<table>
<thead>
<tr>
<th>Resource</th>
<th>Emission Factor (kg CO$_2$eq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina Sulfate</td>
<td>0.069</td>
</tr>
<tr>
<td>Ammonia</td>
<td>2.647</td>
</tr>
<tr>
<td>Biochar</td>
<td>-0.381</td>
</tr>
<tr>
<td>Cellulose</td>
<td>2.301</td>
</tr>
<tr>
<td>Corn Steep Liquor</td>
<td>1.612</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>0.042</td>
</tr>
<tr>
<td>Diammonium Phosphate</td>
<td>1.211</td>
</tr>
<tr>
<td>Electricity (kg CO$_2$eq/kWh)</td>
<td>-0.479</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.783</td>
</tr>
<tr>
<td>Manure*</td>
<td>-0.074</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>0.589</td>
</tr>
<tr>
<td>Urea</td>
<td>1.942</td>
</tr>
</tbody>
</table>

* All values gathered from GREET.net except Manure (47)

Biomass fast pyrolysis, hydroprocessing and anaerobic digestion for gasoline and power production: the hydroprocessing scenario’s material and energy inputs are corn stover, manure and natural gas, and the outputs include electricity, biochar, and gasoline. Other potential resources such as process chemicals are considered to be used in quantities with negligible GHG impacts. We assume that the corn stover is locally (20-mile radius) sourced from a U.S. Midwest location. Cow manure is available within a 5-mile radius. Natural gas is based on the U.S. conventional natural gas mixture. The anaerobic digestion power generation displaces electricity from the U.S. national grid. Biochar is sequestered as described by Han et al. (48) with over 80% of the biochar carbon remaining under soil after a period of 100 years.

Biomass pyrolysis, fractionation, and anaerobic digestion for ethanol, phenolic oil and power production: the fractionation scenario’s material and energy inputs include cellulose, glucose, ammonia, alumina sulfate, manure, corn stover, corn steep liquor, diammonium phosphate, and urea. Its outputs are phenolic oils, biochar, electricity, and ethanol.

**TECHNO-ECONOMIC ANALYSIS (TEA)**

Techno-economic analysis was employed to estimate the minimum fuel-selling price (MFSP) of gasoline for scenario I and ethanol and phenolic oil for scenario II. MFSP is the lowest biofuel price that achieves a 10% internal rate of return (IRR) over the project lifetime. We employed a 20-year discounted cash flow rate of return (DCF-ROR) analysis based on the methodology developed by NREL (41). The DCF-ROR calculates the Net Present Value (NPV) of annual
revenues, expenses, and investment costs. Annual revenues include the sale of by-products at specified prices and biofuel at the MFSP. Annual expenses include material and energy costs, fixed (labor, maintenance, insurance) costs, depreciation, and income tax. Investment costs consists of equipment purchase and installation, indirect project costs, working capital, and loan interest. All costs quantified in the two scenarios are presented on a 2011 basis. Table 2 shows the material and energy prices for the two biorefinery scenarios. Table 3 shows the common economic assumptions for both scenarios.

As shown, the only common materials across both scenarios are corn stover and manure. We assumed a delivered corn stover feedstock price of $83 per tonne at the biorefinery gate, and a manure price of $5 per tonne. Economic assumptions for pyrolysis and hydroprocessing are described in more details in the paper by Li et al. (33). Anaerobic digestion economic assumptions are described in Aui et al.(5), and ethanol economic assumptions are based on Humbird et al.(41).

Table 2. Hydroprocessing and fractionation scenario material and energy prices

<table>
<thead>
<tr>
<th>Material/Energy</th>
<th>Price</th>
<th>Units</th>
<th>Material/Energy</th>
<th>Price</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Stover</td>
<td>83</td>
<td>$/tonne</td>
<td>Corn Stover</td>
<td>83</td>
<td>$/tonne</td>
</tr>
<tr>
<td>AD Manure</td>
<td>5</td>
<td>$/tonne</td>
<td>AD Manure</td>
<td>5</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>5.68</td>
<td>$/MMBtu</td>
<td>Sulfuric Acid, 93%</td>
<td>897</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Pyrolysis Catalyst</td>
<td>11.02</td>
<td>$/kg</td>
<td>Ammonia</td>
<td>449</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Hydrotreating Catalyst</td>
<td>34.2</td>
<td>$/kg</td>
<td>Corn Steep Liquor</td>
<td>56.8</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Hydro Cracking Catalyst</td>
<td>34.2</td>
<td>$/kg</td>
<td>Diammonium Phosphate</td>
<td>987</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Hydrogen Plant Catalysts</td>
<td>360</td>
<td>$/kscf H₂</td>
<td>Glucose</td>
<td>580</td>
<td>$/tonne</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----</td>
<td>-----------</td>
<td>---------</td>
<td>-----</td>
<td>---------</td>
</tr>
<tr>
<td>Boiler Chemicals</td>
<td>3.10</td>
<td>$/kg</td>
<td>Host nutrients</td>
<td>822</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Cooling Tower Chemicals</td>
<td>4.00</td>
<td>$/kg</td>
<td>Sulfur Dioxide</td>
<td>304</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Calcium Acetate</td>
<td>0</td>
<td>$/kg</td>
<td>Caustic (as pure)</td>
<td>150</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Sand &amp; Ash</td>
<td>22.0</td>
<td>$/tonne</td>
<td>FGD Lime</td>
<td>199</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Wastewater Treatment</td>
<td>0.09</td>
<td>$/kg COD</td>
<td>Makeup Water</td>
<td>1.39</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Off-Gas</td>
<td>0</td>
<td>$/kg</td>
<td>Disposal of Ash</td>
<td>6.61</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Makeup Water</td>
<td>1.01</td>
<td>$/1000 gal</td>
<td>Process Water</td>
<td>0.2</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Boiling Feed Water</td>
<td>1.01</td>
<td>$/1000 gal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process Water</td>
<td>1.01</td>
<td>$/1000 gal</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Common economic assumptions for the hydprocessor and fractionation scenarios

<table>
<thead>
<tr>
<th>Price</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>8410</td>
<td>Hours</td>
</tr>
<tr>
<td>20</td>
<td>Years</td>
</tr>
<tr>
<td>10</td>
<td>%</td>
</tr>
<tr>
<td>35</td>
<td>%</td>
</tr>
<tr>
<td>8</td>
<td>%</td>
</tr>
<tr>
<td>10</td>
<td>Years</td>
</tr>
<tr>
<td>40</td>
<td>%</td>
</tr>
<tr>
<td>3</td>
<td>Years</td>
</tr>
<tr>
<td>[0.6, 0.32, 0.08]</td>
<td>By Year</td>
</tr>
</tbody>
</table>

The process models of the two scenarios are developed in Aspen Plus v.10. Material and energy balances across unit operations were employed to size and cost equipment using Aspen Process Economic Analyzer or public sources such as NREL reports. Equipment costs were scaled using
the Economies of Scale Law (49) based on the input mass flows as shown in Equation 1. A scaling exponent of 0.72 was assumed, which is typical of thermochemical facilities. The Fixed Capital Investment is estimated by multiplying the total purchased equipment cost by an installation factor of 3.73 as described by Peters and Timmerhaus(50). The total project investment (TPI) is equal to the equipment costs times a LANG Factor assumed here to be 4.02 in both scenarios.

\[
\frac{C_2}{C_1} = \left(\frac{M_2}{M_1}\right)^n
\]

\(C\)=cost, \(M\)=mass flow, \(n\)=scaling exponent, and \(1,2\)=base, scaled-up values.

SENSITIVITY ANALYSIS

The sensitivity of cost estimates and greenhouse gas emission results to various key parameters is investigated by varying their values by a nominal ±20% from their base case assumption. This approach helps identify key process and economic parameters that could help reduce costs and emissions for each process based on their relative impacts. The TEA sensitivity analysis investigates the impact of liquid fuel output, operating hours, fixed capital, corn stover price, IRR, project lifetime, AD manure price, AD biochar-rich solid digestate credit, AD liquid effluent credit, and the natural gas price on the MFSP. The LCA sensitivity analysis evaluates the impacts of the electricity, biochar, corn stover, natural gas, manure, corn steep liquor, diammonium phosphate, ammonia, glucose, and alumina sulfate on the lifecycle greenhouse gas emissions.

RESULTS AND DISCUSSION

Table 4 summarizes the key results obtained for both scenarios. Gasoline production from 2000 metric tonne per day of corn stover for the pyrolysis, anaerobic digestion, and hydroprocessing system was estimated at 60.5 million gallons per year. The fractionation scenario generates 11.5 million gallons per year of ethanol and 7.13 million gallons per year of phenolic oil, or 16 million gallons of gasoline equivalent (GGE) biofuel. Capital costs for the hydroprocessing and fractionation scenarios are estimated at $643 and $288 million, respectively. Annual operating
costs for gasoline production are around 168 million dollars and 108 million dollars for ethanol and phenolic oil production. The MFSP for the two scenarios are $2.77 and $1.20 ($1.41/GGE) per gallon, respectively. Table 4 also includes the GHG emission estimates for the two scenarios. Hydroprocessing scenario has emissions of –9.6 gm CO₂/MJ gasoline, and fractionation scenario has emissions of –16.6 gm CO₂/ MJ ethanol and phenolic oil suggesting that both of these processes potentially achieve carbon negative biofuel production.

Table 4. Comparison of hydroprocessing and fractionation scenario costs, fuel yield, minimum fuel-selling price, and greenhouse gas emissions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Hydroprocessing Scenario</th>
<th>Fractionation Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital cost (millions $)</td>
<td>643</td>
<td>288</td>
</tr>
<tr>
<td>Annual operating cost (millions $)</td>
<td>167.7</td>
<td>108.03</td>
</tr>
<tr>
<td>Fuel yield (million gallons/year)</td>
<td>60.5</td>
<td>11.5-Ethanol 7.13-Phenolic oil (16 gge)</td>
</tr>
<tr>
<td>Minimum fuel selling price (MFSP)</td>
<td>$2.77</td>
<td>$1.2 ($1.41 /gge)</td>
</tr>
<tr>
<td>Greenhouse gas emissions (GHG)(g CO₂/MJ Fuel)</td>
<td>-9.6</td>
<td>-16.6</td>
</tr>
</tbody>
</table>

GGE: gallons of gasoline equivalent

Table 5 shows the by-products produced and revenue earned in the two scenarios. Electricity production and revenue earned are 105,000 MWhr/year and $6.74 million per year for both the
scenarios. The biochar-rich solid and liquid digestate production in the anaerobic digestion system are around 0.11 million tonne per year for both scenarios. The digestate revenues earned in the two scenarios are around $3.7 million per year which sums up the total earned revenue to $10.44 million per year.

Table 5. By-products (electricity and digestate) production and revenues for the two scenarios

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Hydroprocessing/Fractionation Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount produced (million tonne/year)</td>
</tr>
<tr>
<td>Electricity</td>
<td>105,000 MW-hr/year</td>
</tr>
<tr>
<td>Biochar-rich Solid Digestate</td>
<td>0.10</td>
</tr>
<tr>
<td>Liquid Digestate</td>
<td>0.014</td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
</tbody>
</table>

TECHNO-ECONOMIC ANALYSIS

The total capital cost for the fractionation production scenario is around 55% less than for the hydroprocessing production scenario as shown in Figure 2. For the hydroprocessing scenario, bio-oil stabilization, pretreatment of feedstock and pyrolysis along with boiler account for around 82% of the total equipment cost. For the fractionation scenario, pyrolytic recovery of bio-oils, boiler and wastewater treatment plant account for around 79% of the total equipment cost.
Figure 2. Installed equipment costs for the hydroprocessing and fractionation scenarios

Figure 3 shows the contribution of different factors to the annual operating costs for both scenarios. Feedstock cost and return on investment (ROI) contribute the most in both cases. For the hydroprocessing scenario, corn stover contributes $58 million per year and an annual return on investment (ROI) of $46 million. Power generation from anaerobic digestion provides a revenue of $7 million per year. For the fractionation scenario, corn stover and ROI contribute $58 and $21 million per year, respectively. The uncertainty associated with these costs estimates is ±30% because the analysis represents a preliminary engineering design.
Figure 3. Annual Operating Costs for gasoline, and ethanol and phenol production with anaerobic digestion power generation

Figure 4 illustrates the economic sensitivity of the two scenarios to key process parameters. The hydrotreatment scenario (4a) is highly sensitive to its corresponding fuel output. A 20% decrease in the gasoline yield will increase the MFSP by around 69 cents and increasing it by 20% will decrease the MFSP by 46 cents. The facility operating hours has a similar impact on the MFSP. Fixed capital costs, corn stover price, and the expected IRR are next in importance with a directly proportional relationship with the MFSP. The MFSP of the fractionation scenario (4b) is highly sensitive to the phenolic oil output in comparison to the same for ethanol. A 20% increase in the phenolic oil production decreases the ethanol MFSP by about 18 cents per gallon of the transportation fuel. After hours of plant operation, the next two parameters affecting the MFSP most are corn stover price and fixed capital, both being directly proportional to the MFSP of the
fractionation scenario. Corn stover price is more sensitive than fixed capital, and with ±20% in feedstock input, the MFSP varies by around ±$0.13 per gallon of transportation fuel. These results suggest that the performance and robustness of the integrated facilities are important for their commercial viability.

**Figure 4.** Sensitivity analysis of (a) gasoline and (b) ethanol production with anaerobic digestion to power minimum fuel-selling price. Labels include the baseline values for each parameter.

LIFE CYCLE ANALYSIS
Figure 5 shows the distribution of GHG emission sources and sinks for the two scenarios. Corn stover is the primary source of emissions in both cases with contributions of 4 and 9.5 gm of CO$_2$eq per MJ for gasoline and ethanol and phenolic oil, respectively. Electricity is the primary GHG emission avoidance factor with 7.8 and 16 gm of CO$_2$eq per MJ of gasoline and ethanol and phenolic oil displaced from the U.S. grid. Both the scenarios produce a similar amount of electricity. However, the normalized GHG emission values differ due to a greater parasitic energy load and higher output of ethanol and phenolic oil together in the fractionation scenario. Biochar rich digestates also contribute towards reducing CO$_2$ emissions for both the scenarios, the numbers being 6.5 and 11 gm of CO$_2$eq per MJ of gasoline and ethanol and phenolic oil.
**Figure 5.** Lifecycle greenhouse gas emissions for integrated gasoline or ethanol and phenol production with anaerobic digestion to power

LCA sensitivity analysis results are shown in Figure 6. By-product credits for electricity and biochar have the greatest impact on the GHG emissions for both scenarios (6a and 6b). A 20% increase in the electricity emission factor results in a 16% decrease in gasoline emissions and 19.5% decrease in ethanol and phenolic oil emissions. Similarly, increasing the biochar quantity by 20% decreases the emissions by around 13% for both the scenarios. Corn stover and manure emissions are also significant. However, manure emissions are inversely proportional to fuel emissions because using manure for biofuel production results in avoided methane emissions. In the hydroprocessing scenario, natural gas use has a similar impact on GHG emissions as manure. Varying other resources required at the biorefinery by 20% results in GHG changes of less than 2%.
CONCLUSIONS

This study compares the production of two integrated biorefinery designs for producing gasoline and ethanol and phenolic oils as well as electricity. Both scenarios employ a pyrolysis system configured for producing bio-oil for hydroprocessing to gasoline or fractionating pyrolytic sugars for fermentation to ethanol. In both scenarios, the pyrolysis biochar mixes with cow manure in an anaerobic digester for electricity generation.

The process design shows that a 2000 metric tonne per day biorefinery generates a gasoline output of 60.5 million gallons per year for the hydroprocessing scenario, and an ethanol and phenolic oil output of 11.5 (ethanol) and 7.13 (phenolic oil) million gallons per year (16 million gallons of GGE) for the fractionation scenario. Both scenarios generate around 105,000 MWhr of electricity and about 0.11 million tonnes of biochar-rich solid and liquid digestate annually. The fractionation scenario additionally produces 0.25 million tonnes of phenolic compounds per year.

Figure 6. Sensitivity analysis of the integrated (a) gasoline and (b) ethanol and phenol with anaerobic digestion power generation lifecycle greenhouse gas emissions. Labels include the baseline values for each parameter.
Techno-economic analysis estimates indicate MFSP of $2.77 and $1.2 ($1.41 /gge) per gallon of gasoline and ethanol and phenolic oil, respectively. Lifecycle GHG emissions were estimated at -9.6 and –16.6 gm CO$_2$e per MJ of gasoline and ethanol and phenolic oil, respectively. Sensitivity analysis shows that displacement credits from power generation and biochar have a significant impact on the lifecycle GHG emissions. These results suggest that the fractionation scenario not only produces transportation fuel (ethanol and phenolic oils) but could also generate additional revenue given a carbon capture and sequestration market. The hydroprocessing scenario achieves a higher biofuel to feedstock energy efficiency suggesting that it provides a better use of renewable resources. Therefore, both process designs could provide a cost-competitive approach to carbon negative biofuel production.

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REFERENCES

1. Leonard MD, Michaelides EE, Michaelides DN. Energy storage needs for the substitution of fossil fuel power plants with renewables. Renew Energy. 2020;


Assessment Report of the Intergovernmental Panel on Climate Change. 2014;


38. Monlau F, Sambusiti C, Antoniou N, Barakat A, Zabaniotou A. A new concept for enhancing energy recovery from agricultural residues by coupling anaerobic digestion and


46. International Organization for Standardization. ISO 14040-Environmental management -


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TOC. Block diagram depicting the co-generation of transportation fuel and power along with solid and liquid digestates for the two integrated scenarios, namely- Hydroprocessing scenario and Fractionation scenario.