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ACS Sustainable Chemistry & Engineering

Research Article

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Fuels and Chemicals from Equine-Waste-Derived Tail Gas Reactive Pyrolysis Oil: Technoeconomic Analysis, Environmental and Exergetic Life Cycle Assessment

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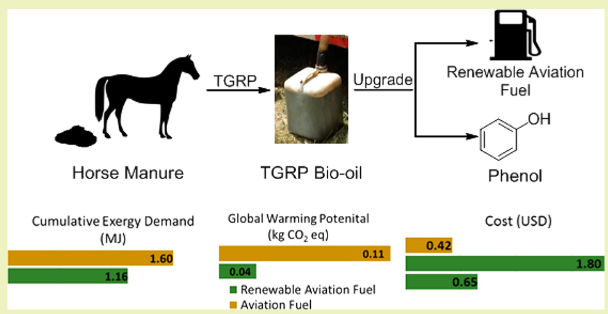
Supporting Information

ABSTRACT: Horse manure, the improper disposal of which, imposes considerable environmental costs, constitutes an apt feedstock for conversion to renewable fuels and chemicals when tail gas reactive pyrolysis (TGRP) is employed. TGRP is a modification of fast pyrolysis that recycles its noncondensable gases and produces a bio-oil low in oxygen concentration and rich in naphthalene. Herein, we evaluate the coproduction of phenol as a value-added renewable chemical, alongside jet-range fuels within distributed TGRP systems using techno-economic analysis and life cycle assessment. We investigate the metrics global warming potential (GWP), cumulative exergy demand (CExD), and cost for the conversion of 200 dry metric tons per day of horse manure to bio-oil and its subsequent upgrade to hydrocarbon fuel and phenolic chemicals. Assigning credits for the offset of the coproducts, the net GWP and CExD of TGRP jet fuel are 10 g of CO_2 eq and 0.4 MJ per passenger kilometer distance traveled, respectively. These values are considerably lower than the GWP and CExD of petroleum-based aviation fuel. The minimum fuel selling price of the TGRP jet fuel (\$1.35−\$1.80 L^{-1}) is estimated to be much greater than that of petroleum-based aviation fuel (\$0.42 L^{-1}), except under optimized fuel conversion and coproduct market conditions (\$0.53−\$0.79 L^{-1}) when including a market price for carbon.



KEYWORDS: *Renewable jet fuel, Phenolic compounds, Equine waste, Life cycle assessment, Greenhouse gas emissions, Social cost of carbon, Exergy analysis*

INTRODUCTION

Horse owners in North America pay an estimated \$50 million dollars per month[1] to properly dispose of 7 million tons of equine waste (horse manure and bedding);[2,3] this is a cost that reaps no economic value. On the other hand, turning the feedstock into a value-added product could be a cost-effective means of using rather than disposing of the resource. One avenue for recovering value from horse manure is to convert it to biofuels and chemicals using thermochemical processes, such as fast pyrolysis.[4,5] Such a strategy could support a renewable economy using biomass resources,[6−8] abate climate change, and support the development of rural communities. The successful contribution of biofuels to a renewable energy economy requires that they are energy efficient and cost-effective and that they do not introduce additional environmental impacts.[9] Currently, resource efficiency and cost limit the commercialization of biofuels. To date, biofuels cannot compete with petroleum-derived products such as aviation fuel (\$0.42 L^{-1}),[10] given the historic fluctuations and more recent drop in the price of petroleum, most noticeably demonstrated by gasoline (\$0.87 L^{-1} in 2008 to \$0.61 L^{-1} in 2015[11]). Hence, added value can be sought in the production of biobased chemicals, which may sell for a higher unit price than liquid fuels, alongside biofuels.[8]

In 2004, the U.S. Department of Energy (DOE) created a single biomass program that merged previous programs for biofuels, biopower, and biobased products.[12] The objective of this merger was to promote biorefineries producing multiple products, including higher-value chemicals, along with fuels and

Received: May 22, 2017
Revised: August 28, 2017
Published: September 4, 2017

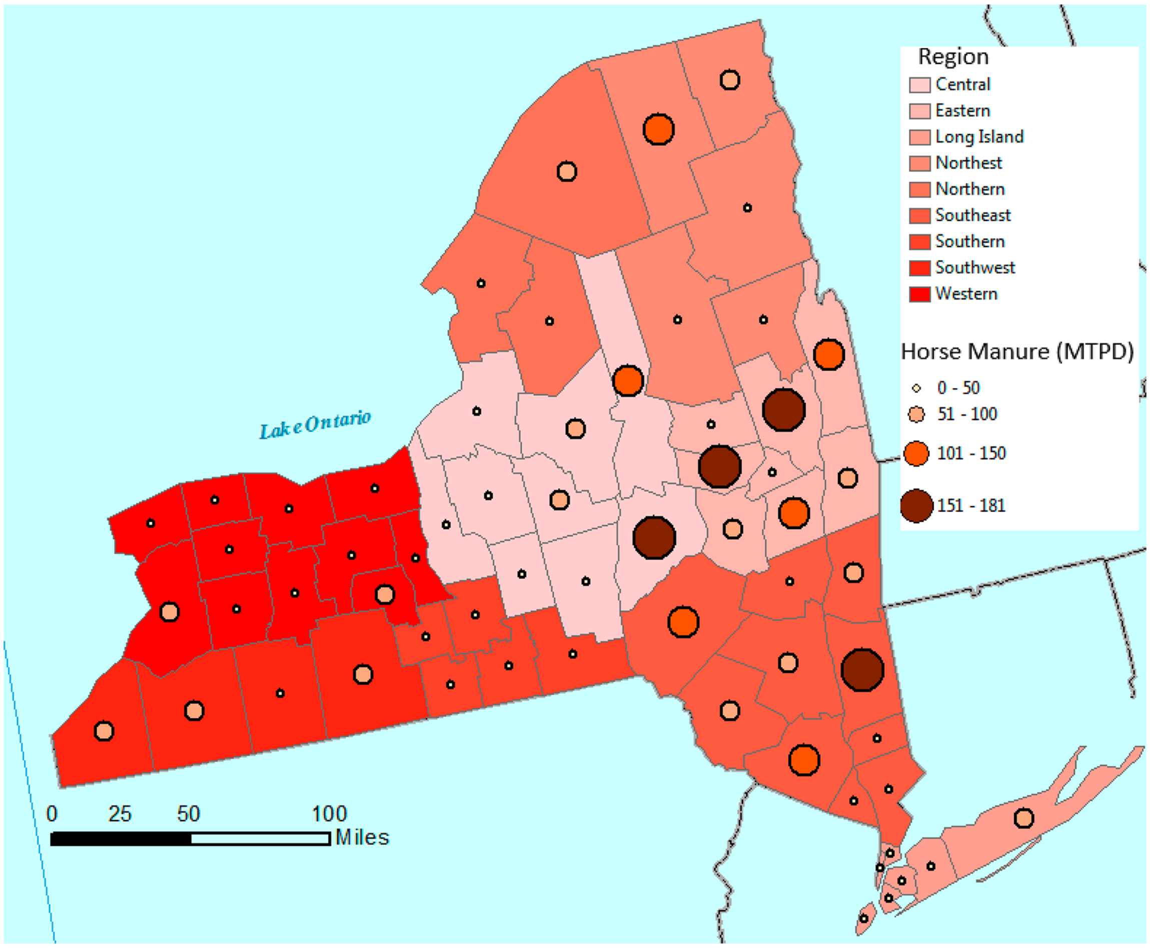


Figure 1. New York State map divided into counties. Color blocks represent the regions in New York State and graduated symbols represent horse manure availability in metric tons per day. Distributed pyrolysis systems scaled up to 200 MTPD would be feasible in multiple locations in New York State.

power.[12] Phenol, which is one of such chemicals present in pyrolysis oil, is examined in this paper. Phenol is a relatively valuable chemical commodity that sells for ~\$1.3 kg^{-1}[13] (compared to aviation fuel at \$0.5 kg^{-1}) and is typically synthesized from crude oil distillates through the cumene process.[14] In addition, phenolic compounds are used as partial phenol substitutes in the phenol formaldehyde resol resin process.[15,16]

With the goal of co-producing value-added chemicals, Mullen et al.[5,17] used tail gas reactive pyrolysis (TGRP), which is a variation of fast pyrolysis in which the noncondensable gases generated during the reaction are recycled into the reactor, to convert horse manure to a bio-oil rich in naphthalenes that could increase the yield of value-added chemicals.[17] Unlike fast pyrolysis, TGRP creates a reductive atmosphere in the pyrolysis reactor, which results in a highly aromatic bio-oil with lower oxygen content than bio-oil produced from fast pyrolysis.[17]

The reactive oxygenated compounds present in fast pyrolysis bio-oil render it incompatible with petroleum refinery infrastructure. The oxygenated compounds of TGRP oil are predominantly phenols (see Table S1 in the Supporting Information (SI)),[18] which, because of their thermal stability, can be distilled and recovered at relatively high purity, compared with fast pyrolysis bio-oil.

The oxygen-poor hydrocarbons obtained after distillation of TGRP oil can further undergo hydrodeoxygenation (HDO) over common catalysts to yield almost completely deoxygenated hydrocarbons that can be directly blended in a petroleum refinery (drop-in) as well as high levels of concentrated phenols that can potentially be separated. HDO has been widely studied as a method of upgrading fast pyrolysis bio-oil and, as such, has been the subject of techno-economic analysis (TEA) and life cycle assessment (LCA) studies.[19−21] These include studies on the LCA of technologies and developments for the production and upgrading of fast pyrolysis bio-oil that are focused on upgrading via hydrotreating and hydrocracking with corn stover[20,22] and poplar[19] as feedstocks. One study[23] concluded that the majority of the environmental impact is due to direct emissions to air and the production of natural gas and electricity consumed in the process. Another study[22] showed that greenhouse gas (GHG) emissions of biofuel produced from upgraded fast pyrolysis oil may be reduced by 88%, relative to gasoline, and 94%, relative to diesel fuel, exceeding the renewable fuel standard-2 (RFS-2) requirements, which states that the life cycle GHG emission reduction threshold for any biomass-based biofuel is 50%.

The overall objective of the current study is to use LCA and TEA to examine the environmental performance and cost of isolating and extracting value-added chemicals, in this case, phenol and its derivatives, and fuel from TGRP oil produced from horse manure, and compare it to the dual-stage HDO upgrading process that is required for bio-oil produced from

DOI: 10.1021/acssuschemeng.7b01609
ACS Sustainable Chem. Eng. 2017, 5, 8804−8814

fast pyrolysis. HDO upgrading consists of mild hydrotreating, followed by severe hydrotreating, which represents a sequence of unit operations that result in a stable bio-oil.[24] We use experimental results from Elkasabi et al., in whose study TGRP oil from three feedstocks (horse manure, eucalyptus and switchgrass) was analyzed. Whereas other studies performed comparative LCA of renewable fuels using biomass such as forest residue,[25] this study exclusively focuses on the use of horse manure, because of the favorable quality of its TGRP bio-oil and that the waste feedstock is available in New York State and Pennsylvania.[4,18,26] While horse manure can be disposed of via spreading, composting, and hauling,[27] these methods come with high capital and operating costs to comply with regulations and they still result in poor water quality.[28] Herein, we evaluate the conversion of horse manure to fuels as an alternative to disposal.

■ METHODS

Techno-economic analysis and life cycle assessment (ISO 14040)[29] were used to investigate the economic and life cycle environmental and exergetic performance of processing horse manure using TGRP and upgrading the TGRP oil to phenol and jet-range fuel. Experimental data from Elkasabi et al.[18] were used to construct thermodynamic conversion models using Aspen Plus software,[30] which, in turn, were integrated into a comprehensive life cycle inventory that considers feedstock provision, biomass conversion, TGRP-oil upgrading to phenols and jet-range fuel, and final consumption.

Biomass Supply and Logistics. Biomass supply was investigated to guarantee security of horse manure supply in the production of TGRP fuel in units of a 200 t per day (MTPD) projected capacity.[8] To illustrate the satisfactory supply potential of horse manure in New York State, we set spatial boundaries using a geographic information system (GIS) map. Data from the USDA 2012 census of agriculture[31] were merged with an equine waste study in New York State.[26]

We estimated the total equine waste generated as the product of the number of farms across the state and the quantity of waste generated per farm. The total amount of equine waste available in New York State was estimated as the product of the total number of farms (10 207) taken from the USDA 2012 census[31] and the average dry equine waste generated per farm (0.17 MRPD) taken from Shayya et al.[26]

Our study evaluated the production of TGRP oil, assuming a daily supply of 200 t of horse manure, which could be supported given the available supply in New York State. Horse manure, having a potential higher heating value of 19.5 GJ per dry metric ton[26] (seeTable S2 in the SI), represents ~25% of the total equine waste,[26] and the supply data on a county level was adapted accordingly, with respect to the obtained equine waste generation data.

Furthermore, we used Arc GIS[32] to determine possible locations of the facility. We used county-level horse manure supply data to predict likely locations for constructing 200 MTPD production facilities; however, more-detailed logistics studies would consider additional factors such as road and rail infrastructures for feedstock transport, and access to labor.[33,34] We limit feedstock transport to an average distance (radius) of 80.5 km (50 mile), similar to prior literature on feedstock-biorefinery logistics,[33,35] assuming that, beyond this radius, the environmental impact and cost of transportation of biomass become disproportionate.

The GIS map for the supply logistics of horse manure (Figure 1) indicates that, in most areas of New York, there will be some generation of horse manure within a 80.5 km radius average. More details on data calculations for the map are found in Table S2.

Although TGRP technology may be feasible with other types of manure such as cow or poultry manure[36,37] and fast pyrolysis has been used previously on poultry waste, we use horse manure, because of its geographical supply in the Northeast and that it has been tested using TGRP[18] at laboratory scale, yielding bio-oil compositions modeled in this paper.

While a 200 MTPD facility is small in scale, relative to a conventional crude oil facility, we suggest that the TGRP process and subsequent extraction would address waste treatment issues as well as contribute to an existing supply of biojet fuel.

Biomass Conversion. The TGRP and oil upgrading facility is assumed to receive horse manure feeds of 200 MTPD, which is a capacity compatible with the small clusters of the equine industry and a scale on par with small- to medium-sized fast pyrolysis facilities that could take agricultural residues[38] and forestry biomass.[39] The TGRP oil yield from horse manure is assumed to be 36.9 wt %, based on previous experimental work.[5] Major processing steps include biomass preparation, TGRP oil production, and TGRP oil upgrade. Biomass preparation and fast pyrolysis have been studied previously,[4] and these results are used to inform the current study. In this study, we build a 200 MTPD biomass conversion model using Aspen Plus,[30] based on TGRP processing conditions analogous to the work of Hammer et al.,[4] who studied fast pyrolysis at a smaller scale of 5 MTPD, by increasing the process scale, adding a preheater, a blower, and recycling the stream of noncondensable gases into the fluidized bed (see Figure S1 in the SI).

The Aspen Plus model simulated for the conversion step was based on experiments that treated manure; however, in commercial production, equine waste, which consists of both manure and bedding, would be used as feedstock. The LCA feedstock harvest step includes manure and bedding collection but the conversion step assumes only the manure portion is converted to fuels and chemicals, giving a lower bound estimate of production volume. Also, because elemental compositions of horse manure and bedding are similar,[18] bio-oil yield would not vary significantly.

The LCA and TEA in this paper used data from previously published bench-scale experiments[5,18] that demonstrated the upgrading of TGRP oil through extraction of bio-oil distillates and separation of phenols.

Aspen Plus[30] was used for process modeling to establish mass and energy balances of the studied TGRP process, scaled to 200 MTPD of horse manure. Furthermore, it was used to estimate utility inputs such as electricity costs for operating pumps and compressors and water utilities for cooling operations. Data for the preprocessing used in the fast pyrolysis Aspen Plus models of Hammer et al.[4] were applied to this TGRP model. The model was extended with the upgrading process of TGRP oil (distillation, extraction, and hydrogenation), using published experimental results.[5,18]

In the upgrading process, the thermodynamic models used for the unit operations vary, depending on the operation and the input streams. For instance, we used the Peng−Robinson and RK-Soave equations of state in the simulation for major units such as reactors, vessels, and coolers, because they are suitable for modeling hydrocarbon systems. In the simulation, the condensed TGRP oil was heated to 150 °C from 25 °C using medium pressure steam (Figure S3 in the SI). The heated oil was fed into a flash drum as a single-stage distillation process; we estimated a phase-equilibrium separating the vapor phase (VOC1 representing volatiles) from the liquid (see Figure S3 in the SI). The resulting liquid S10 (volatiles with a melting point of ≥150 °C) stream (see Figure S3) was heated to 420 °C before entering another flash drum. Because of the high melting point of biorenewable coke (modeled as benzopyrene), it exited the flash drum as liquid and was separated from the process.

The vapor phase (VOC1 stream; see Figure S3) was cooled to 90 °C and entered a decanter to remove any excess water from the process. The water-free volatiles stream (VOC2) was mixed with a cooled stream (VOC2B), which exited as a vapor from the second flash drum. After distillation, the distillates underwent a two-step extraction process that separated the phenols from the hydrocarbon stream. The first process step (Figure S4 in the SI) was a phenol extraction; NaOH entered the stoichiometric reactor, which was operated at 138 °C, deprotonating the phenols (phenol and cresols) by increasing alkalinity, giving sodium phenoxide and sodium cresolate as phenolic salts. In the second step (shown in Figure S4), the mixture

DOI: 10.1021/acssuschemeng.7b01609
ACS Sustainable Chem. Eng. 2017, 5, 8804−8814

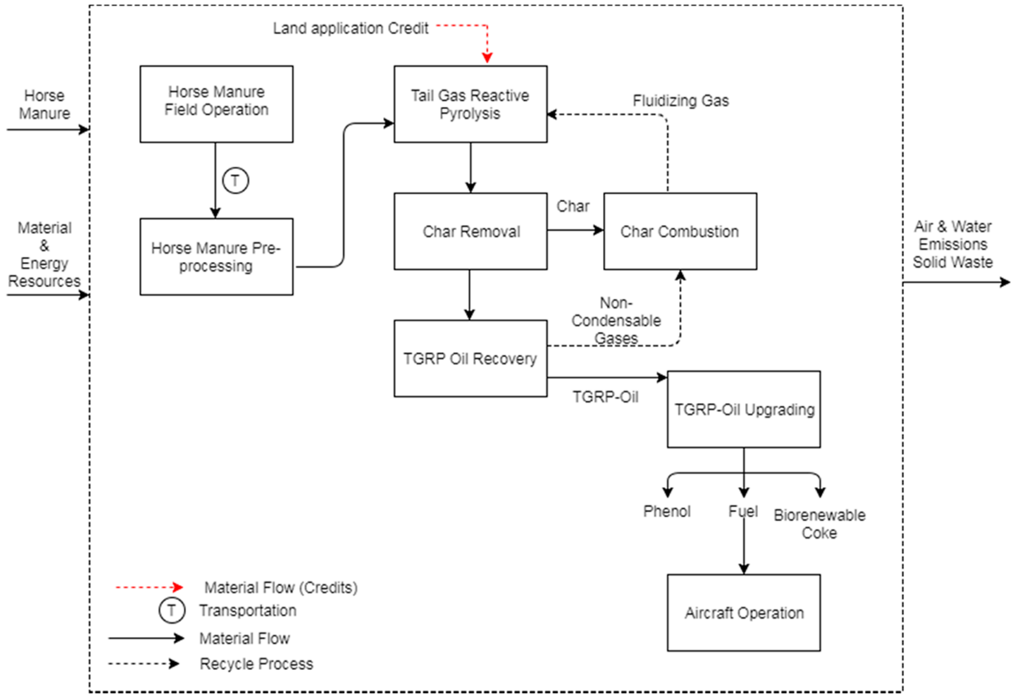


Figure 2. Life cycle system boundary for the production of fuel and phenol from horse manure via TGRP and upgrading through isolation and extraction of TGRP-oil distillates.

with phenolic salts was acidified with HCl and decanted, forming phenols in one stream and aqueous NaCl in the other stream. The hydrocarbon stream, consisting of olefins and aromatics, was hydrogenated in two stages (see Figure S5 in the SI). Both stages were performed in continuous stirred tank reactors (CSTRs): RXTR3, which was operated at 80 °C, 50 atm, and RXTR4, which was operated at 200 °C, 75 atm.

Life Cycle Assessment. The primary product that we evaluate is the fuel product with the phenol chemical serving as coproduct. The upgraded TGRP-fuel produced is similar in composition to aviation fuel; thus, we assume it will serve those markets. Hence, the functional unit was defined as 1 MJ of fuel and 1 person-kilometer (PKM) of travel by aircraft. The co-produced phenol is compared with petroleum-based phenol made using the cumene-phenol or hock process, which is an industrial process used to produce both phenol and acetone from benzene and propylene. A LCA model was constructed with Simapro[40] software, using input parameters specified in the feedstock harvest and collection, and the mass and energy balances derived from the chemical process model developed in Aspen Plus. The metrics that we evaluated, using life cycle impact assessment (LCIA), were the 100 year global warming potential (GWP) for CO_2, CH_4, and N_2O, according to IPCC,[41] and the cumulative exergy demand (CExD).[42] These metrics were used to describe the products (jet-range fuels and phenol) of the separation and upgrading of condensed TGRP oil. We used the GWP-100 metric in accordance to the benchmark for new biofuel standards given by RFS-2, which states that advanced biofuels must reduce life cycle GHG emissions by 50%, according to the advanced fuel designation.[43] While many biofuel LCA studies include GWP as a life cycle assessment metric,[44−46] CExD has not been as widely used.[47] Exergy is a thermodynamic measure of the maximum theoretical available work from a substance if it were to achieve equilibrium with the environment. Since exergy is a measure of available work, it represents a more nuanced and complete indicator of resource use, compared to cumulative energy consumption (CED).[48−50] Energy can be converted to different forms, but exergy is consumed in all processes. CExD also takes into account the consumption of nonenergetic raw materials. However, for non-renewable energy intensive products, results are similar to CED.

The system boundary (Figure 2) of this study is from well to flight; whereby the end of life of the fuels produced coincides with their use.

Data used for the life cycle inventory model include the material and energy inputs for conversion of horse manure to upgraded biofuel (Figure 2). Inputs such as electricity reflect the region's supply, the Northeast Power Coordinating Council (NPCC) grid. We assumed that the average distance the horse manure is transported from individual sites to the equine facility is 80.5 km.[35] The equine facility will be the major site to which the other surrounding farms can deliver their horse manure. After delivery, the horse manure is dried as a preprocessing step (Figure 2).

Allocation of environmental burdens in multiple product systems such as this, in which fuels and phenols are coproduced, is required in LCA. ISO 14040-44[29] recommends that the allocation methods used shows the physical relationship, such as mass and energy content, or other significant variables, such as economic value of the products.[51] In the TGRP process, allocation of the impact between oil and char was done on a mass basis (90% oil, 10% char), since mass allocation is more appropriate for a mixture of chemical and fuel. In the TGRP oil upgrade, we use mass, energy, and economic allocation, similar to previous studies,[52,53] because the effect of phenols extraction can vary, depending on the allocation method used. Herein, mass fractions, market price, and energy values are shown in Table S5 in the SI. Energy values were obtained from Aspen Plus results of HHV and price references are listed in Table S7 in the SI. System expansion was used in the impact calculations, because phenols are produced as coproducts; hence, we seek to capture changes in environmental impacts as a consequence of displacing petroleum-based phenols.

Process inputs for the TGRP process (Table S3) and TGRP oil upgrading (Table S4) were used to construct the life cycle inventory (LCI). Fuel and coke are produced in the highest quantity, followed by phenol and sodium chloride (Table S5); these values are used to inform the LCI. Fractions of energy, mass, and market price (see Table S6 in the SI) are used to allocate LCIA results to individual TGRP products. We assume the TGRP-fuel produced will be used in a short haul plane that travels less than 1609 km, similar to the Boeing 737−800W currently used by United Airlines−Eco-skies.[54] According to the specifications of the Boeing 737−800W, we assume the aircraft is a 162-seater with a fuel efficiency of 1.1 kg PKM^{-1}.[54]

Finally, we examine the sensitivity of feedstock transportation and credits from the avoided GHG emissions from manure disposal on life cycle GWP.

DOI: 10.1021/acssuschemeng.7b01609
ACS Sustainable Chem. Eng. 2017, 5, 8804−8814

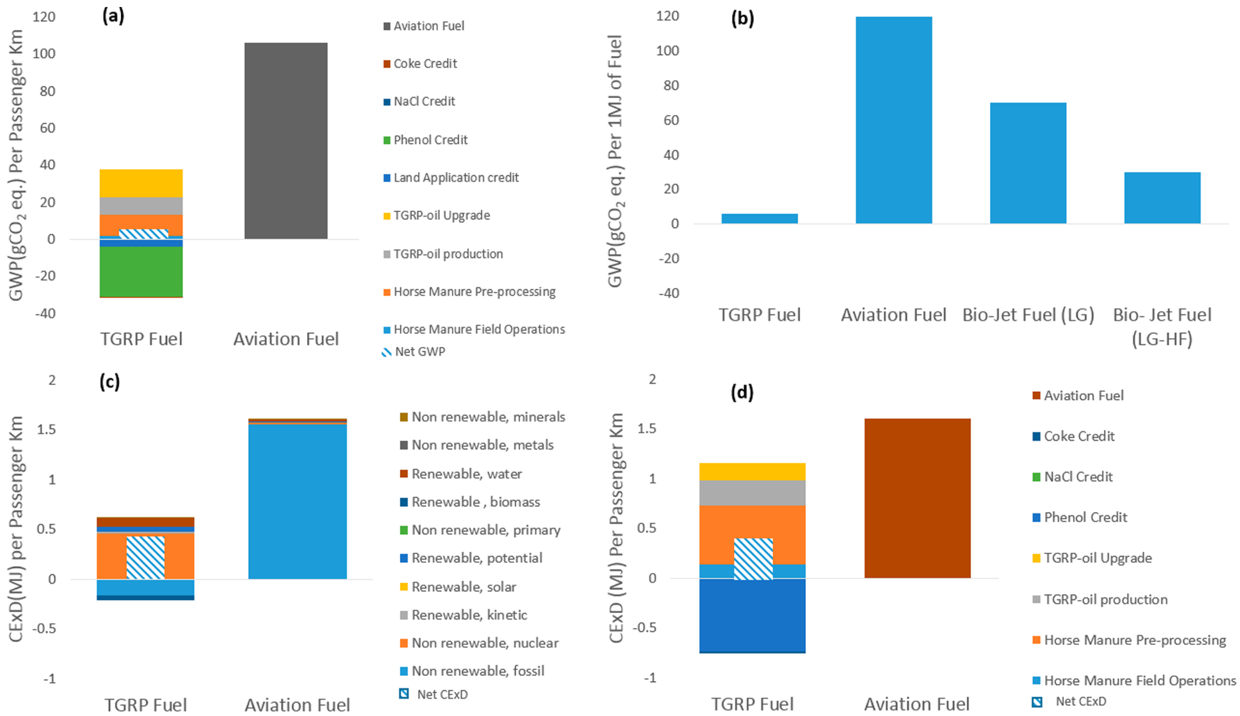


Figure 3. Life cycle environmental impact of TGRP fuel using system expansion. (a) GWP comparing TGRP fuel to aviation fuel per passenger kilometer. (b) GWP comparing TGRP fuel to aviation fuel and other biojet fuels produced from the bioconversion of poplar biomass per 1 MJ of fuel produced.[64] (c) CExD comparing TGRP fuel to aviation fuel per PKM by natural resource contribution. (d) CExD comparing TGRP fuel to aviation fuel per PKM by process type. LG refers to lignin gasification, and LG-HF refers to lignin gasification and hog fuel.

Techno-economic Analysis. To calculate the incremental cost of adding a TGRP oil upgrading system to a fast pyrolysis operation, the material and energy flows obtained from Aspen Plus were used to size the major equipment in the upgrade process. We estimated capital costs based on previous reports[7,38,55] and used the Aspen Plus Capital Cost estimator software.[56] Costs were estimated using a desired rate of return of 10% and projected in 2013 U.S. dollars, using a cost basis from the Aspen Process Economic Analyzer. All other assumptions made in the TEA are found in the SI.

In addition, a sensitivity analysis was conducted to examine the effects that different model assumptions such as variation in the cost of individual raw materials (hydrogen, catalyst, and feedstock), market price of the major coproduct (phenol), and the biofuel yield have on the minimum fuel selling price (MFSP). To investigate the relationship between environmental and economic impacts of the processes, we use the social cost of carbon (SCC), which is a method that internalizes the cost of GHG emissions (and savings).

RESULTS AND DISCUSSION

Process Yield, Energy Use, and Production Volume. In the modeled TGRP facility, 200 MTPD of horse manure (8300 kg h^{-1}) are fed into the system, producing ~74 t of TGRP oil per day (3075 kg h^{-1}), corresponding to a yield of 36.9% on a mass basis. The heat for the pyrolysis process is transferred from the char combustor by fluidization sand. Fuels, phenols, sodium chloride, and biorenewable coke are separated or formed during the TGRP oil upgrade. In the upgrade process, energy is internally generated by the enthalpies of solution and exothermic reactions such as the cooling of volatiles serve as a heating source for the flash drums, heaters, and separators.

The analysis shows that available horse manure supply in New York State could yield ~4.3 million gallons per year of biojet fuel (Table S2). Although we do not base our study on a regional scale, if we were to include equine farms in the Northeast region, biojet fuel supply from Pennsylvania alone would add an additional 5.7 million gallons per year (Table S2). Given that the 4.3 million gallons produced would be 100% renewable jet fuel and that biorefineries may blend 25% biobased and 75% petroleum-based fuel in the near term (c. 2020),[57] New York State's equine waste jet fuel production would supply 5.5 billion gallons of 25%/75% biojet fuel to the market. Also, 4.3 million gallons per year is a conservative estimate, since we only consider horse manure (25% of the total equine waste) and not horse bedding. If all equine waste were converted with the same bio-oil yield for horse manure and bedding, then New York State could produce a total of 172 million gallons per year and meet ~3% of the total U.S aviation fuel demand.[58]

Life Cycle Metrics. The life cycle GWP and CExD were calculated for the production of fuel and its coproduct (phenols) from the upgrade of TGRP oil, using functional units of 1 MJ of fuel (see Figures S6 and S8 in the SI) and 1 PKM (Figures 3a and 3d). Because of the different values of the mass, price, and energy content of the coproducts, the allocation results found in the SI vary by method. The high market price of phenol (\$1.28 kg^{-1}), compared to fuels (\$0.5 kg^{-1}), translates to a low economic allocation for both the GWP and CExD of fuel.

Compared to other allocation methods, the fuel product has a higher GWP when allocated by mass, because of its high mass fraction among all product flows (see Figure S6). Moreover, regardless of the allocation method, the TGRP fuel has a lower GWP than aviation fuel on a well-to-wheel basis. Herein, we assumed similar GHG emissions from the distribution distance of TGRP fuel and aviation fuel, because of similar distances from refinery to pump. The impact of horse manure biofuel is almost entirely caused by its cradle-to-gate emissions, whereas the major share of the GWP of petroleum-based aviation fuel

DOI: 10.1021/acssuschemeng.7b01609
ACS Sustainable Chem. Eng. 2017, 5, 8804−8814

comes from operation, i.e., CO_2 emissions during aviation fuel combustion. This is because the TGRP upgraded fuel is assumed to have zero net GHG emissions during combustion, because its carbon is biogenic. Overall, the analysis suggests that the TGRP-fuel emits <10% (10 g of CO_2 eq per PKM) of the GHGs of aviation fuel (110 g of CO_2 eq per PKM) (Figure 3a). The GWP of the TGRP upgraded fuel product shown in Figure 3b meets the RFS-2[43] standards; hence, the TGRP fuel product is environmentally preferable, relative to aviation fuel on a life cycle basis. When the GWP of the TGRP process is allocated according to economic value, the GWP of phenol is slightly higher (9%) than that of petroleum-based phenol (30 g CO_2 eq per PKM of fuel)[40] (excluding the end-of-life impact of phenol applications), because of its high economic value, but lower using mass and energy allocations (see Figure S6). This validates the results of other studies[59,60] that have argued that different allocation methods determine the outcome of the environmental impacts on the products and coproducts. Also, this suggests that it is more beneficial to separate the phenols in the TGRP upgrade process than to produce only fuels (as is the conventional hydrogenation (HDO) method).[19] Using system expansion yields a higher net GWP for TGRP-fuel than when it is allocated on an economic, mass or energy basis (Figure S6). This is mostly because, in all of the allocation methods, a large share of the GWP is attributed to the byproducts, mainly phenol and coke. The total impact of the TGRP process is identical for all allocation methods, but a reduced GWP for TGRP fuel induced by shifting the impact to phenol or coke is artificial. Therefore, in the interest of the functional unit defined, i.e., the production of 1 MJ equivalent of TGRP-fuel or 1 PKM of distance traveled, we opt to discuss only system expansion hereafter.[25,61−63] This means that the entire GWP of the TGRP process is allocated to the fuel, and afterward corrected for the credits achieved by phenol and coke production, offsetting phenol from the cumene process and coke as byproducts from the production of liquid fuels from crude oil. Nonetheless, the entire GWP of the TGRP process (10 g CO_2 eq), producing the fuel, coke, and phenols, is still significantly lower than the GWP of petroleum-based aviation fuel (110 g of CO_2 eq)[40] combined with phenol from the cumene process (30 g of CO_2 eq), per PKM of distance traveled.

A previous study[64] determined that the GWP (Figure 3b) of the conversion of poplar biomass to drop-in biojet fuel via the bioconversion platform ranges from 30 g of CO_2 eq to 70 g of CO_2 eq per MJ of fuel burned, depending on the hydrogen generation method used in the hydrogenation steps. Biojet fuel (LG) represents a fuel for which the hydrogen for upgrading comes from lignin gasification (LG) and natural gas is used for heat and steam. Biojet (LG-HF) represents a fuel produced from a process that uses lignin gasification for hydrogen generation and hog fuel (HF) for heat and steam. When comparing this range to the GHG emissions from the current process (TGRP oil upgrade) without the credits from the coproducts (40 g CO_2 eq per MJ), and the various process contributions, the GHG credit for phenol (30 g of CO_2 eq) is larger than the extra impact of the separation process (Figure 3a). In addition, we explore the effects of not disposing the manure and including the GHG emissions as a credit (Figure 3b). These results show that the average GHG emissions from land application reduce the TGRP fuel GHG emissions to 4.4 g of CO_2 eq.

The results for CExD assessment are given in Figures S8 and S9 in the SI, in addition to Figures 3c and 3d. Previous studies used exergy assessment to evaluate the production of biofuels, such as biodiesel and ethanol.[49,65−68] Most relevant for our study is the work of Keedy et al.,[49] who used CExD as an assessment metric for evaluating the sustainability of bio-oil production via fast pyrolysis using three feedstocks, one of which was horse manure. When analyzing the CExD metric, the trend in allocation results (Figure S8) is similar to the GWP results; whereby the phenol contributes the highest CExD in economic allocation, compared to the other coproducts. According to the Ecoinvent database[69,70] from which data were drawn, the CExD for the production and combustion of aviation fuel is 1.8 MJ per MJ of fuel. This value is ∼28% greater than the CExD of the TGRP-fuel produced in this study without coproduct credits (1.3 MJ per MJ of fuel).

Figures 3c and 3d present the life cycle environmental impact of CExD per person kilometer (PKM) of travel by aircraft passenger (as in Figure 3a for GWP). These figures compare CExD of TGRP fuel with aviation fuel. Credits are also displayed for the TGRP fuel. The dashed bar for TGRP fuel indicates the net CExD (including credits). Figure 3c includes the contribution of CExD by resource for the net amount. Figure 3d indicates the TGRP contribution by process and details credits. Both figures indicate the cumulative exergy destruction per passenger kilometer is much higher for aviation fuel, compared to TGRP fuel. Figure 3d indicates that this is true, even without credits. The positive TGRP area on Figure 3d represents the CExD for total production. Of the individual process contributions shown on Figure 3d, the results indicate that the majority of the CExD in the overall process is attributed to horse manure preprocessing. The bulk of the energy consumed in the preprocessing step is from electricity used to operate milling, drying, and conveying equipment. This indicates that the material and energy needs of the preprocessing step could be targeted for CExD reduction. Figure 3c provides a breakdown of the net CExD by resource. The majority of the resource inputs used to produce aviation fuel are derived from fossil fuels (petroleum, natural gas, coal). A significant contribution to the CExD of the TGRP fuel is attributable to electricity production. The NPCC grid resources are ∼50% fossil (including petroleum, natural gas) and 31% nuclear on an energy basis. However, the CExD percentages are 75% nuclear and 24% fossil. This results in the larger nuclear contribution to CExD on Figure 3c (compared to the fossil contribution). Note the fossil contribution is considered a credit, because of the production of phenol and coke.

Figure S9 in the SI compares the CExD of phenol extracted in the TGRP process with the phenol produced by the cumene process. The former demands either more or less exergy than the latter, depending on the allocation method used. With energy and mass allocations, the CExD of phenol is smaller than the CExD of the cumene process, whereas, with economic allocation, the CExD of phenol is greater than the CExD in the cumene process. This difference due to allocation method choice is a result of phenol having a higher market value than fuel and the other coproducts.

Global Warming Potential Sensitivity. Diverting horse manure from agricultural lands for fuel production may avoid GHG emissions. Manure is often land applied in agriculture to recycle nutrients. When manure is disposed by land, it releases GHGs predominantly in the form of N_2O and CH_4, because of the presence of inorganic nitrogen and microbic available

DOI: 10.1021/acssuschemeng.7b01609
ACS Sustainable Chem. Eng. 2017, 5, 8804−8814

sources of carbon and water.[71] These emissions are in the range of 16 400−33 500 g of CO_2 eq per ton of manure,[72] depending on the size of the farm. By using thermochemical conversion to dispose of the manure, we can reduce CO_2 emissions from land application by 88%−94% (as shown in Figure S12 in the SI). A scenario that includes the GHG emissions released from land application as a credit (Figure 3b) shows that the average GHG emissions from the TGRP fuel process reduces to 4.4 g of CO_2 eq.

In addition, we examined the sensitivity of GWP on feedstock transportation by doubling the horse manure transportation distance to the equine facility. This increases the GHG emission by 0.5 g of CO_2 eq per passenger kilometer (5% increase in the total GHG emissions), which is a small amount that aligns with prior literature[62,73] on the transport of biomass feedstocks for biofuels.

Techno-economic Analysis. We estimate the capital and operating costs of TGRP bio-oil upgrading operations from the Aspen Plus simulations, and compare these incremental costs to fast pyrolysis to produce bio-oil from prior research[38] (see Table 1). Since TGRP and fast pyrolysis use the same equipment, are identical in scale, and the only difference between the two is that the TGRP process recycles the noncondensable gases, whereas fast pyrolysis uses the gases for process energy; we assume that the differences in costs between the two are negligible. The additional capital cost of bio-oil upgrading operations that produce value-added products (jet fuel, phenols, and green coke) is one-third ($7.7 million) of the cost of fast pyrolysis[38] ($24.7 million), which produce bio-oil alone (see Table 1). The project capital cost was determined based on 5% per year working capital,[74] which is a percentage of total capital expense per period showing the amount required to operate the facility until the revenue from product sales is sufficient to cover costs.[56]

Table 1. Capital and Operating Costs of Fast Pyrolysis and the Incremental Cost of TGRP Upgrading

	fast pyrolysis[a]	TGRP upgrade
total project capital costs ($)	**24 700 000**	**7 680 000**
annual operating costs ($/yr)	**9 360 000**	**4 510 000**
raw material	4 280 000	1 950 000
utilities	768 000	313 000
total operating labor and maintenance costs	1 130 000	1 060 000
total additional fixed operating cost	712 000	423 000
depreciation (10 yr, straight line)	2 470 000	768 000
total revenue ($/yr)		**5 620 000**
coproduct sales		3 020 000
sales from fuels		2 600 000
MFSP of bio-oil from fast pyrolysis and subsequent TGRP upgrade ($/L)	**1.1[b]−1.8[c]**	

[a]Data taken from ref 38. [b]MFSP for Option B (free feedstock). [c]MFSP for Option A (feedstock price = $0.055 kg $^{-1}$).

An economic life span of 10 years was chosen for this study for a side-by-side comparison with a similar 200 MTPD fast pyrolysis study.[38] The cost of raw materials and market prices of products are shown in Table S7. The labor cost is estimated from the number of full-time equivalents required for operating the TGRP upgrade process for 7920 h per year. We use two operators per shift at a unit cost of $20 per operator per hour and one supervisor per shift with a unit cost of $35 per supervisor per hour. The total additional fixed operating costs include facility overhead and operating charges.

Total revenue consists of sales of the main product of the upgrade and byproducts. The price of fuel used in this analysis is based on the current price of aviation fuel; consequently, the outcome of this comparative study may change based on future market conditions. Sodium chloride (NaCl) and water (H_2O) are considered waste products of the process; hence, they have a negative monetary value and incur waste treatment costs of $0.002 kg^{-1} (from ref 75) and $0.074 kg^{-1} (from ref 74), respectively.

Using the economic analysis of Pourhashem et al.[38] with the incremental costs of TGRP upgrade, the MFSP of the final upgraded TGRP fuel is estimated to be $1.8 L^{-1} of fuel (MFSP Option B, Table 1), which is comparable to a similar study by Carracso et al.,[55] who investigated the conversion of forest residue to biodiesel through fast pyrolysis and catalytic upgrading. The MFSP for Option A in Table 1, assumes the agricultural residue feedstock cost from Pourhashem et al.,[38] $0.055 kg^{-1} to approximate the cost of collecting and properly hauling the horse manure to the conversion facility and contrasts it with the Option B MFSP, a lower limit in which horse manure is assumed to be given freely[4] by the farmers as an alternative to paying for disposal and thus is $0 kg^{-1}. Option A represents a conservative approximation of feedstock cost, given that the cost of a waste such as horse manure is expected to be low, or possibly zero or negative (if the horse keeper has to pay to have the manure hauled offsite for treatment). However, horse manure is an agricultural waste product with no value; therefore, the assumed feedstock cost of $0 kg^{-1} (MFSP Option B, Table 1) is plausible, reducing the MFSP to $1.1 L^{-1}. An investment analysis over a project life of 10 years results in a net present value of $1.6 million; hence, the project is economically feasible under the assumptions made.

Jones et al.[7] evaluated the production of fuels via pyrolysis and HDO upgrade and found a positive net present with a minimum fuel selling price (MFSP) of $0.54 L^{-1}, which is far below the MFSP for the TGRP oil upgrade process; $1.1 L^{-1}. This variation in MFSP can be attributed to the significant difference in scale between the two processes; the biomass supply needed for the HDO process is 10 times higher than the distributed TGRP fuel process.

Sensitivity Analysis. The MFSP is most sensitive to feedstock cost and yield and, to a smaller extent, on the market prices of phenol and coke, but hydrogen and catalyst costs do not have a significant effect on the MFSP, because they are used in small quantity, compared to the other raw materials in the process (Figure S10 in the SI). The MFSP value showing sensitivity analysis to feedstock cost depicts a significant reduction from $1.8 L^{-1} to $1.1 L^{-1} (Table S9) when the feedstock is treated as a waste ($0 kg^{-1}), hence making TGRP fuel more economically competitive, compared to the base case. If the price of feedstock were to double, assuming that it has to be purchased from the farmers, the MFSP increases significantly to $2.4 L^{-1}. This can be the case if equine waste is in high demand and its supply is limited. Also, because the market price of green coke can change drastically,[76] it is important to see the effect of this change on the MFSP. However, the tornado plot shows little variation in MFSP due to changes in the price of coke; hence, the MFSP is not too sensitive to the price of coke.

If the yield increases by 25%,[20,77] the MFSP decreases significantly to $1.4 L^{-1}. Similarly, if the market selling price of

DOI: 10.1021/acssuschemeng.7b01609
ACS Sustainable Chem. Eng. 2017, 5, 8804−8814

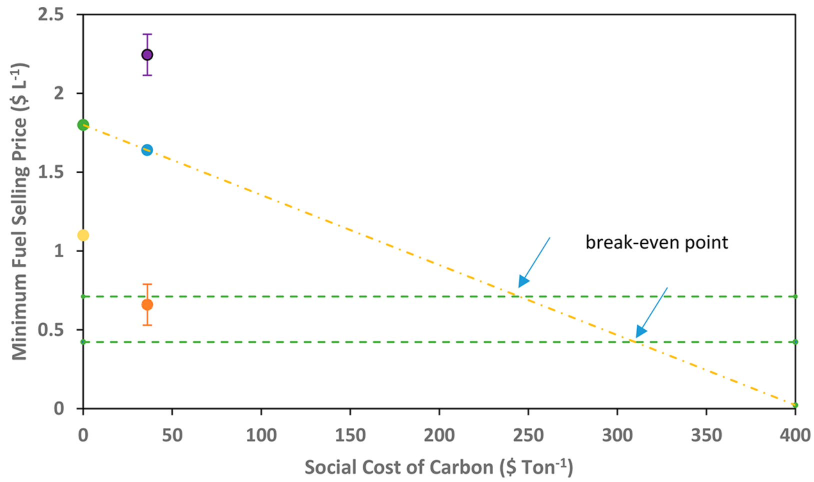


Figure 4. Effect of social cost of carbon on the minimum fuel selling price. [Legend: blue circle, Option A with SCC = $36/ton,[67] baseline scenario and a feedstock price of $0.055/kg; purple circle, Option A with SCC = $36/ton,[67] upper bound conditions from the sensitivity analysis (tornado plot) and high cost of raw materials, low yield, and a low selling price of coproducts; orange circle, Option B with SCC = $36/ton,[67] low cost of raw materials, high yield, and a low selling price of coproducts; green circle, Option A without SCC, baseline scenario, and a feedstock price of $0.055/kg; yellow circle, Option B without SCC, baseline scenario, and a feedstock price of $0/kg; orange dashed line, MFSP for option A at varying SCC (curve shows break-even points (arrows) with petroleum-based aviation fuel); and green dashed line, price range of petroleum-based aviation fuel (2014–2017).]

phenol increases, the MFSP decreases, and if the selling price decreases, the MFSP increases. This implies that increasing process yields, increasing the price of coproducts and reducing the price of feedstocks, can render the process economically feasible.

Environmental and Economic Implications for Advanced Fuel Development and Policy. To fully account for the climate change mitigation benefits of biofuels and support policy decisions in their investment, it is important to include both internal and external costs and measure both direct and indirect costs of a process or product. In this section, we estimate all internal costs associated with TGRP and aviation fuel production and consider the social cost of carbon (SCC), an external cost.[78] The United States Environmental Protection Agency (U.S. EPA)[79] uses SCC to estimate the climate benefits of set standards. The SCC is a monetary value estimating the economic damages caused by a marginal increase in carbon dioxide emissions in a defined year. In order to overcome the high MFSP, SCC is expressed as a revenue equivalent to the difference in the monetary value of GHG emissions between the renewable fuel and petroleum-based aviation fuel. Using the 2007 year SCC value of $36 with a 3% discount rate,[79] the TGRP SCC value is $930 000 yr^{-1}, which is a quantity that represents the reduction in economic damages associated with CO_2. Using Option A (MFSP, Table 1) while including the SCC, the MFSP decreases to $1.64 L^{-1}. When varying the discount rate (2.5%, 3%, and 5%) and statistics (average and 95th percentile)[80] applied to the SCC, the MFSP will vary from $1.35 L^{-1} to $1.74 L^{-1}. In order to break even with the MFSP of aviation fuel ($0.42 L^{-1}), the SCC would need to be as high as $354 per metric ton, based on the assumption that the original SCC of $36 has been underestimated.

Finally, to understand how sensitive the MFSP is to variability in the SCC, a sensitivity analysis (Figure 4) was carried out, using scenarios reflecting the highest and lowest MFSP. When the cost of raw materials (feedstock, hydrogen, and catalyst) is high, yield is low and coproduct (phenol and coke) selling prices are low, the MFSP ranges from $2.11 to $2.38 L^{-1}. On the other hand, a scenario that includes the lowest price of raw materials, higher yields, and a high selling price of coproducts reduces the MFSP to a range of $0.53-$0.79 L^{-1}, which could be competitive with the price of petroleum-based aviation fuel on the market. If we add a manure management fee of $0.008/L, this would have a small effect on the MFSP, reducing it from $0.66/L to $0.65/L. Therefore, when all fuel conversion parameters are optimized, as would be expected of the *n*th biofuel conversion facilities,[81] and when external costs are reflected in the market price of energy, it is possible to economically produce low carbon jet-range fuels and value-added chemicals through TGRP technology.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01609.

Supporting life cycle inventory data, coproduct allocation parameters and results, bio-oil characteristics, feedstock logistics and supply, and economic data are summarized; process flow diagrams from Aspen Plus simulations show details of feedstock conversion and fractionation to fuels and phenolic compounds (PDF)

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Notes

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ACKNOWLEDGMENTS

Funding for this work was provided by the U.S. Department of Agriculture under USDA-NIFA No. 2012-10008-20271. We thank four anonymous reviewers, whose comments improved the manuscript.

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SUPPORTING INFORMATION

The supporting information consists of 18 pages, including cover page, containing 12 figures and 9 tables.

Fuels and chemicals from equine waste derived tail gas reactive pyrolysis oil: techno-economic analysis, environmental and exergetic life cycle assessment

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SUPPORTING FIGURES

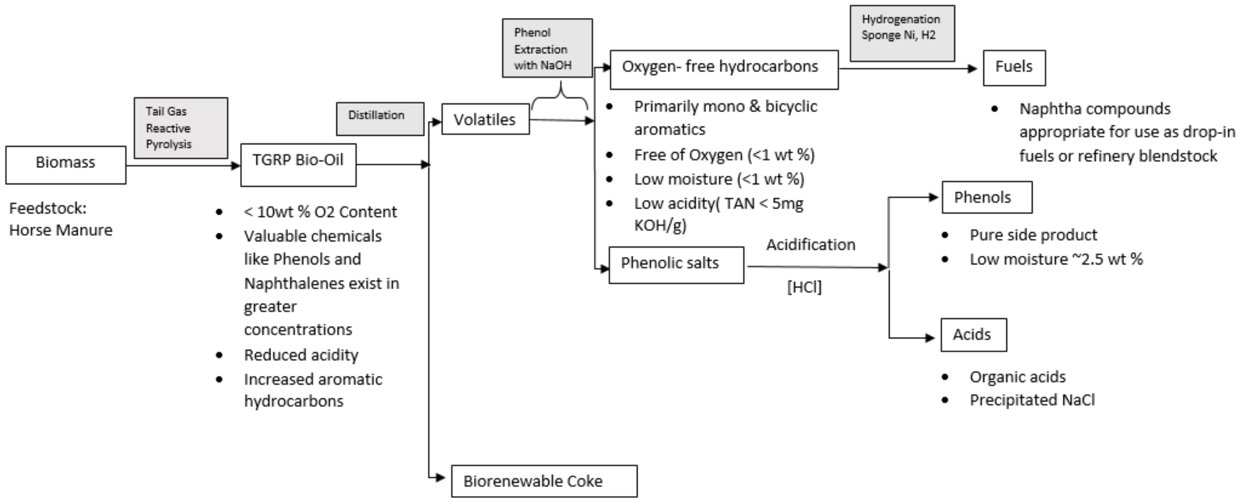

Figure S1. Process flow diagram for tail gas reactive pyrolysis of horse manure to bio-oil and further upgrade through distillation and extraction of the bio-oil distillates, forming value-added chemicals and fuels.

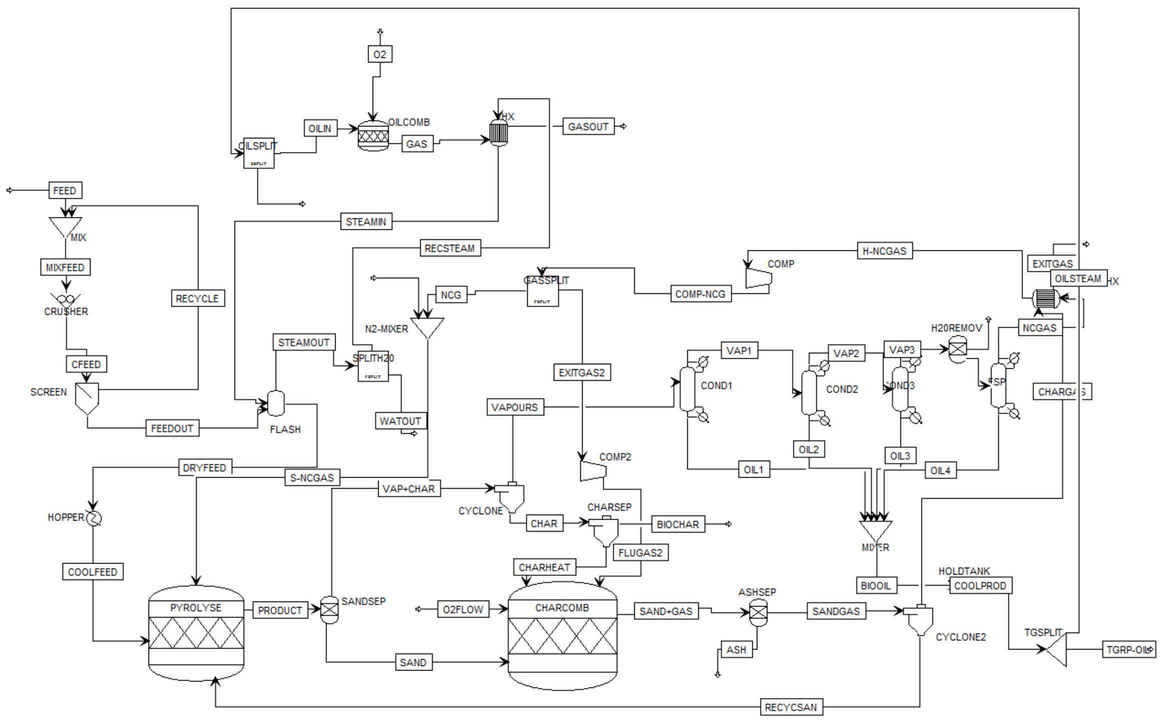

Figure S2. TGRP -Oil production

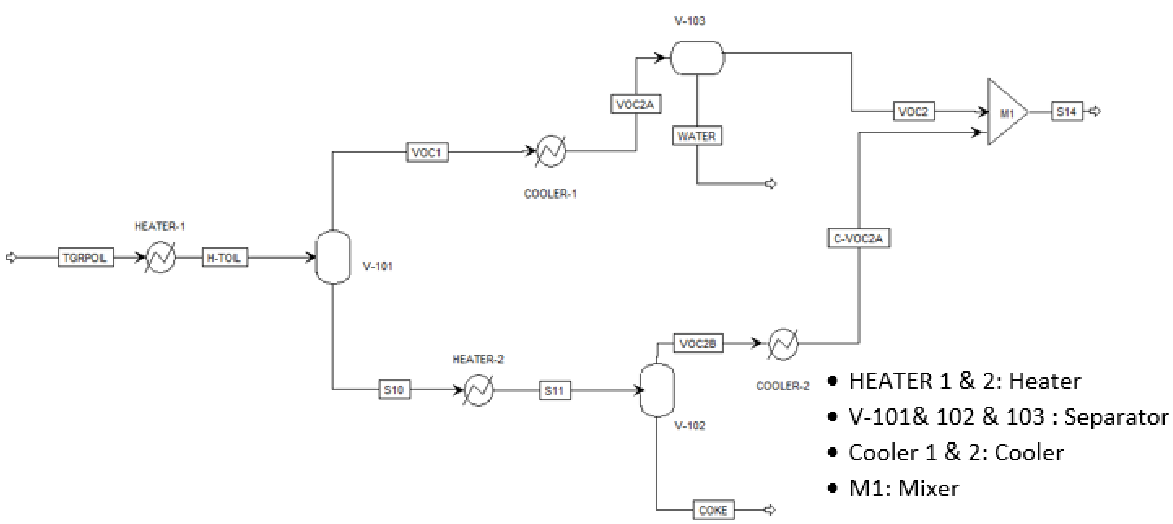

Figure S3. Aspen Plus process flow diagram showing a TGRP oil distillation process that separates the oxygenated oil into volatiles and bio-renewable coke. The volatiles are further upgraded by isolation and extraction of TGRP-oil, while the bio-renewable coke can be used as green coke.

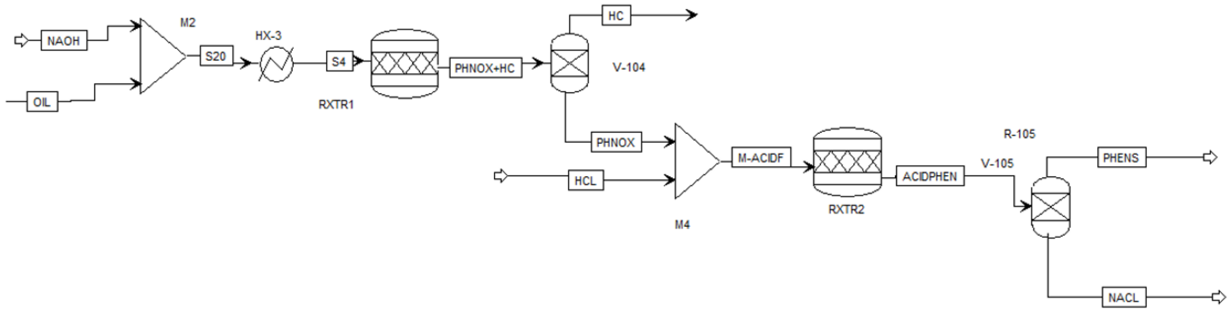

Figure S4. Phenol Extraction

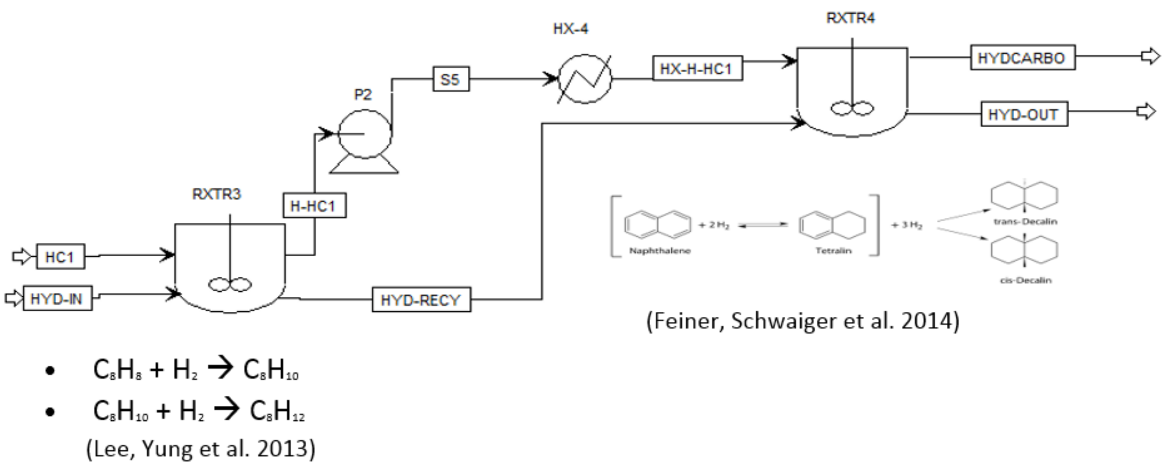

Figure S5. Two-step hydrogenation procedure consisting of (1) olefin hydrogenation at 80 °C [1] and (2) aromatics hydrogenation at 200 °C [2] . RXTR 3 and RXTR 4 represent the stoichiometric reactors used, P2 represents the pump and HX-4 is for the heater.

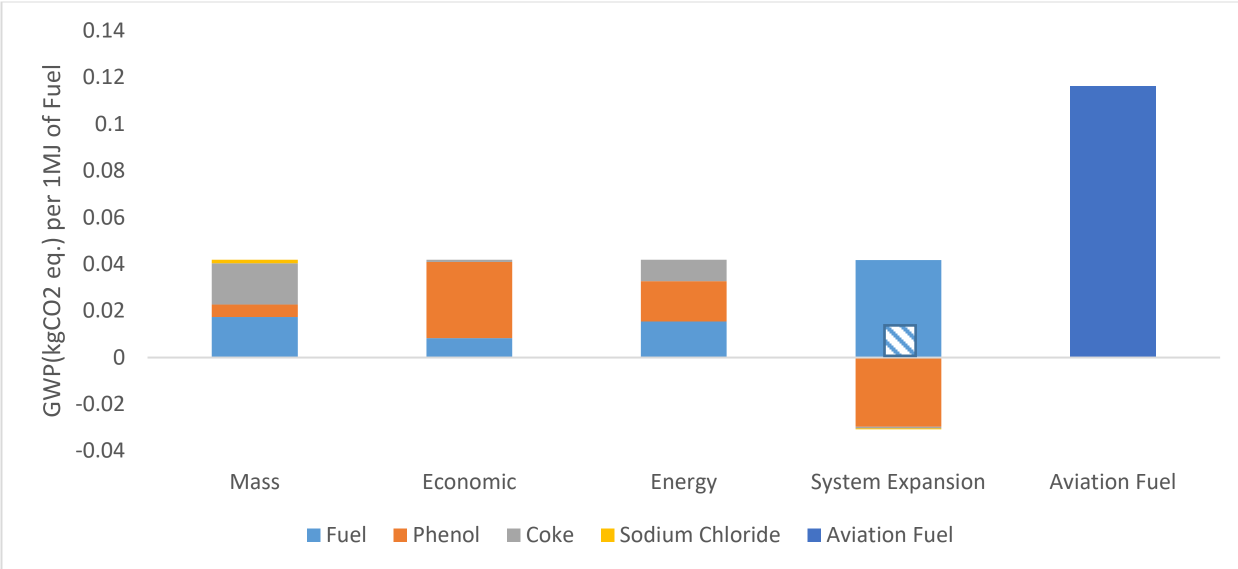

Figure S6. Contribution of the products and co-products to global warming potential per 1MJ of Fuel produced based on the economic, mass and energy allocations. The figure compares these allocations to the GWP of Low –Sulfur diesel extracted from Simapro [3]. Total GWP for economic, mass and energy allocations are the same but the percent of GWP allocated to each product is different.

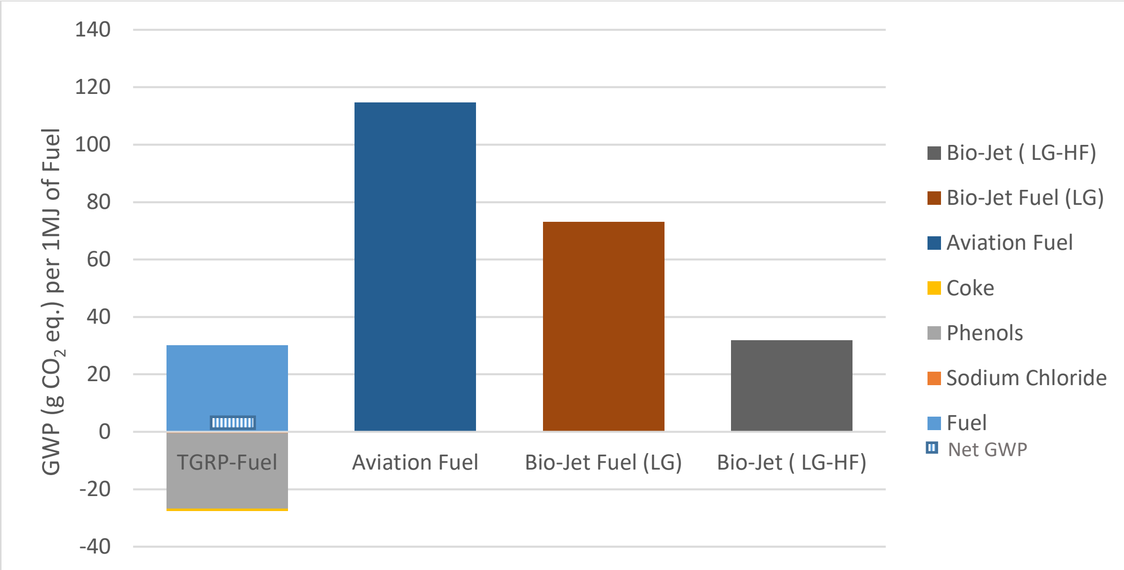

Figure S7. Global warming potential of TGRP fuel compared to aviation fuel and bio-jet fuel from other bio-fuel processes using system expansion.

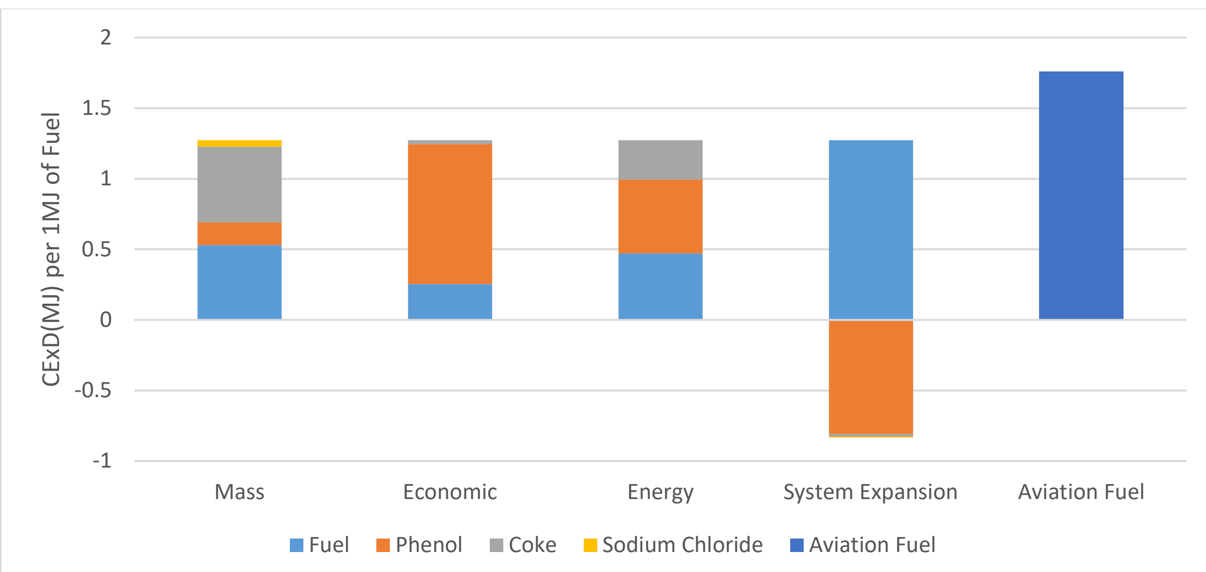

Figure S8. Contribution of the products and co-products to cumulative exergy demand per 1MJ of Fuel produced based on the economic, mass and energy allocations. The figure compares these allocations to the CExD of Low –Sulfur diesel extracted from Simapro [3]. Tot Total CExD for economic, mass and energy allocations are the same but the percent of CExD allocated to each product is different.

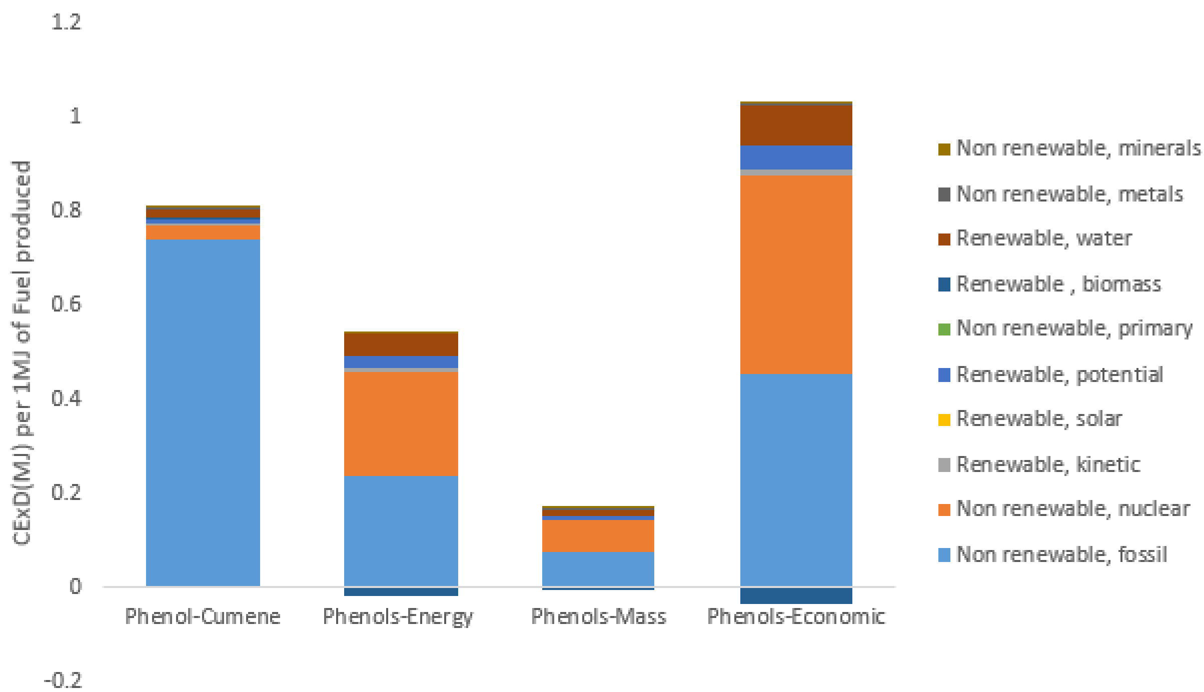

Figure S9. Cumulative Exergy demand (MJ) of phenol per 1MJ of Fuel produced. Phenol form the cumene process is compared with phenol form the TGRP process using mass, energy and economic allocations.

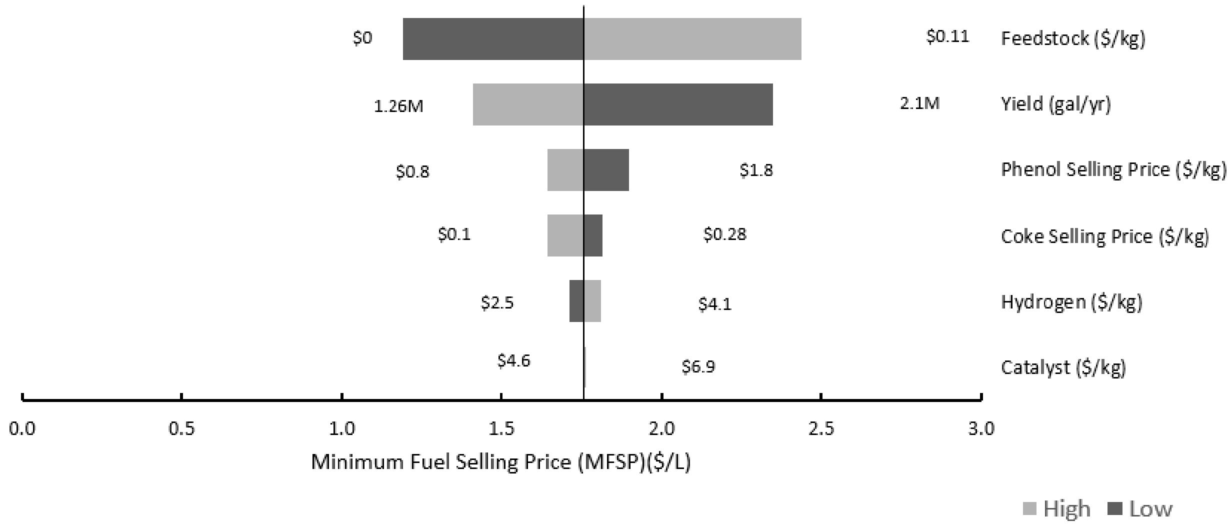

Figure S10. Tornado plot that shows the financial sensitivities of the TGRP upgrade process. The economic analysis includes the TGRP oil production and its upgrade to fuels and phenols.

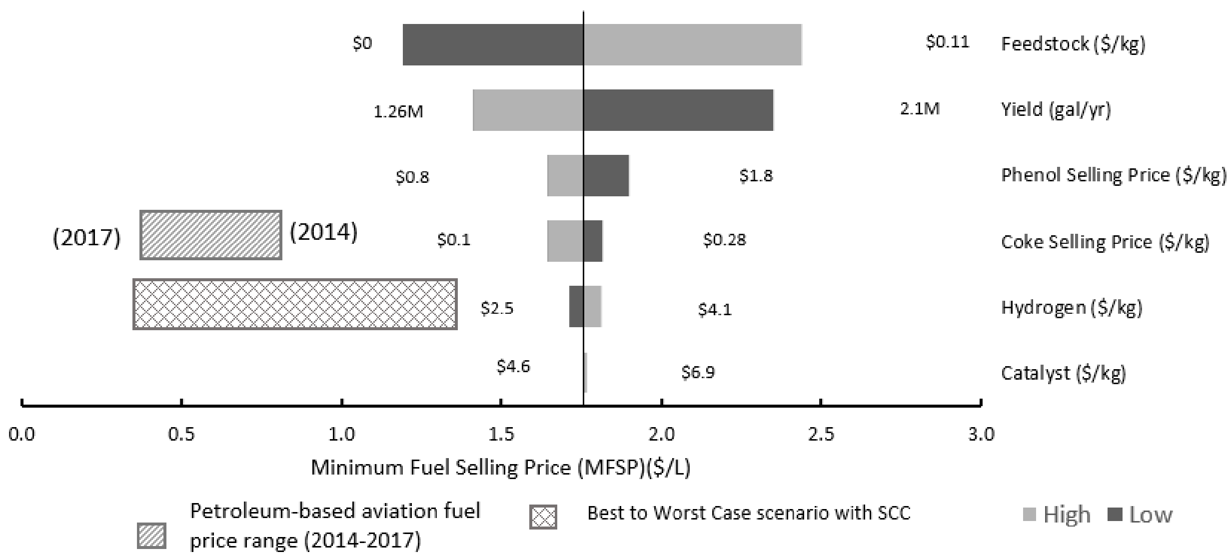

Figure S11. Aviation price range and minimum fuel selling price of best to worst case scenario.

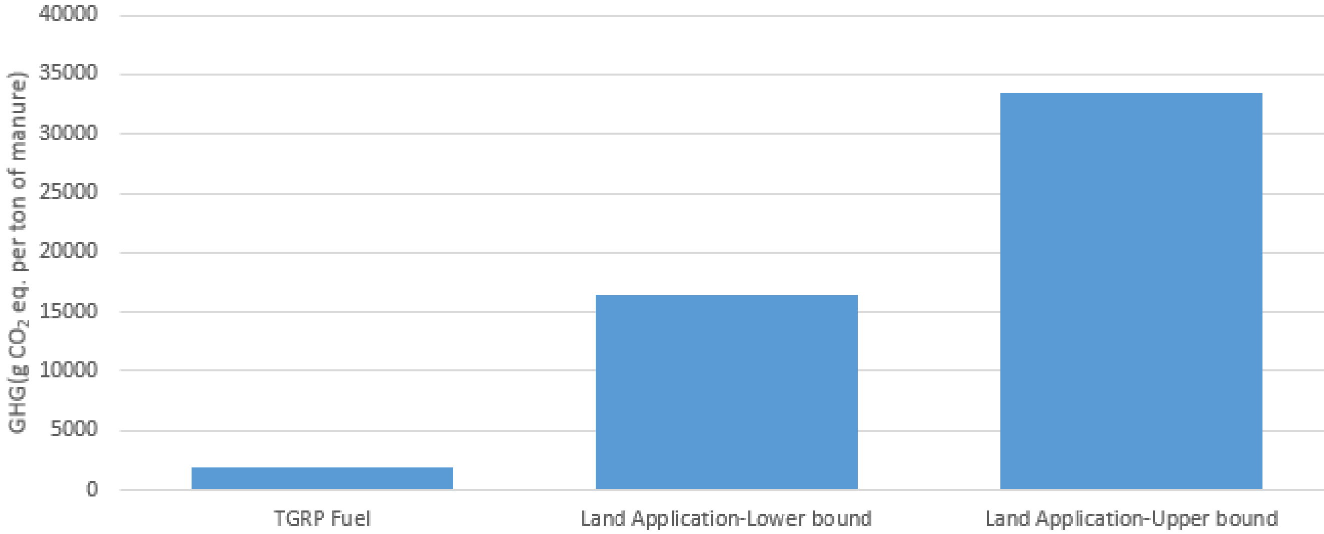

Figure S12. GHG emissions per ton of manure from TGRP fuel and land application

The literature shows that depending on the practice and farm size, GHG emissions per ton of manure range from 16,400 to 33,500 g CO_2-eq [4] for land-application. Although the cited literature does not give sufficient breakdown for the N_2O and CH_4 emissions, it details that the major source of emissions is N_2O from land application. We calculated the amount of GHG emissions from the TGRP fuel per ton of horse manure and this value is between 88% - 94% less than the GHG emissions from land application.

SUPPORTING TABLES

Table S1. Composition of horse manure biomass and oils from Tail Gas Reactive Pyrolysis and Fast Pyrolysis [5]

Process(Feedstock)	Horse Manure (Dry Basis)	TGRP oil (Manure)	Traditional Fast Pyrolysis Oil (Manure)
Wt.%			
Phenols/Cresols		4.31	4.04
Naphthalenes		16.83	0.34
Acetic acid/Acetol		0.23	8.04
Wt. % [6]			
C	48.43	79.53	67.35
H	5.98	5.75	6.82
N	1.21	3.54	2.31
O	38.43	11.18	23.52
S	0.07		
Moisture (wt %)	0	2.08	7.31

Table S2. Equine waste generated in New York State. The dry residue estimates were based on an average of 41.7lb/stall/day (on dry residue basis. Potential energy value estimates based on samples Average higher heating value (dry) of 19.5MJ/kg[7]. The moisture content of horse manure is about 48 wt. % and the manure is assumed stored in open storage areas at the end of the barn for a very brief period. In the pre-processing step, the manure is dried in an oven at 150˚F. In addition, the manure is ground in the pre-processing step and this process of grinding removes moisture via heat transfer.

Equine[1] per farm	**No. of farms**	**Total No. of equine**	**Average No. of equine per farm**	**Dry residue to be generated (lb./d)**	**Potential energy value (MJ/day)**
1 to 24	9,514	59,083	6	259	2,293
25 to 29	529	17,329	33	1365	12,097
55 to 99	131	8,267	63	2629	23,305
>= 100	33	5,478	166	6916	61,303
Total	10,207	90,157	9	368	3,262

Total Horse manure (lb/day)	**1,126,963**
Total Horse manure (kg/hr)	21,299
Bio-Fuel Produced (kg/hr)	**1,948**
Bio-Fuel Density (lb/cu.ft)	59
Bio-Fuel Produced in **New York State** (gallons/yr)	**4,311,283**
Bio-Fuel Produced in **Pennsylvania** (gallons/yr)	**5,733,585**[8]

[1]Equine includes horses and ponies. More details on location are provided in the equine waste study [7].

Table S3. Inventory data for TGRP oil Production per 1MJ of fuel produced

Item	Amount	Unit	Ecoinvent Database Module
Outputs			
Tail Gas Reactive Pyrolysis Oil	2620	kg	
Biochar	1040	kg	
Resources			
Water	55600	kg	Water, process, surface
Oxygen	33300	kg	Oxygen
Nitrogen	134000	kg	Nitrogen
Materials & Fuels			
Preheated Horse manure	8300	kg	User defined
Nitrogen	188	kg	Nitrogen, liquid, at plant/RER U
Ash	420	kg	Ash I
Electricity & Heat			
Electricity for Pyrolysis	65500	MJ	Electricity, medium voltage {NPCC, US only}| market for | Alloc Def, U
Emissions to air			
Oxygen	31200	kg	Oxygen
Nitrogen	134000	kg	Nitrogen, atmospheric
Carbon dioxide	4500	kg	Carbon dioxide, biogenic
Waste			
Ash	420	kg	Coal ash in landfill U
Water	57200	kg	Wastewater, average [9]| market for | Conseq, U

Table S4. Inventory data for TGRP oil Upgrade per 1MJ of Fuel produced

Item	Amount	Unit	Ecoinvent Database Module
Outputs			
Hydrocarbons(Fuels)	760	kg	
Hydrogen	27	kg	
Phenols	230	kg	Phenol {RoW}| production | Alloc Def, U
Sodium Chloride	66	kg	Sodium chloride, powder {RoW}| production | Alloc Def, U
Biorenewable coke	770	kg	Coke {RoW}| coking | Alloc Def, U
Resources			
Water	1.81	m^3	Water, unspecified natural origin, US
Materials and Fuels			
TGRP oil	2620	kg	User Defined
Hydrogen Chloride	45	kg	Hydrochloric acid, without water, in 30% solution state {RoW}| hydrochloric acid production, from the reaction of hydrogen with chlorine | Alloc Def, U
Hydrogen	47	kg	Hydrogen (cracker) E
Nickel (Catalyst)	1.2	kg	Nickel, 99.5% [9]| nickel mine operation, sulfidic ore | Alloc Def, U
Sodium Hydroxide	45	kg	Sodium hydroxide, without water, in 50% solution state [9]| market for | Alloc Def, U
Waste			
Water	1830	kg	Wastewater, average [9]| market for | Conseq, U
Utilities			
Electricity	32	MJ	Electricity, medium voltage {NPCC, US only}| market for | Alloc Def, U
Steam	970	kg	Steam, for chemical processes, at plant/RER U

Table S5. Mass, Price and Energy values of all products and co-products in the TGRP upgrade process. The mass and energy values were obtained from the Aspen Plus Simulation and price sources are cited in Table S7.

	Mass (kg)	Price ($/kg)	Energy (MJ/kg)
Fuel	759	0.5	46.3
Sodium Chloride	66	0.0*	0.0
Phenols	231	1.3	51.5
Coke	767	0.16	27.6

*****Sodium Chloride is considered $0 since it is in small quantities and will be disposed.

Table S6. Allocation Percentages Used

	Mass (%)	Price (%)	Energy (%)
Fuel	41.6%	20.0%	37%
Sodium Chloride	3.6%	0.0%	0%
Phenols	12.7%	77.8%	41%
Coke	42.1%	2.2%	22%

Table S7. Pricing References

	Price	Reference
Hydrogen($/kg)	3.33	[10]

Process water($/MT)	0.032	[10]
Electricity($/kWh)	0.061	[10]
Natural Gas($/MMBTU)	5	[10]
Steam ($/1000lb)	5.25	[10]
Phenol($/kg)	1.28	[11]
Catalyst($/kg)	4.61	[12]
HCl($/kg)	0.22	[11]
NaOH($/kg)	0.4	[11]
Coke($/kg)	0.036	[11]
NaCl($/kg)	0.2	[13]

Table S8. Techno economic analysis assumptions for the Tail gas reactive pyrolysis upgrade process. Assumptions are based on literature, Pourhashem et al, 2013 model, PNNL 18284 and Aspen Process Economic Analyzer. Utility pricing are shown in Table S7.

Period Description		**Year**
Number of weeks per period	Weeks/Period	52
Number of period for analysis		20
Tax Rate	Percent/Period	39
Interest Rate/Desired Rate of Return	Percent/Period	20
Economic Life of Project	Period	10
Salvage value	Percent	0
Depreciation Method		Straight Line
Escalation Parameter		
Project Capital Escalation	Percent/Period	5
Products Escalation	Percent/Period	5
Raw Material Escalation	Percent/Period	3.5
Operating and Maintenance Labor Escalation	Percent/Period	3
Utilities Escalation	Percent/Period	3
Project Capital Parameters		
Working Capital Percentage	Percent/Period	15
Operating Costs Parameters		
Operating Supplies	Cost/Period	25
Laboratory Charges	Cost/Period	25
Operating Charges	Percent/Period	25
Plant Overhead	Percent/Period	30
General and Administrative Expenses	Percent/Period	8

Facility Operation Parameters		
Facility Type		Specialty Chemical Processing Facility
Operating Mode		Continuous Process-24hrs
Length of Start-up Period	Weeks	20
Operating Hours per Period	Hours/Period	7,920
Process Fluids		Liquids and Gases
Operating Unit Costs		
Labor Unit Costs		
Operator	cost/operator/H	20
Supervisor	cost/Supervisor/H	30
Utility Unit Costs		
Electricity	cost/KWH	0.07
Portable Water	cost/M3	0
Fuel	cost/MEGAWH	27

Table S9. Itemized cost in dollar per liter of fuel produced.

	Fast Pyrolysis [14] + Upgrade ($ L^{-1})	
Cost	Option A	Option B
Raw materials	0.98	0.31
Utilities	0.17	0.17
Total labor cost	0.35	0.35
Total additional fixed operating costs	0.18	0.18
Depreciation	0.52	0.52
Co-product credit	(0.44)	(0.44)
MFSP ($ L^{-1})	**1.8**	**1.1**

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