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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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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 non-condensable gases and produces a bio-oil low in oxygen concentration and rich in naphthalene. Herein, we evaluate the co-production 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 co-products, 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 co-product market conditions ($0.53-$0.79 L^{-1}) when including a market price for carbon.

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] 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 like 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 of biofuels.[8]

In 2004, the US Department of Energy (DOE) created a single biomass program that merged previous programs for biofuels, bio-power, and biobased products.[12] The objective of this merger was to promote biorefineries producing multiple products, including higher-value chemicals, along with fuels and power.[12] Phenol, one of such chemicals present in pyrolysis oil, is examined in this paper. Phenol is a relatively valuable chemical commodity that sells for ~ 1.3kg^{-1}$ [13] (compared to aviation fuel at $0.5 kg^{-1}) and is typically synthesized from crude oil distillates through the

cumene process[14]. Additionally, 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), a variation of fast pyrolysis in which the non-condensable 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 (Table S1 in SI)[18], which due to 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 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. Hydrodeoxygenation (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 hydrodeoxygenation (HDO) upgrading process that is required for bio-oil produced from fast pyrolysis. HDO upgrading consists of mild hydrotreating followed by severe hydrotreating, a sequence of unit operations that result in a stable bio-oil[24]. We use experimental results from Elkasabi, *et al* (2015); 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 due to 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 by spreading, composting and hauling[27], these methods come with high capital and operating costs to comply with regulation and 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 metric tons 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 metric tons 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] (supporting information (SI) - Table S2), comprises about 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

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and rail infrastructures for feedstock transport, and access to labor.[33-34] We limit feedstock transport to an average distance of 80.5 km (50 mile) radius 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 generation of horse manure within a 80.5 km radius average. More details on data calculations for the map are found in the 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 due to its geographical supply in the North East 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 posit that the TGRP process and subsequent extraction would address waste treatment issues as well as contribute to an existing supply of bio-jet fuel.
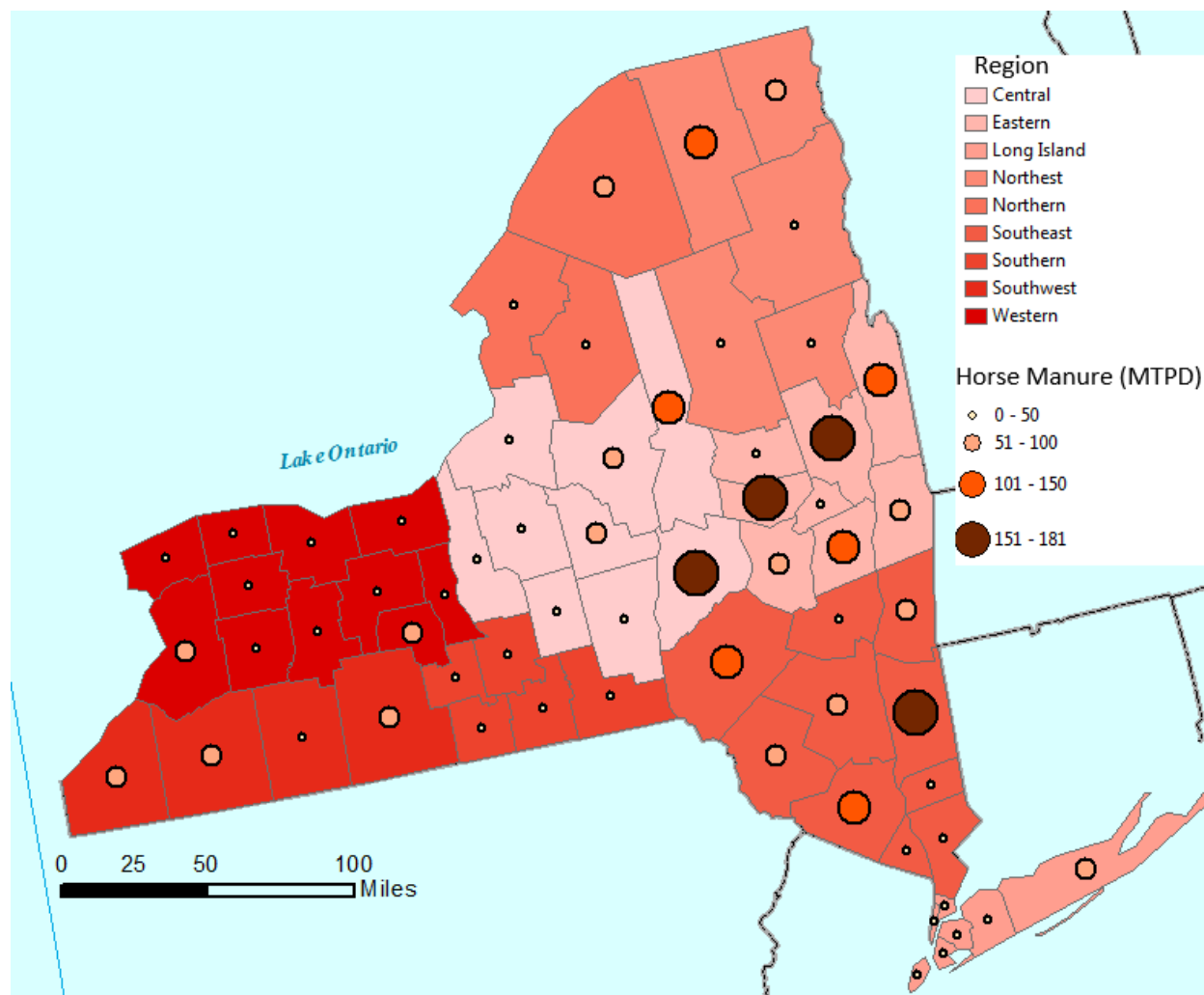
Figure 1. New York State map divided into counties. Color blocks represent the regions in New York State and graduated symbols represent horse manure availability in metric tons per day. Distributed pyrolysis systems scaled up to 200 MTPD would be feasible in multiple locations in New York State.

Biomass Conversion

The TGRP and oil upgrading facility is assumed to receive horse manure feeds of 200 MTPD, 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 pre-heater, a blower and recycling the stream of non-condensable gases into the fluidized bed (Figure S1).

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 pre-processing 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].

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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 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 (Figure S3 in SI). The resulting liquid S10 (volatiles with melting point $\geq$ 150 ˚C) stream (Figure S3 in SI) was heated to 420 ˚C before entering another flash drum. Due to 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-Figure S3 in SI) 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 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 in SI), the mixture 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 (Figure S5 in SI). Both stages were carried out in continuous stirred tank reactors (CSTR) RXTR3, operated at 80 ˚C, 50 atm, and RXTR4, operating at 200 ˚C, 75 atm.

Life Cycle Assessment

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The primary product we evaluate is the fuel product with the phenol chemical serving as co-product. 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, 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 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 into different forms, but exergy is consumed in all processes. CExD also takes into account the consumption of non-energetic 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.
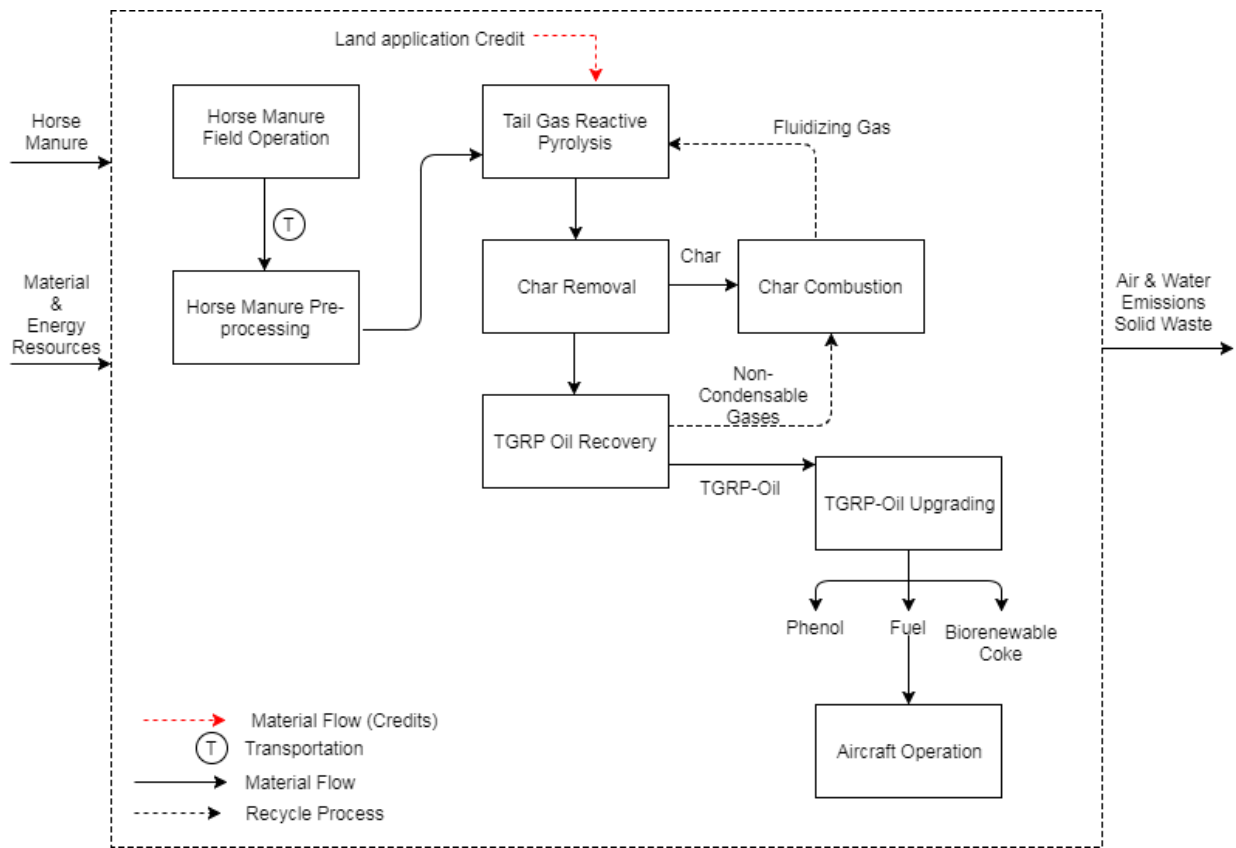

Figure 2. Life cycle system boundary for the production of fuel and phenol from horse manure via TGRP and upgrading through isolation and extraction of TGRP- oil distillates.

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 co-produced, is required in LCA. ISO 14040-44 [29] recommends that the allocation methods used shows the physical relationship like 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 co-products, 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 in SI) and TGRP oil upgrading (Table S4 in SI) 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 in SI); these values are used to inform the LCI. Fractions of energy, mass, and market price (Table S6 in 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 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.

1 *Techno-Economic Analysis*

2   To calculate the incremental cost of adding a TGRP oil upgrading system to a fast pyrolysis

3   operation, the material and energy flows obtained from Aspen Plus were used to size the major

4   equipment in the upgrade process. We estimated capital costs based on previous reports[7, 38, 55] and

5   used the Aspen Plus Capital Cost estimator software [56]. Costs were estimated using a desired rate

6   of return of 10% and projected in 2013 U.S. dollars using a cost basis from the Aspen Process

7   Economic Analyzer. All other assumptions made in the TEA are found in the SI.

8   In addition, a sensitivity analysis was conducted to examine the effects that different model

9   assumptions such as variation in the cost of individual raw materials (hydrogen, catalyst and

10   feedstock), market price of the major co-product (phenol), and the biofuel yield have on the

11   minimum fuel selling price (MFSP). To investigate the relationship between environmental and

12   economic impacts of the processes we use social cost of carbon (SCC), a method that internalizes

13   the cost of GHG emissions (and savings).

14

15   **Results and Discussion**

16   ***Process Yield, Energy Use, and Production Volume***

17   In the modeled TGRP facility, 200 MTPD of horse manure (8,300 kg.h^{-1}) are fed into the system,

18   producing about 74 metric tons of TGRP oil per day (3075 kg.h^{-1}), corresponding to a yield of

19   36.9% on a mass basis. The heat for the pyrolysis process is transferred from the char combustor

20   by fluidization sand. Fuels, phenols, sodium chloride and biorenewable coke are separated or

21   formed during the TGRP oil upgrade. In the upgrade process, energy is internally generated by

22   enthalpies of solution and exothermic reactions such as the cooling of volatiles; serving as a

23   heating source for the flash drums, heaters, and separators.

24   The analysis shows that available horse manure supply in New York State could yield about 4.3

25   million gallons per year of bio-jet fuel (SI Table S2). Although we do not base our study on a

26   regional scale, if we were to include equine farms in the North-East region, bio-jet fuel supply

27   from Pennsylvania alone would add an additional 5.7 million gallons per year (SI Table S2). Given

28   that the 4.3 million gallons produced would be 100% renewable jet fuel and that bio-refineries

29   may blend 25% bio-based and 75% petroleum-based fuel in the near term (c. 2020), [57] New York

30   State's equine waste jet fuel production would supply 5.5 billion gallons of 25%/75% bio-jet fuel

31   to the market. Also, 4.3 million gallons per year is a conservative estimate since we only consider

32   horse manure (25% of the total equine waste) and not horse bedding. If all equine waste were

33   converted with the same bio-oil yield for horse manure and bedding, then New York State could

34   produce a total of 172 million gallons per year and meet about 3% of total U.S aviation fuel demand

35   [58].

36   ***Life Cycle Metrics***

37   The life cycle GWP and CExD were calculated for the production of fuel and its co-product

38   (phenols) from the upgrade of TGRP oil, using functional units of 1 MJ of fuel (Figures S6 and S8

39   in SI) and 1 PKM (Figures 3a and 3d). Due to the different values of the mass, price and energy

40   content of the co-products, the allocation results found in the supporting information vary by

41   method. The high market price of phenol ($1.28 kg^{-1}) compared to fuels ($0.5 kg^{-1}) translates into

42   a low economic allocation for both the GWP and CExD of fuel.

43   Compared to other allocation methods, the fuel product has a higher GWP when allocated by

44   mass, because of its high mass fraction among all product flows. (Figure S6 in SI). Moreover,

45   regardless of the allocation method, the TGRP-fuel has a lower GWP than aviation fuel on a well-

46   to-wheel basis. Herein, we assumed similar GHG emissions from the distribution distance of

15

47 TGRP fuel and aviation fuel, due to similar distances from refinery to pump. The impact of horse

48 manure biofuel is almost entirely caused by its cradle-to-gate emissions, whereas the major share

49 of the GWP of petroleum based aviation fuel comes from operation, i.e. CO_2 emissions during

50 aviation fuel combustion. This is because the TGRP upgraded fuel is assumed to have zero net

51 GHG emissions during combustion, as its carbon is biogenic. Overall, the analysis suggests (Figure

52 3a) that the TGRP-fuel emits less than 10% (10 g of CO_2 eq. per PKM) of the GHGs of aviation

53 fuel (110 g of CO_2 eq. per PKM). The GWP of the TGRP upgraded fuel product shown in Figure

54 3b meets the RFS-2[43] standards; hence, the TGRP fuel product is environmentally preferable

55 relative to aviation fuel on a life cycle basis. When the GWP of the TGRP process is allocated

56 according to economic value, the GWP of phenol is slightly higher (9%) than that of petroleum

57 based phenol (30g CO_2 eq. per PKM of fuel) [40] (excluding the end-of-life impact of phenol

58 applications) due to its high economic value, but lower using mass and energy allocations (Figure

59 S6 in SI). This validates the results of other studies [59-60] that have argued that different allocation

60 methods determine the outcome of the environmental impacts on the products and co-products.

61 Also, this suggests that it is more beneficial to separate the phenols in the TGRP upgrade process

62 than to produce only fuels (as is the conventional hydrogenation (HDO) method)[19]. Using system

63 expansion yields a higher net GWP for TGRP-fuel than when it is allocated on an economic, mass

64 or energy basis (Figure S6 in SI). This is mostly because in all of the allocation methods, a large

65 share of the GWP is attributed to the byproducts, mainly phenol and coke. The total impact of the

66 TGRP process is identical for all allocation methods, but a reduced GWP for TGRP fuel induced

67 by shifting the impact to phenol or coke is artificial. Therefore, in the interest of the functional unit

68 defined, i.e. the production of 1 MJ equivalent of TGRP-fuel or 1 PKM of distance traveled, we

69 opt to discuss only system expansion hereafter [25, 61-63]. This means that the entire GWP of the

16

70   TGRP process is allocated to the fuel, and afterwards corrected for the credits achieved by phenol

71   and coke production, offsetting phenol from the cumene process and coke as byproducts from the

72   production of liquid fuels from crude oil. Nonetheless, the entire GWP of the TGRP process (10 g

73   CO_2 eq.), producing the fuel, coke and phenols, is still significantly lower than the GWP of

74   petroleum based aviation fuel (110 g CO_2 eq.) [40] combined with phenol from the cumene process

75   (30 g CO_2 eq.), per PKM of distance traveled.

76   A previous study[64] determined that the GWP (Figure 3b) of the conversion of poplar biomass to

77   drop-in bio-jet fuel via the bioconversion platform ranges from 30 g CO_2 eq. to 70 g CO_2 eq. per

78   MJ of fuel burned, depending on the hydrogen generation method used in the hydrogenation steps.

79   Bio-jet fuel (LG) represents a fuel for which the hydrogen for upgrading comes from lignin-

80   gasification (LG) and natural gas is used for heat and steam. Bio-jet (LG-HF) represents a fuel

81   produced from a process that uses lignin gasification for hydrogen generation and hog fuel (HF)

82   for heat and steam. When comparing this range to the GHG emissions from the current process

83   (TGRP oil upgrade) without the credits from the co-products (40 g CO_2 eq. per MJ), and the various

84   process contributions, the GHG credit for phenol (30 g CO_2 eq.) is larger than the extra impact of

85   the separation process (Figure 3a). In addition, we explore the effects of not disposing the manure

86   and including the GHG emissions as a credit (Figure 3b). These results show that the average GHG

87   emissions from land application reduce the TGRP fuel GHG emissions to 4.4 g CO_2 eq.

88   The results for CExD assessment are given in Figures S8, S9, 3c and 3d. Previous studies used

89   exergy assessment to evaluate the production of biofuels such as biodiesel and ethanol [49, 65-68].

90   Most relevant for our study is the work of Keedy, *et al*. [49], who used CExD as an assessment metric

91   for evaluating the sustainability of bio-oil production via fast pyrolysis using three feedstocks, one

92   of which was horse manure. When analyzing the CExD metric, the trend in allocation results

93 (Figure S8) is similar to the GWP results; whereby the phenol contributes the highest CExD in

94 economic allocation compared to the other co-products. According to the Ecoinvent database[69-70]

95 from which data were drawn, the CExD for the production and combustion of aviation fuel is 1.8

96 MJ per MJ of fuel. This value is approximately 28% greater than the CExD of the TGRP-fuel

97 produced in this study without co-product credits (1.3 MJ per MJ of fuel).

98 Figure 3c and 3d present the life cycle environmental impact of CExD per person kilometer (PKM)

99 of travel by aircraft passenger (as in Figure 3a for GWP). These figures compare CExD of TGRP

100 fuel with aviation fuel. Credits are also displayed for the TGRP fuel. The dashed bar for TGRP

101 fuel indicates the net CExD (including credits). Figure 3c includes the contribution of CExD by

102 resource for the net amount. Figure 3d indicates the TGRP contribution by process and details

103 credits. Both figures indicate the cumulative exergy destruction per passenger kilometer is much

104 higher for aviation fuel compared to TGRP fuel. Figure 3d indicates that this is true even without

105 credits. The positive TGRP area on Figure 3d represents the CExD for total production. Of the

106 individual process contributions shown on Figure 3d, the results indicate that the majority of the

107 CExD in the overall process is attributed to horse manure pre-processing. The bulk of the energy

108 consumed in the pre-processing step is from electricity used to operate milling, drying, and

109 conveying equipment. This indicates that the material and energy needs of the pre-processing step

110 could be targeted for CExD reduction. Figure 3c provides a breakdown of the net CExD by

111 resource. The majority of the resource inputs used to produce aviation fuel are derived from fossil

112 fuels (petroleum, natural gas, coal). A significant contribution to the CExD of the TGRP fuel is

113 attributable to electricity production. The NPCC grid resources are about 50% fossil (including

114 petroleum, natural gas) and 31% nuclear on an energy basis. However, the CExD percentages are

115 75% nuclear and 24% fossil. This results in the larger nuclear contribution to CExD on Figure 3c

116   (compared to the fossil contribution). Note the fossil contribution is considered a credit because of

117   the production of phenol and coke.

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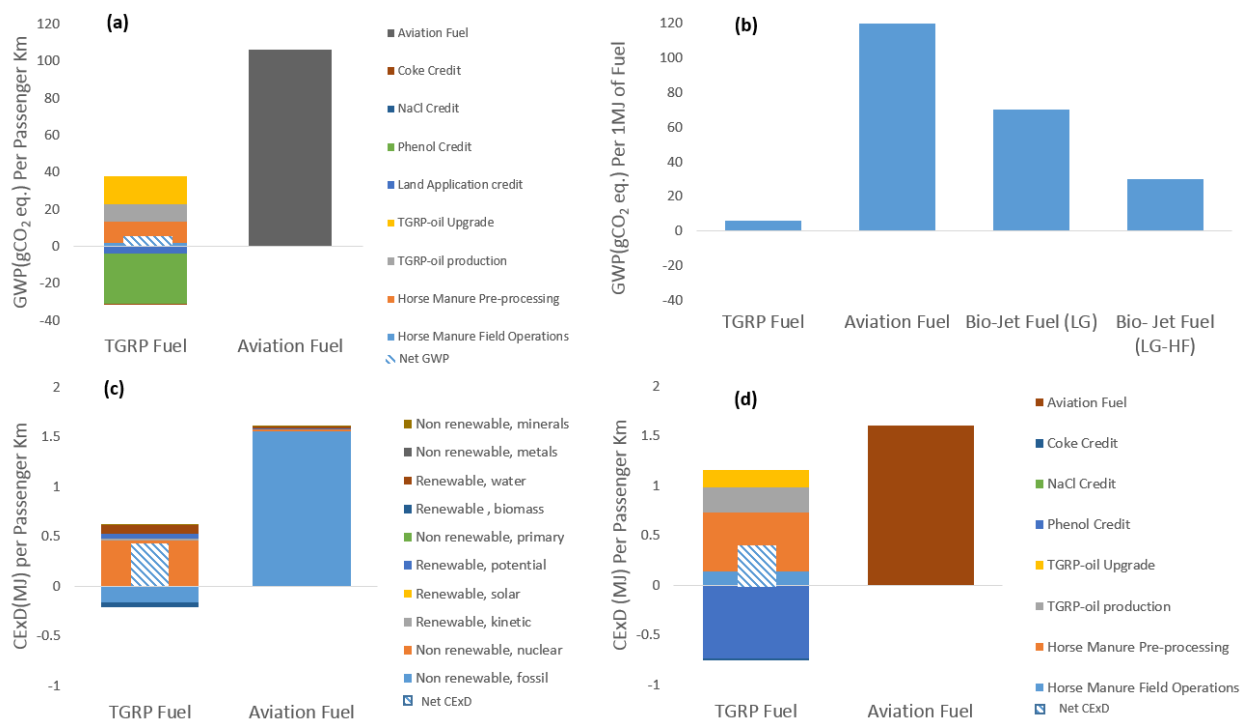
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Figure 3. Life cycle environmental impact of TGRP fuel using system expansion. a) GWP

comparing TGRP fuel to aviation fuel per passenger km. b) GWP comparing TGRP fuel to aviation

fuel and other bio-jet fuels produced from the bioconversion of poplar biomass per 1MJ 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.

126   SI Figure S9 compares the CExD of phenol extracted in the TGRP process with the phenol

127   produced by the cumene process. The former demands either more or less exergy than the latter,

128   depending on the allocation method used. With energy and mass allocations, the CExD of phenol

19

129   is smaller than the CExD of the cumene process whereas with economic allocation, the CExD of

130   phenol is greater than the CExD in the cumene process. This difference due to allocation method

131   choice is a result of phenol having a higher market value than fuel and the other co-products.

132   *Global Warming Potential Sensitivity*

133   Diverting horse manure from agricultural lands for fuel production may avoid GHG emissions.

134   Manure is often land applied in agriculture to recycle nutrients. When manure is disposed by land,

135   it releases GHGs predominantly in the form of N_2O and CH_4 owing to the presence of inorganic

136   N, microbic available sources of carbon and water. [71] These emissions are in the range of 16,400-

137   33,500 g CO_2 eq. per ton of manure [72] depending on the size of the farm. By using thermochemical

138   conversion to dispose of the manure, we can reduce CO_2 emissions from land application by 88%

139   to 94% (as shown in SI- Figure S12). A scenario that includes the GHG emissions released from

140   land application as a credit (Figure 3b) shows that the average GHG emissions from the TGRP

141   fuel process reduces to 4.4 g CO_2 eq.

142   In addition, we examined the sensitivity of GWP on feedstock transportation by doubling the

143   horse manure transportation distance to the equine facility. This increases the GHG emission by

144   0.5g CO2 eq. per passenger kilometers (5% increase in the total GHG emissions), a small amount

145   that aligns with prior literature [62, 73] on the transport of biomass feedstocks for biofuels.

146   *Techno-economic Analysis*

147   We estimate the capital and operating costs of TGRP bio-oil upgrading operations from the

148   Aspen Plus simulations, and compare these incremental costs to fast pyrolysis to produce bio-oil

149   from prior research[38] (Table 1). Since TGRP and fast pyrolysis use the same equipment, are

150   identical in scale, and the only difference between the two is that the TGRP process recycles the

20

151   non-condensable gases whereas fast pyrolysis uses the gases for process energy, we assume the

152   differences in costs between the two are negligible. The additional capital cost of bio-oil upgrading

153   operations that produce value-added products (jet fuel, phenols and green coke) is one third ($7.7

154   million) the cost of fast pyrolysis[38] ($24.7 million), which produce bio-oil alone (Table 1). The

155   project capital cost was determined based on 5% per year working capital [74] , which is a percentage

156   of total capital expense per period showing the amount required to operate the facility until the

157   revenue from product sales is sufficient to cover costs [56].

158   An economic life span of 10 years was chosen for this study for a side by side comparison with

159   a similar 200 MTPD fast pyrolysis study [38]. The cost of raw materials and market prices of products

160   are shown in Table S7 in SI. The labor cost is estimated from the number of full time equivalents

161   required for operating the TGRP upgrade process for 7920 hours per year. We use two operators

162   per shift at a unit cost of $20 per operator per hour and one supervisor per shift with a unit cost of

163    $35 per supervisor per hour. The total additional fixed operating costs include facility overhead

164   and operating charges.

165   Total revenue consists of sales of the main product of the upgrade and by-products. The price of

166   fuel used in this analysis is based on the current price of aviation fuel; consequently, the outcome

167   of this comparative study may change based on future market conditions. Sodium chloride and

168   water are considered waste products of the process; hence, they have a negative monetary value

169   and incur waste treatment costs of $0.002 kg^{-1} [75] and $0.074 kg^{-1} [74], respectively.

170   **Table 1.** Capital and operating costs of fast pyrolysis and the incremental cost of TGRP upgrading.

	Fast Pyrolysis[38]	TGRP Upgrade
Total Project Capital Costs ($)	24,700,000	7,680,000
Annual Operating Costs (in $/year)	9,360,000	4,510,000

Raw material	4,280,000	1,950,000
Utilities	768,000	313,000
Total Operating Labor & Maintenance Costs	1,130,000	1,060,000
Total Additional Fixed Operating Cost	712,000	423,000
Depreciation (10 years, straight line)	2,470,000	768,000
Total Revenue ($/year)		**5,620,000**
Co-product Sales		3,020,000
Sales from Fuels		2,600,000
MFSP of bio-oil from fast pyrolysis and subsequent TGRP upgrade ($/L)	**1.1ᵃ-1.8ᵇ**	

171 a. MFSP for Option B (Free Feedstock)
172 b. MFSP for Option A (Feedstock price $0.055 kg $^{-1}$)
173

174   Using the economic analysis of Pourhashem *et al*. [38] with the incremental costs of TGRP

175   upgrade, the MFSP of the final upgraded TGRP-fuel is estimated to be $1.8 L^{-1} of fuel (MFSP

176   Option B-Table 1), which is comparable to a similar study by Carracso, *et al* [55], who investigated

177   the conversion of forest residue to bio-diesel through fast pyrolysis and catalytic upgrading. The

178   MFSP for Option A in Table 1, assumes the agricultural residue feedstock cost from Pourhashem

179   *et al.*[38], $0.055 kg^{-1} to approximate the cost of collecting and hauling properly haul the horse

180   manure to the conversion facility and contrasts it with the Option B MFSP, a lower limit in which

181   horse manure is assumed to be given freely[4] by the farmers as an alternative to paying for disposal

182   and thus is $0 kg^{-1}. Option A represents a conservative approximation of feedstock cost given that

183   the cost of a waste like horse manure is expected to be low, or possibly zero or negative (if the

184   horse keeper has to pay to have the manure hauled offsite for treatment). However, horse manure

185   is an agricultural waste product with no value, thus, the assumed feedstock cost of $0 kg^{-1} (MFSP

186   Option B-Table 1) is plausible, reducing the MFSP to $1.1 L^{-1}. An investment analysis over a

187   project life of 10 years results in a net present value of $1.6 million; hence, the project is

188   economically feasible under the assumptions made.

189   Jones *et al* [7] evaluated the production of fuels via pyrolysis and HDO upgrade and found a

190   positive net present with a minimum fuel selling price (MFSP) of $0.54 L^{-1}, which is far below the

191   MFSP for the TGRP oil upgrade process; $1.1 L^{-1}. This variation in MFSP can be attributed to the

192   significant difference in scale between the two processes; the biomass supply needed for the HDO

193   process is 10 times higher than the distributed TGRP-fuel process.

194   ***Sensitivity Analysis***

195   The MFSP is most sensitive to feedstock cost and yield, and to a smaller extent on the market

196   prices of phenol and coke, but hydrogen and catalyst costs do not have a significant effect on the

197   MFSP because they are used in small quantity compared to the other raw materials in the process

198   (Figure S10). The MFSP value showing sensitivity analysis to feedstock cost depicts a significant

199   reduction from $1.8 L^{-1} to $1.1 L^{-1} (Table S9 in SI) when the feedstock is treated as a waste ($0

200   kg^{-1}), hence making TGRP fuel more economically competitive compared to the base case. If the

201   price of feedstock were to double, assuming it has to be purchased from the farmers, the MFSP

202   increases significantly to $2.4 L^{-1}. This can be the case if equine waste is in high demand and its

203   supply is limited. Also, because the market price of green coke can change drastically [76], it is

204   important to see the effect of this change on the MFSP. However, the tornado plot shows little

205   variation in MFSP due to changes in the price of coke; hence, the MFSP is not too sensitive to the

206   price of coke.

207   If the yield increases by 25% [20, 77], the MFSP decreases significantly to $1.4 L^{-1}. Likewise, if

208   the market selling price of phenol increases, the MFSP decreases, and if the selling price decreases,

209   the MFSP increases. This implies that increasing process yields, increasing the price of co-products

210   and reducing the price of feedstocks can render the process economically feasible.

211

212   ***Environmental and Economic Implications for Advanced Fuel Development and Policy***

213   To fully account for the climate change mitigation benefits of biofuels and support policy

214   decisions in their investment, it is important to include both internal and external costs and measure

215   both direct and indirect costs of a process or product. In this section, we estimate all internal costs

216   associated with TGRP and aviation fuel production and consider the social cost of carbon (SCC),

217   an external cost[78]. The United States Environmental Protection Agency (U.S. EPA)[79] uses SCC to

218   estimate the climate benefits of set standards. The SCC is a monetary value estimating the

219   economic damages caused by a marginal increase in carbon dioxide emissions in a defined year.

220   In order to overcome the high MFSP, SCC is expressed as a revenue equivalent to the difference

221   in the monetary value of GHG emissions between the renewable fuel and petroleum-based aviation

222   fuel. Using the 2007 year SCC value of \$36 with a 3% discount rate[79], the TGRP SCC value is

223   \$930,000 yr^{-1}, a quantity representing the reduction in economic damages associated with CO_2.

224   Using Option A (Table 1-MFSP) while including the SCC, the MFSP decreases to \$1.64 L^{-1}. When

225   varying the discount rate (2.5%, 3% and 5%) and statistics (average and 95th percentile)[80] applied

226   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

227   of aviation fuel (\$0.42 L^{-1}), the SCC would need to be as high as \$354 per metric ton based on the

228   assumption that the original SCC of \$36 has been underestimated.

229   Finally, to understand how sensitive the MFSP is to variability in the SCC, a sensitivity analysis

230   (Figure 4) was carried out using scenarios reflecting the highest and lowest MFSP. When the cost

231   of raw materials (feedstock, hydrogen and catalyst) is high, yield is low and co-product (phenol

24

232 and coke) selling prices are low, the MFSP ranges from \$2.11 to \$2.38 L^{-1}. On the other hand, a

233 scenario that includes the lowest price of raw materials, higher yields and high selling price of co-

234 products reduces the MFSP to a range of \$0.53-\$0.79 L^{-1}, which could be competitive with the

235 price of petroleum-based aviation fuel on the market. If we add a manure management fee of

236 \$0.008/L, this would have a small effect on the MFSP, reducing it from \$0.66/L to \$0.65/L.

237 Therefore, when all fuel conversion parameters are optimized as would be expected of n[th 81] biofuel

238 conversion facilities, and when external costs are reflected in the market price of energy, it is

239 possible to economically produce low carbon jet-range fuels and value-added chemicals through

240 TGRP technology.
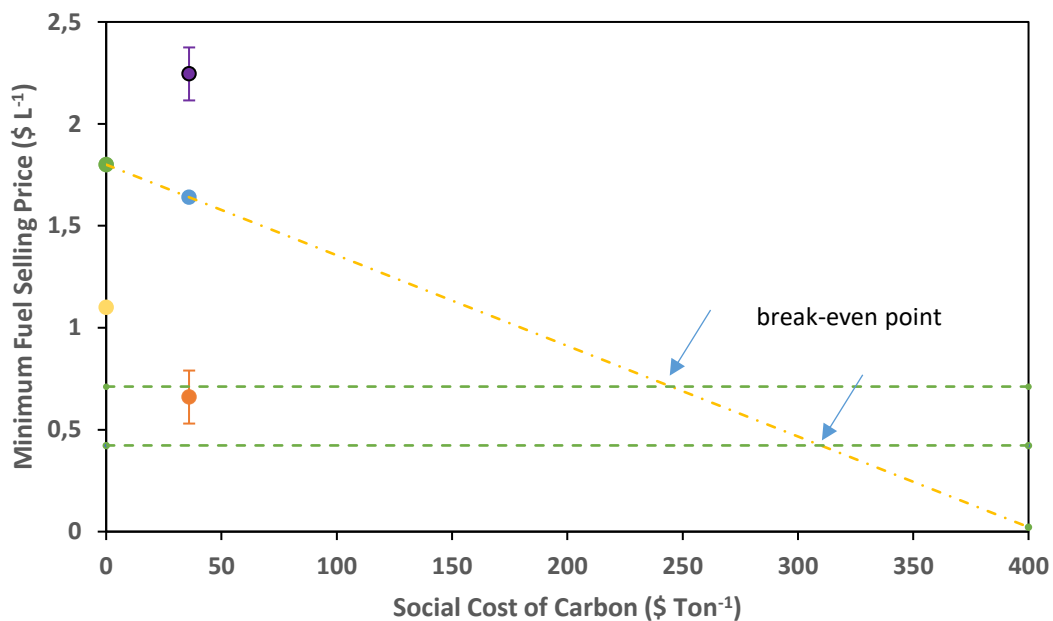
241

242

243 ● Option A with SCC of \$36/ton [67], baseline scenario and feedstock Price of \$0.055/kg

● Option A with SCC of \$36/ton [67], upper bound conditions from the sensitivity analysis (tornado
244 plot) and high cost of raw materials, low yield, low selling price of co-products

● Option B with SCC of \$36/ton [67], low cost of raw materials, high yield, low selling price of co-
245 products

● Option A without SCC, baseline scenario and feedstock price of \$0.055/kg
246 ● Option B without SCC, baseline scenario and feedstock price of \$0/kg

---- MFSP for option A at varying SCC; curve shows break-even points (arrows) with petroleum-
based aviation fuel

---- Price range of petroleum based aviation fuel (2014-2017)

247

248

249

250 **Figure 4.** The effect of social cost of carbon on the minimum fuel selling price.

251 **Associated Content:**

252 **Supporting Information:**

253 Supporting life cycle inventory data, co-product allocation parameters and results, bio-oil

254 characteristics, feedstock logistics and supply, and economic data are summarized; process flow

255 diagrams from Aspen Plus simulations show details of feedstock conversion and fractionation to

256 fuels and phenolic compounds (PDF).

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518   **For Table of Contents Use Only**

519   **Table of Contents (TOC) Graphic:**
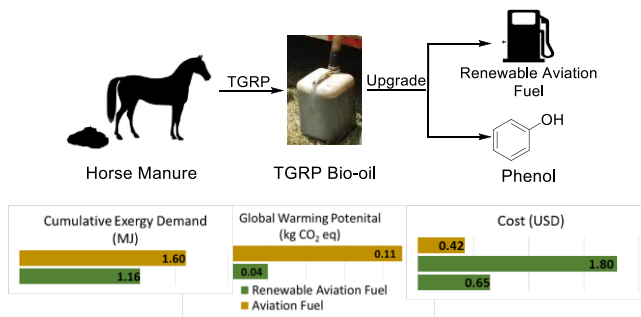
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521   LCA and TEA are used to evaluate renewable jet-range fuels and phenolic compounds by tail gas

522   reactive pyrolysis of equine waste.

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

Yetunde. E. Sorunmu[1], Pieter Billen[1, 4], Yaseen Elkasabi[2], Charles. A. Mullen[2], Nelson. A. Macken[3], Akwasi. A. Boateng[2], Sabrina Spatari[1]*

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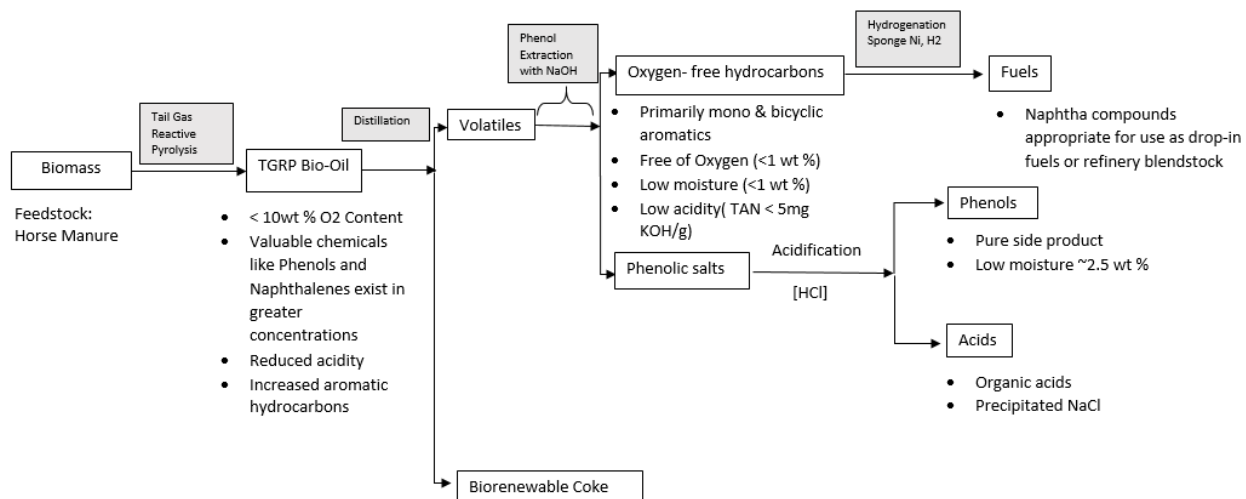
SUPPORTING FIGURES

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.
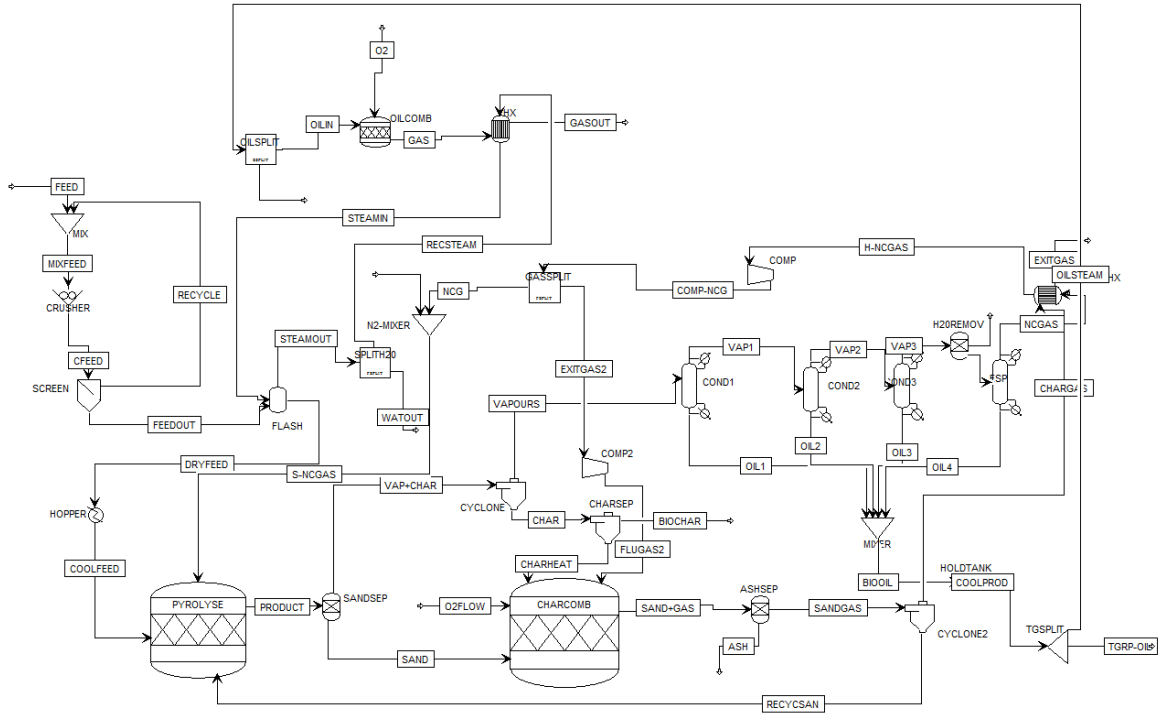
Figure S2. TGRP -Oil production

- HEATER 1 & 2: Heater
- V-101 & 102 & 103 : Separator
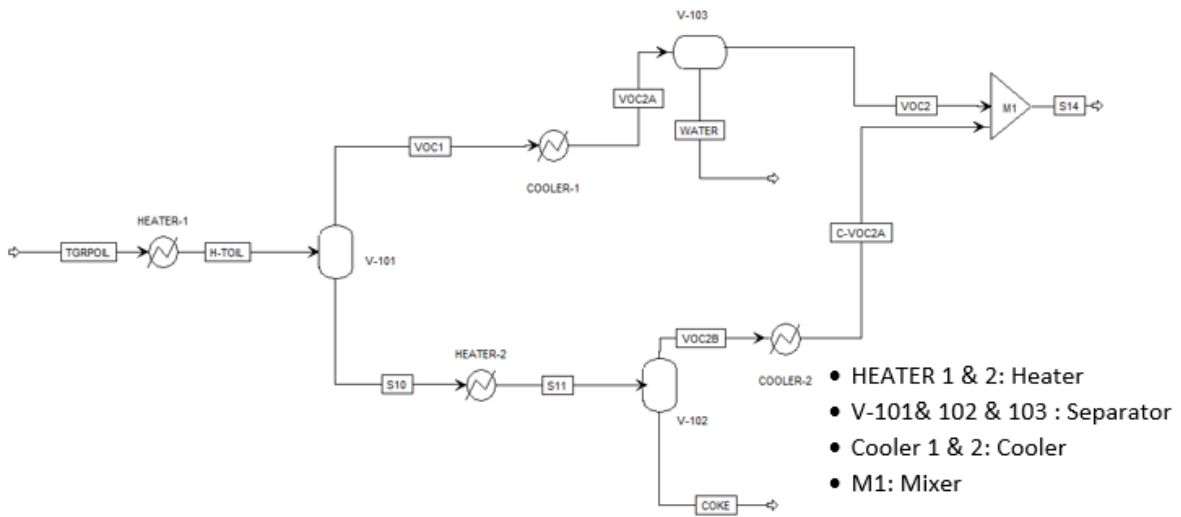- Cooler 1 & 2: Cooler
- M1: Mixer

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.
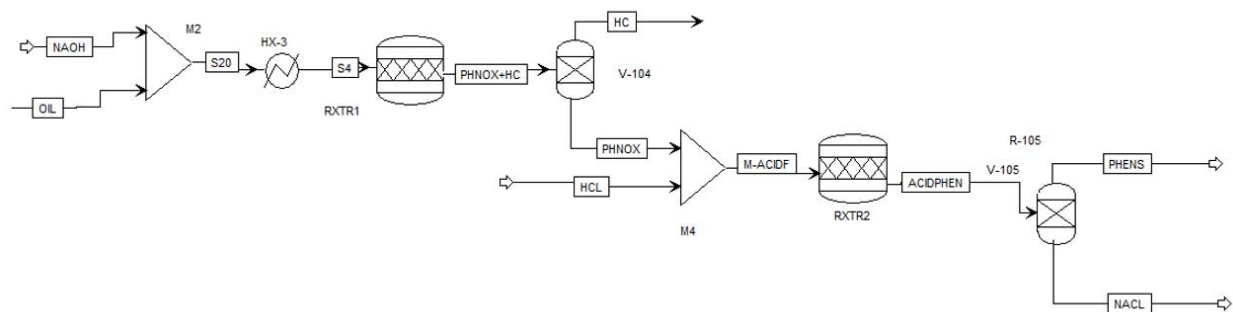
Figure S4. Phenol Extraction
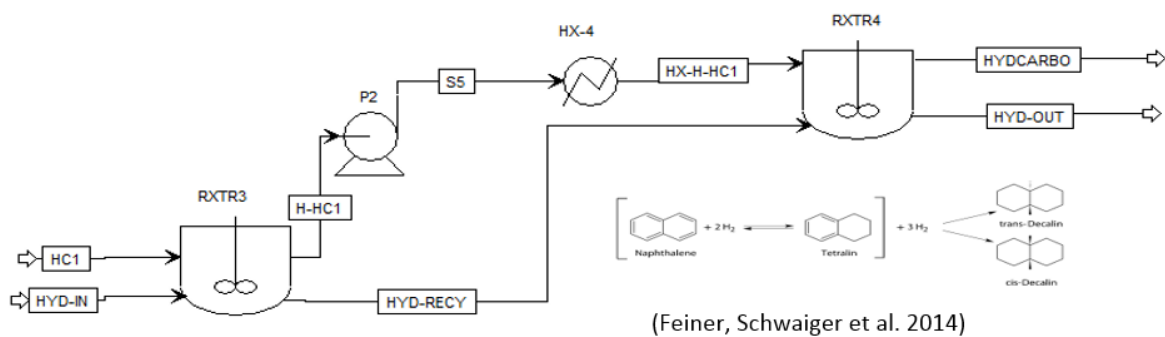
- $C_8H_8 + H_2 \rightarrow C_8H_{10}$
- $C_8H_{10} + H_2 \rightarrow C_8H_{12}$
(Lee, Yung et al. 2013)

(Feiner, Schwaiger et al. 2014)

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.
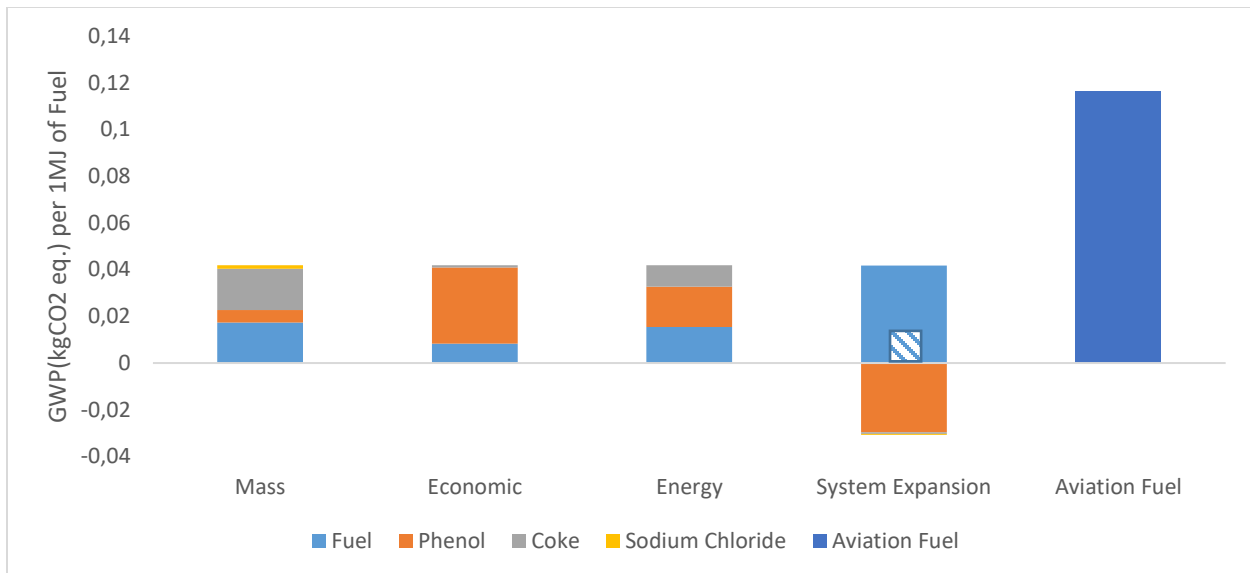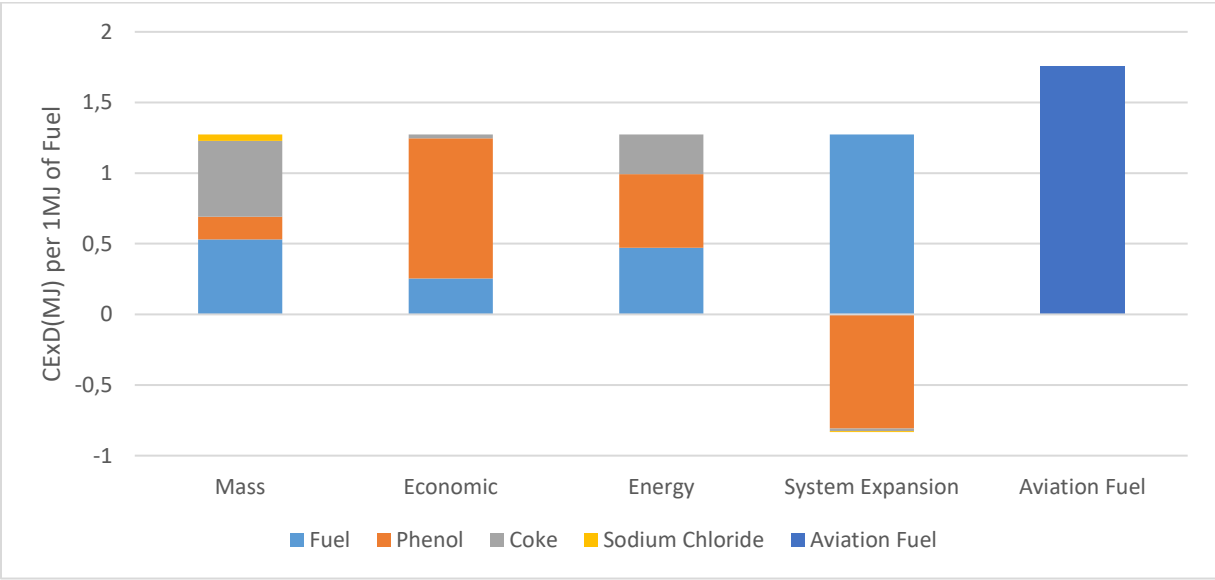

Figure S8. Contribution of the products and co-products to cumulative exergy demand per 1MJ of Fuel produced based on the economic, mass and energy allocations. The figure compares these allocations to the CExD of Low –Sulfur diesel extracted from Simapro [3]. Total CExD for

economic, mass and energy allocations are the same but the percent of CExD allocated to each
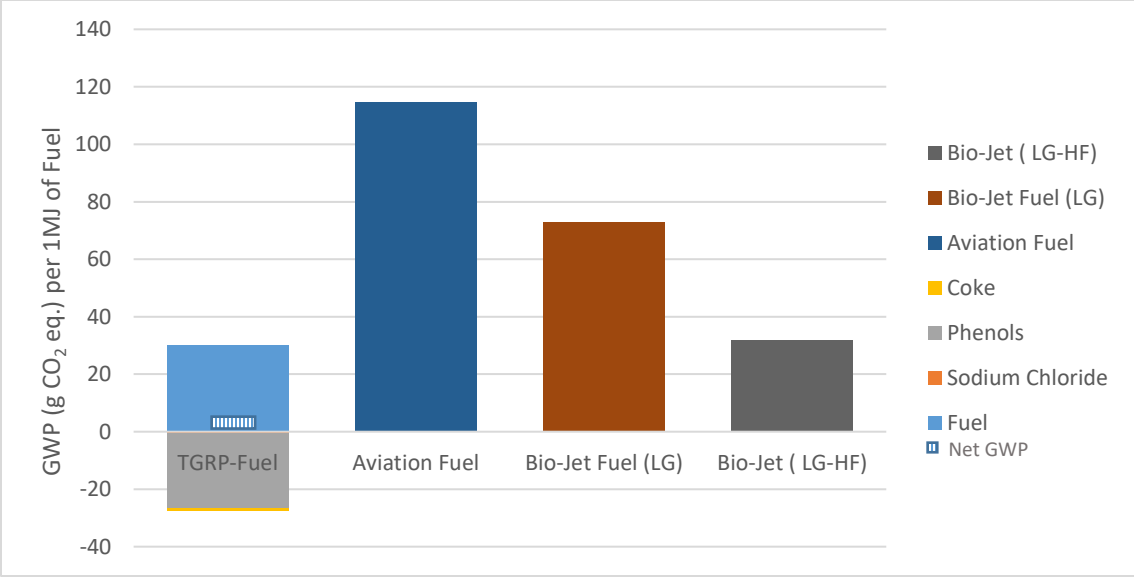
product is different.
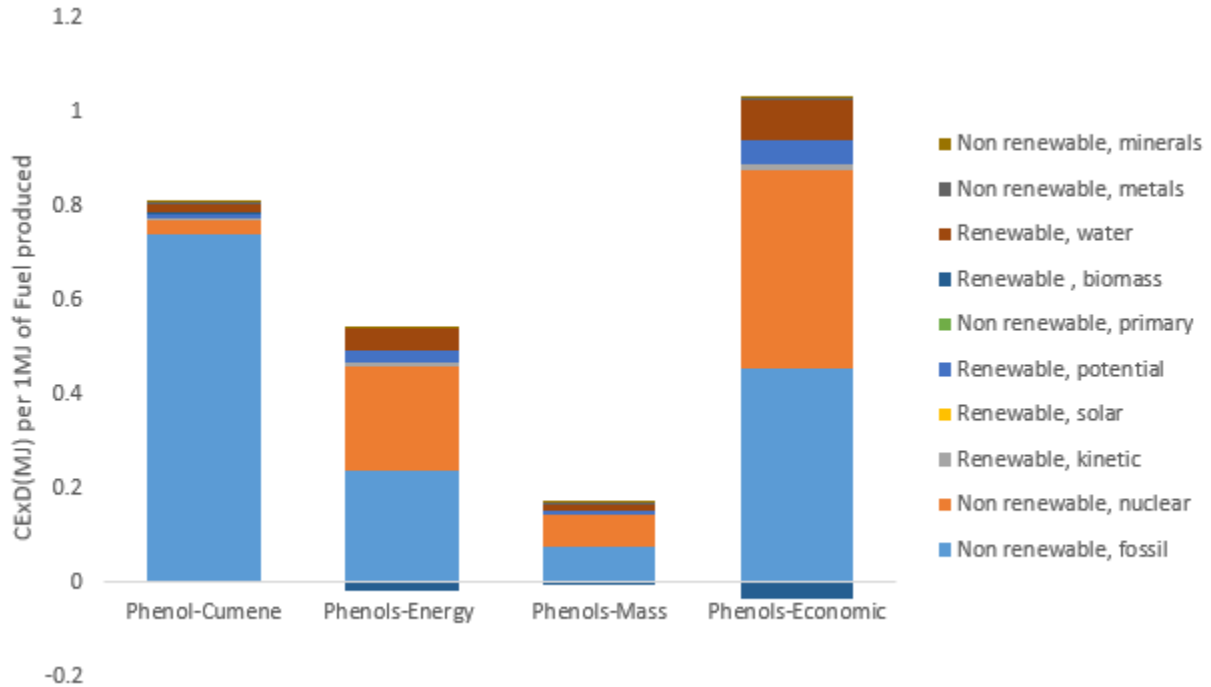
Figure S9. Cumulative Exergy demand (MJ) of phenol per 1MJ of Fuel produced. Phenol form

the cumene process is compared with phenol form the TGRP process using mass, energy and

economic allocations.
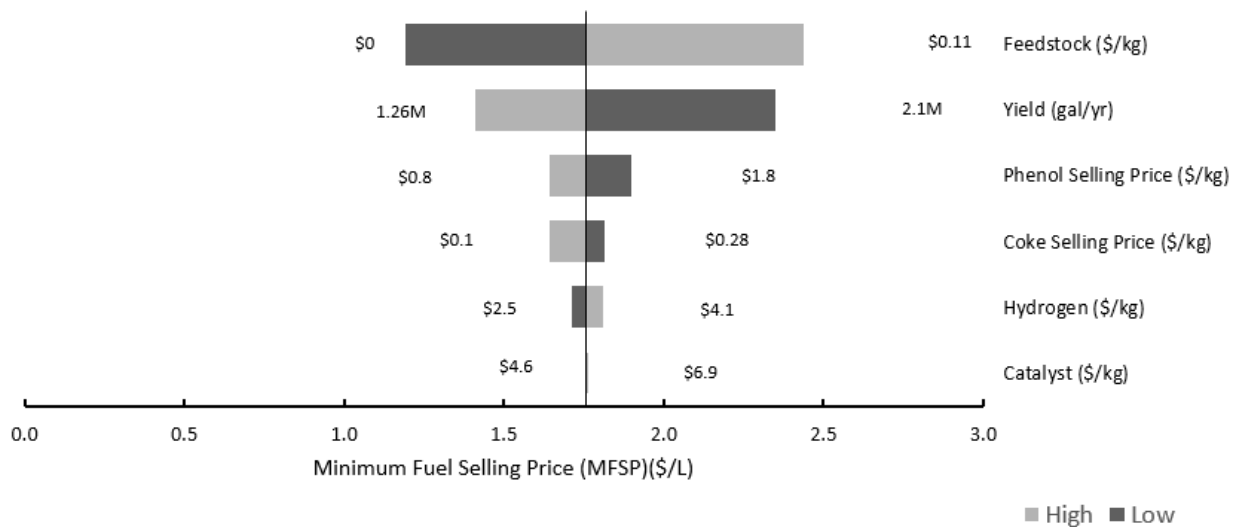
Figure S10. Tornado plot that shows the financial sensitivities of the TGRP upgrade process. The economic analysis includes the TGRP oil production and its upgrade to fuels and phenols.
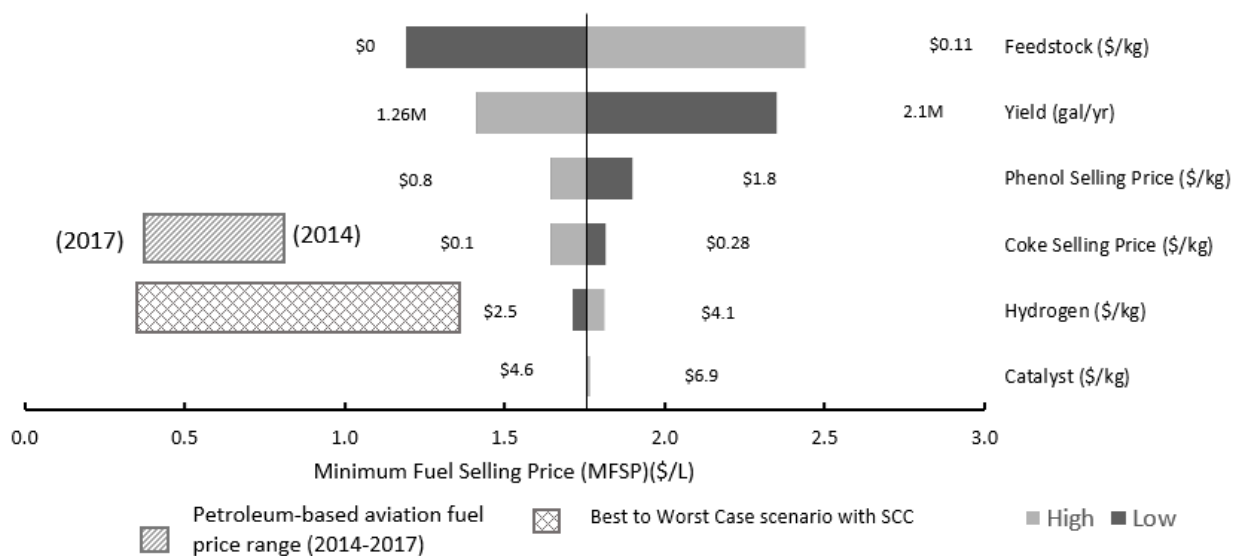
Figure S11. Aviation price range and minimum fuel selling price of best to worst case scenario.
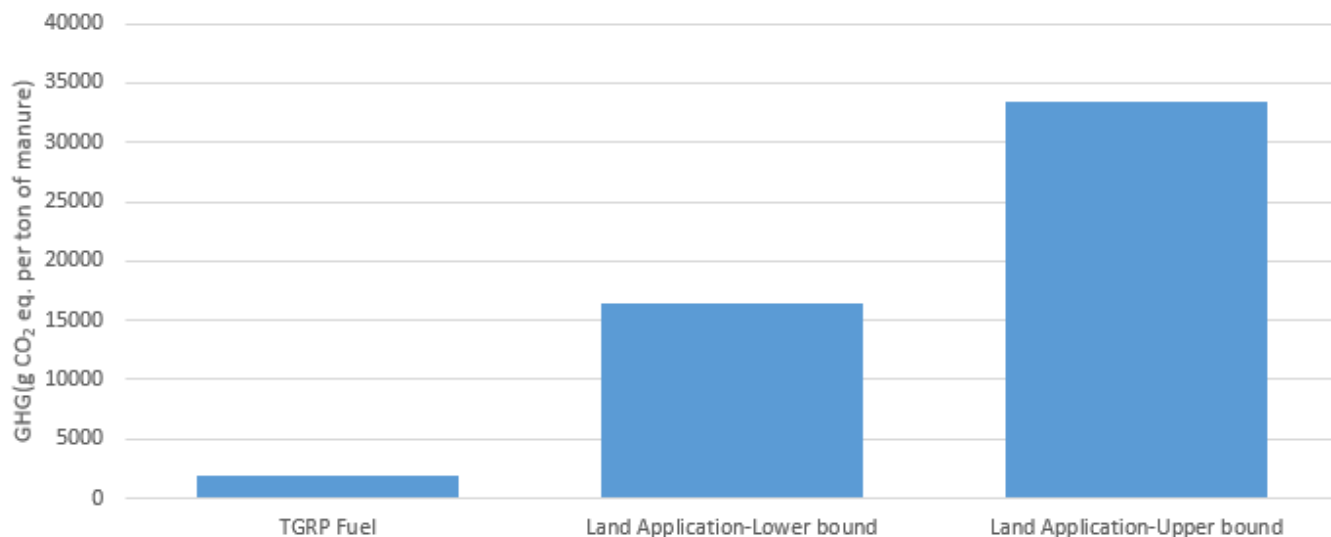
Figure S12. GHG emissions per ton of manure from TGRP fuel and land application

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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