

Investigating the techno-economic trade-offs of hydrogen source using a response surface model of drop-in biofuel production via bio-oil upgrading

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Abstract: This study presents a parametric fitting of the economics of bio-oil stabilization and hydroprocessing to naphtha and diesel range blend fuel. The data is fit with a response surface model (RSM). Technical variables evaluated in this study are rate of bio-oil upgrading and natural gas input rate. Economic variables considered include bio-oil, natural gas, hydrogen, catalyst, capital, and fossil carbon costs.

Our base case consists of a 1440 tonnes per day bio-oil upgrading biorefinery concept design for the production of naphtha and diesel range blend stock fuels. The RSM represents variation around this base case. The process model includes reforming, stabilization, and hydroprocessing sections. Total project investment for this concept is \$171.5 million or \$2.34 per gallon of bio-oil input capacity. This base case biorefinery generates 71.8 million gallons of fuel (5182 barrels per day) at a minimum fuel selling price (MFSP) of \$2.48 per gallon.

We investigated the techno-economic impacts of different hydrogen sources on the bio-oil upgrading process. Hydrogen from bio-oil reforming results in the lowest biofuel emissions but is not always economical. A portion of available bio-oil should be converted to hydrogen under two main conditions: the cost of hydrogen from bio-oil is lower than procuring hydrogen from other sources and the lost income due to a lower biofuel output; and/or when there is a market or policy constraint limiting fossil fuel use. Results indicate that to minimize fuel costs, the amount of bio-oil upgraded should decrease from $\geq 90\%$ to 80% as bio-oil prices decline from \$1.37 to \$0.70 per gallon

depending on market conditions. Carbon emission constrains such as those mandated by the Renewable Fuels Standard (RFS) could force bio-oil upgrading rates to less than 90%. © 2012 Society of Chemical Industry and John Wiley & Sons, Ltd

Supporting information may be found in the online version of this article.

Keywords: techno-economic analysis; biofuels from bio-oil; response surface model

Introduction

Petroleum remains the predominant source of transportation fuel with a global consumption of more than 84 million barrels per day (BPD). New energy sources are needed to meet growing global demand in a cost-effective and sustainable manner. In 2009, global biofuel production exceeded 1.64 million barrels per day mostly in the form of renewable ethanol.¹ The United States alone generated 875 000 barrels per day of ethanol in 2010.² Ethanol in the USA is marketed to consumers as a 10% blend of ethanol with gasoline (E10) as mandated by the Environmental Protection Agency (EPA).³ The ethanol industry faces a blending wall given the current gasoline consumption rate of 8 993 000 barrels per day. The EPA recently increased the blending limit to 15% for model vehicles 2007 and newer.⁴ This market constraint highlights the opportunity for production of drop-in transportation fuels. Drop-in biofuels consist of hydrocarbon fuels with characteristics similar to those found in petroleum products. Drop-in biofuels are envisioned to be compatible with the prevalent petroleum infrastructure and vehicle technologies.

The Energy Independence and Security Act (EISA) of 2007 mandated the production of 36 billion gallons of biofuels by 2022 with 16 billion generated from cellulosic biomass.⁵ The EPA greatly reduced the 2010 cellulosic biofuel mandate from 100 to 6.5 million gallons underscoring the challenge in converting cellulosic biomass into transportation fuels.⁶ In January of 2010, the US Department of Energy established the National Advanced Biofuels Consortium with \$35 million of public funding and \$14.5 million of partner investment to develop cost effective and sustainable drop-in biofuels that leverage existing refinery infrastructure.⁷ Pyrolysis and catalyst development/upgrading are among the cross-cutting technologies chosen for this project.^{8,9}

Biomass fast pyrolysis with bio-oil upgrading shows promise as a low-cost option for the production of gasoline and diesel.^{10,11} Biomass fast pyrolysis generates a liquid product known as bio-oil with attractive properties for power generation and fuel synthesis.¹² Bio-oil has a density of about 1.2 kg/L and a higher heating value of 16 to 19 MJ/kg.^{13,14} Unlike crude oil, bio-oil contains a significant amount of oxygenated compounds. Experiments have shown that conventional bio-oil can contain between 35 and 40 wt% oxygen content and up to 30 wt% water content.¹³ Oxygenated bio-oil compounds contribute to instability and acidity, and thus the oxygen must be released to make bio-oil compatible with existing refinery equipment. Researchers are pursuing several approaches to deoxygenate and dehydrate bio-oil including catalytic pyrolysis,^{15–17} bio-oil fractionation,^{17,18} and bio-oil stabilization.¹⁹

Bio-oil deoxygenation is a thermally intensive process with important technical and economic implications. This process employs metal catalysts in a high-pressure environment to chemically remove oxygen by forming water and carbon oxides. Process performance suffers from deactivation and poisoning of the metal catalysts because of coke formation and interactions with metal impurities found in the originating feedstock. Bio-oil conversion has been reported to be as high as 42 wt% to naphtha and diesel range hydrocarbons.²⁰ There are currently no commercial biofuel production based on bio-oil upgrading. Therefore, the technical and economic performance of this platform are uncertain. Although techno-economic studies focus on mature technology forecasts known as nth plant designs, commercial enterprises will require multiple facility implementations in order to meet capital and fuel cost targets. Several decision variables, such as reforming technology and feedstock choices, play a major role on process profitability. A better understanding of decision variable impacts can help identify opportunities and challenges of this technology.

Recent publications have analyzed the techno-economic performance of converting biomass to drop-in transportation fuels via fast pyrolysis and bio-oil upgrading.^{11,10} To our knowledge, there are no publications that describe a response surface model (RSM) of the bio-oil upgrading process. This study is therefore the first to present an RSM of bio-oil upgrading to gasoline and diesel. RSM is a novel approach to understanding the technical and economic tradeoffs inherent in the bio-oil upgrading process, and it provides a mathematical formulation suitable for further study of this technology in fields such as economics, supply logistics, and life-cycle analysis.^{21,22}

Background

Biomass fast pyrolysis

Fast pyrolysis is a rapid approach to converting solid biomass into a liquid crude-like product. Pyrolysis is a thermal treatment that takes place at 450 to 600°C and atmospheric pressure in an inert environment.¹² Several process designs have been proposed and operated for biomass fast pyrolysis.²³ The most common designs are based on fluid bed,²⁴ and auger,^{25,26} reactor units. These designs can convert a wide range of feedstock into a high yield of liquid products. These liquid products are commonly known as bio-oil - a dark, viscous mixture of organic compounds. Bio-oil yields of 70 wt% and higher are achievable depending on the feedstock type and operating conditions. Feedstock inorganic content (alkali) plays an important role in the pyrolysis process. Complex interactions between biomass and its alkali metals can adversely impact bio-oil quality.²⁷ Thus, recent research efforts focus on improving the quality and stability of pyrolysis oils.

Biomass fast pyrolysis for biofuel production involves several processing steps common to most thermochemical approaches. Operating parameters vary among implementations, and here we describe common assumptions for fluid bed pyrolysis. First, biomass is pretreated using grinding and drying to meet particle sizes of 1–5 mm and moisture content of around 7 wt%. The pre-treated biomass is converted in the pyrolysis reactor into a vapor stream with entrained solid particles. The solid particles, a mixture known as bio-char that is rich in carbon and plant nutrients, are collected using high efficiency cyclones. The clean vapors are sent to a

condensation system which can consist of a simple quench unit or several heat exchangers with staged exit temperatures. Some designs include an electro-static precipitator (ESP) to collect aerosols and condensable compounds that escape from the heat exchanger system. Non-condensable gases consisting mostly of carbon oxides and light gases are typically recycled within the process to recover heat. A portion of the collected solids could be combusted to provide process heat. Bio-oil requires stabilization prior to long term storage. This is due to the unstable, acidic, corrosive, and viscous nature of bio-oil mixtures, which continue to interact at room temperature.²⁸ Following stabilization, bio-oil can be converted into naphtha and diesel range fuels using conventional hydroprocessing technologies.

The combination of fast pyrolysis and bio-oil upgrading is not commercially available at this time due to economic and technological challenges. Researchers are investigating the potential for small-scale (less than 200 ton per day), mobile fast pyrolysis units,^{29,30} as an approach to reduce feedstock transportation costs. This study bases its assumptions on bio-oil from mobile fast pyrolysis units with 100 dry ton per day capacity and \$50 per dry ton feedstock prices.³¹ The US billion ton study update estimates that 79 million dry tons of forest and wood residues are available at costs of \$40 per dry ton or less.³² These mobile units produce bio-oil at prices of about \$0.94 per gallon.

Recent reports investigated the economics of biofuel production via biomass fast pyrolysis and bio-oil upgrading. Estimates from these investigations suggest that biofuel costs from mature commercial implementations of this technology would be between \$1.80 and \$3.50 per gallon.^{20,33,11,10} Risk analysis indicates that bio-oil based biofuel prices could be as high as \$8.00 per gallon today due to key technological challenges.¹¹

Response surface methodology

Response surface methodology is a mathematical and statistical analysis technique to study the influence of several variables on a target variable.³⁴ The outcome is a fitted function, which can serve as a reasonable approximation to the real model when the error is small.

A common approach to RSM is to develop an initial linear model for a given target variable y and decision variables x_i where $i \in \{1, 2, 3, \dots\}$. Equation (1) shows an example

linear model. Higher order models such as Eqn (2) are required to reduce fit errors in regions where the response is non-linear.³⁴

$$y = a \times x_1 + b \times x_2 \quad (1)$$

$$y = a \times x_1 + b \times x_2 + c \times x_1 \times x_2 \quad (2)$$

RSM techniques are commonly used in experimental studies in combination with design of experiment (DOE) techniques. The typical approach is to develop a DOE that would efficiently allow for the proper quantification of variable sensitivities and experimental uncertainty. A DOE can drastically reduce the number of tests required for an experimental study. Modeling studies employ RSM and other strategies to generate reduced order models (ROMs) that fit complex data.^{35–37}

An RSM of bio-oil and gas reforming

Bio-oil upgrading is a complex process with numerous parameters that could affect the technical, economic, and environmental performance of the process. Technical variables considered in this study include fraction of bio-oil converted to fuel and merchant hydrogen input. Economic variables include costs for bio-oil, natural gas, hydrogen, and carbon. The benefit of an RSM is the ability to simultaneously study the impact of multiple variables. Table 1 describes the decision variables and their value ranges.

An illustrative example related to this study is the reforming of bio-oil and natural gas. Here we employ Aspen Plus 7.3TM to calculate mass and energy balances of thermochemical processes. Reforming is a thermal process that takes place at high temperature (above 800°C) to convert carbonaceous fuel into hydrogen and light hydrocarbons. Methane steam reforming is widely used in industry to generate hydrogen.³⁸ We are unaware of bio-oil reforming commercial units. Natural gas typically contains 60 to 80 wt% methane, which has a high hydrogen to carbon ratio. Similarly, bio-oil reforming generates renewable hydrogen. The differing compositions, economic, and environmental costs of bio-oil and natural gas present an opportunity to optimize hydrogen production based on given criteria.

The following example evaluates a RSM for the yield, feedstock cost, and carbon emissions of generating hydrogen from varying inputs of bio-oil and natural gas. Equation (3) shows equations for bio-oil and natural gas steam reforming

in which symbols *a* through *e* represent model coefficients and *i* is the intercept. The decision variables are the rates of bio-oil and natural gas fed into the reformer, which varied here between 100 and 2000 metric tonnes per day.

$$\left\{ \begin{array}{l} x_1 \\ x_2 \\ H_{2, \text{yield}} \\ H_{2, \text{feedstock cost}} \\ H_{2, \text{carbon emissions}} \end{array} \right. = \left\{ \begin{array}{l} = \text{Bio Oil}_{\text{flow rate}} \\ = \text{Natural Gas}_{\text{flow rate}} \\ = a \times x_1 + b \times x_2 + c \times x_1^2 + d \times x_2^2 + e \times x_1 \times x_2 + i \\ = a \times x_1 + b \times x_2 + c \times x_1^2 + d \times x_2^2 + e \times x_1 \times x_2 + i \\ = a \times x_1 + b \times x_2 + c \times x_1^2 + d \times x_2^2 + e \times x_1 \times x_2 + i \end{array} \right. \quad (3)$$

Figure 1 displays the process flow diagram for bio-oil and natural gas reforming to produce hydrogen. The reforming process modeled in this study follows the design published by Spath *et al.*³⁹ This concept employs a sulfur removal unit with a ZnO catalyst to reduce sulfur content to less than 1 parts per million by volume in order to preserve the reforming catalyst. The reformer is modeled as an equilibrium (RGIBBS) reactor operating at 850°C and 26 bar with a temperature approach of –150°C. The temperature approach restricts methane conversion to a target of 70 wt-%. The water-gas-shift reactor (WGS) enhances hydrogen output by converting CO and water to H₂ and CO₂. The steam-to-carbon mole ratio employed in this model is 2:1. WGS is modeled as a stoichiometric equilibrium reactor operating at 288°C and 25 bar. We assume an 85% hydrogen recovery rate. Hydrogen production feedstock costs are based on a

Table 1. Response surface coefficient values for hydrogen yield, cost, and fossil carbon emissions from natural gas and bio-oil reforming. Decision variables vary from 100 to 2000 metric tonnes per day.

Coefficient	Hydrogen yield	Feedstock cost	Carbon emissions
a	–0.0908	0.2783	–0.0456
b	0.0907	–0.3302	0.0541
c	0.1068	–0.3301	0.0439
d	–0.1066	0.4779	–0.0784
e	–0.0001	–0.1636	0.0269
intercept	0.258	0.8289	0.062
units	kg H ₂ /kg feed	\$/kg	kg CO ₂ eq/kg H ₂

\$0.94/gallon bio-oil,³¹ and \$0.16/m³ (\$4.65/1000 scf) natural gas prices.⁴⁰

Figure 2 shows the hydrogen yields, feedstock costs, and carbon emissions for natural gas and bio-oil reforming. Based on the assumptions employed in this example, hydrogen yields increase from 0.18 kg of H₂ per kg of fuel

to over 0.32 kg H₂ with higher fractions of natural gas use. Feedstock costs decrease from \$1.12 per kg of H₂ to \$0.64 per kg of H₂ with higher natural gas usage. On the other hand, fossil carbon emissions increase with natural gas use from 0.012 kg of CO₂eq to over 0.09 kg of CO₂eq per kg of H₂.

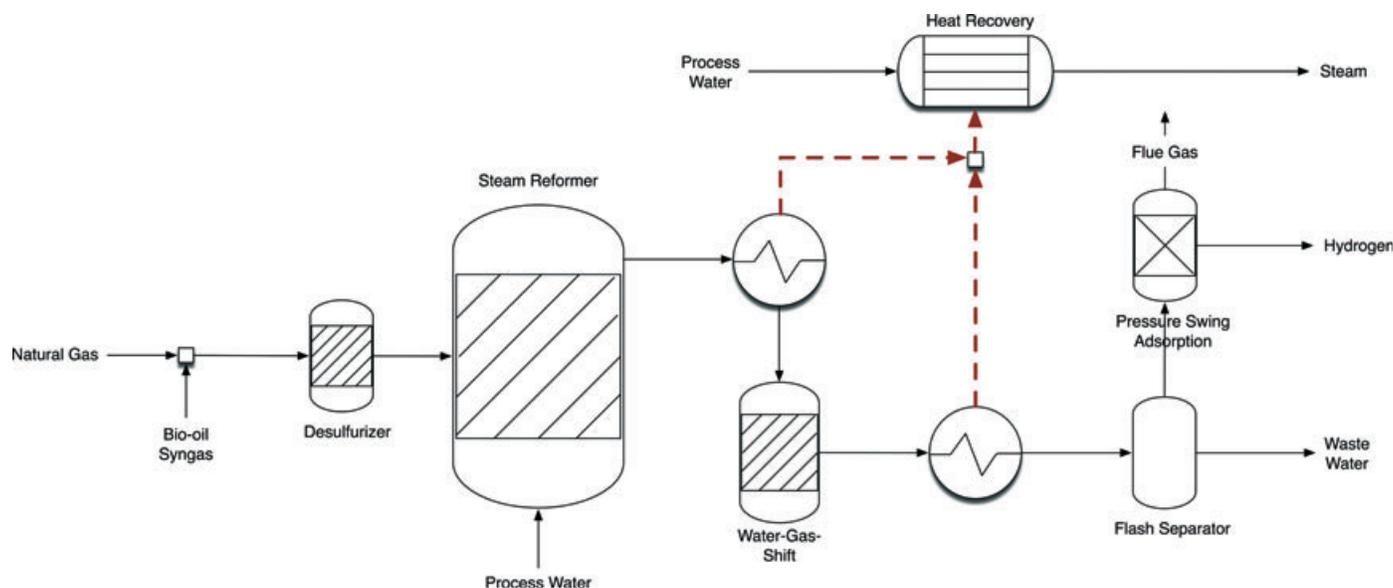


Figure 1. Bio-oil and natural gas steam reforming for hydrogen production.

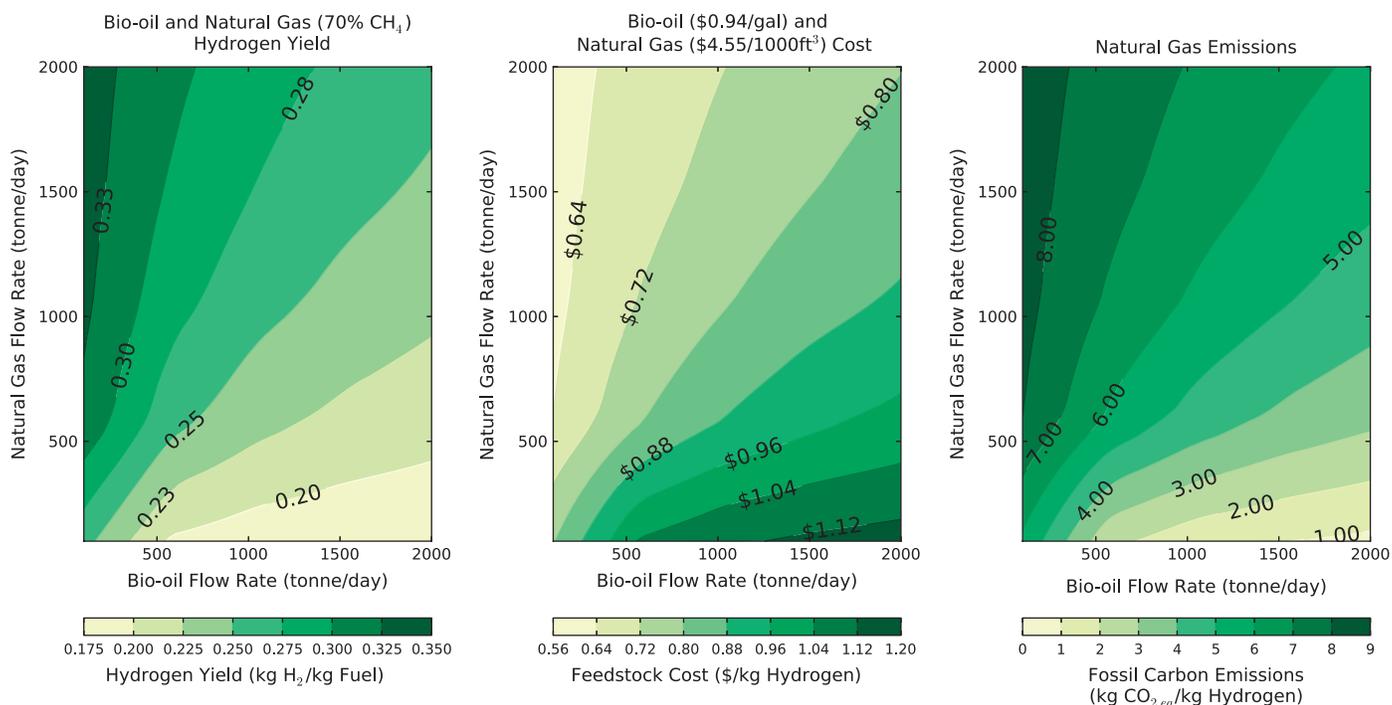


Figure 2. Bio-oil and natural gas steam reforming hydrogen feedstock cost.

Bio-oil upgrading with natural gas reforming to produce transportation fuels

The recent literature describes various approaches to bio-oil upgrading. A key difference between these approaches is the method of procuring requisite hydrogen. Hydrogen for biofuel production could be generated from either fossil,¹⁰ or renewable,¹¹ sources. This model focuses on hydrogen generation from either natural gas or bio-oil using steam reforming. The process employs hydrogen for bio-oil stabilization and also for hydroprocessing to gasoline and diesel as described by work developed at PNNL.^{10,19} Figure 3 shows a simplified process diagram of this upgrading concept.

Process description

Bio-oil upgrading to naphtha and diesel range blend stock fuel employs three main process operations: stabilization, reforming, and hydroprocessing. Bio-oil stabilization removes metals, sulfur, nitrogen, and oxygen compounds yielding bio-oil with improved storage and energy properties.⁴¹ Reforming generates requisite hydrogen for the reforming and hydroprocessing steps.¹¹ Hydroprocessing includes final stage hydrotreating and hydrocracking reactions followed by separations and blending into the desired fractions of naphtha and diesel blend fuels.¹⁰ Biorefineries that hydroprocess bio-oil could consume between 3 and 5 bio-oil wt% hydrogen depending on feed properties and process severity.

Bio-oil upgrading overview

Natural gas is a more economical feedstock for hydrogen production than bio-oil under current US market conditions. Therefore, it is unlikely that facilities implementing this technology would currently employ bio-oil for hydrogen production. Our results suggest that certain market conditions could favor bio-oil reforming such as: regions where natural gas is expensive or scarce, time periods of high natural gas prices, or environmental policies that tax the use of fossil fuels for example. However, employing bio-oil for hydrogen production must not only be cheaper than reforming natural gas, but also justify the lost income from lower biofuel output. A lower biofuel output could be justified when natural gas is expensive. In this case, biorefineries co-located with facilities that generate excess fuel gas would have an advantage.

A bio-oil upgrading biorefinery is a suitable addition to a facility with excess fuel gas or hydrogen. The facility would benefit from higher by-product revenues, and the biorefinery would have a source of inexpensive hydrogen. Because these facilities may have limited amounts of excess fuel gas, the biorefinery may still have to purchase external natural gas in order to maximize fuel output.

The hydrogen sources considered in this study are natural gas, bio-oil, and merchant hydrogen. The base case assumes that all 1440 tonnes per day of bio-oil are upgraded to 634 tonnes per day of gasoline and diesel. This represents

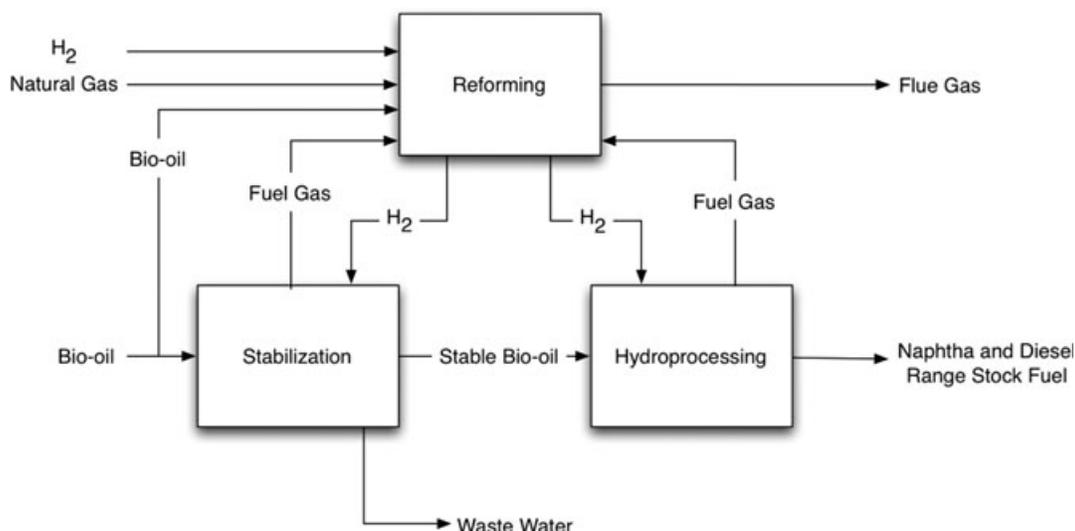


Figure 3. Bio-oil upgrading with natural gas and bio-oil reforming to produce transportation fuels.

a 44-wt% yield of liquid fuels from bio-oil. The base case employs 156 tonnes per day of natural gas. This configuration reforms fuel gas from bio-oil hydroprocessing reactions to maximize the use of renewable hydrogen.

Natural gas is widely available throughout the U.S. and is a logical choice for procuring hydrogen. Methane-steam reforming is a mature commercial process that can convert hydrocarbon fuels to hydrogen at reasonable costs.³⁸ Integrating a reformer into the biorefinery avoids hydrogen storage and transportation costs and improves the use of fuel gas and excess heat from hydroprocessing. On the other hand, dedicating a reformer to a single small-scale biorefinery would neglect benefits from economies of scale. Therefore, it could be advantageous to procure hydrogen from an external source that can be optimized for capacity, cost, or environmental performance. Suitable sources include oil refineries, biomass gasification facilities, and power generation stations. A bio-oil upgrading refinery with a built-in reformer could theoretically choose from these various feedstock sources depending on energy prices. In practice, this flexibility requires additional operation complexity, which is beyond the scope of this study and better suited to dynamic simulations and optimization efforts.

In the absence of natural gas or merchant hydrogen, a portion of the bio-oil could be reformed to generate hydrogen. About a third of the bio-oil could be sufficient to upgrade the remaining feed. A previous study estimated that only 62-wt% of the available bio-oil could be upgraded to transportation fuels in a stand-alone facility.¹¹

Bio-oil stabilization

The bio-oil stabilization section consists of a two-stage hydrotreating process with two separate reactors operating at temperatures and pressure conditions of 240 and 370°C; 175 and 140 bar. A summary of reactor operating conditions is shown in Table 2. Flash separators condense water and stable bio-oil from the reactors' vapor stream. The non-condensable gases are sent to the reforming section. The freewater is treated as waste water and could contain trace quantities of organic compounds, metals, and other impurities. The stable bio-oil is sent to the hydroprocessing section for upgrading and separations. Stabilized bio-oil contains between 0.05 and 5.5 wt-% oxygen which is sufficient for long-term storage but may not meet the feed requirements

for existing crude oil refineries.¹⁹ The remaining oxygenated compounds are better suited to reforming, but they may be difficult to separate. Elemental analysis indicates that hydrotreated bio-oil products with boiling points below 350°C contain less than 0.07-wt% oxygen.¹⁹ Table 3 includes bio-oil stabilization performance and product properties reported in the literature.

Table 2. Bio-oil upgrading reactor operating conditions of key processing units.^{10,39}

Reactor	Temperature (°C)	Pressure (bar)
Hydrotreater 1	240	175
Hydrotreater 2	370	140
Reformer	850	25
Hydrocracker	427	88

Table 3. Properties of bio-oil and upgraded bio-oil products.^{19,46}

Upgrading performance	Bio-oil feed	Stable oil
Carbon, wt-%	73.7	86.9
Hydrogen, wt-%	7.6	10.4
Oxygen, wt-%	15.3	2.2
Nitrogen, wt-%	3.3	0.5
Sulfur, wt-%	0.1	N/A
Oxygen removal, %	–	85
Nitrogen removal, %	–	85
Hydrotreated product properties	Naphtha	Diesel
Boiling point	<180°C	180–350°C
Yields, ²⁰ wt-%	21	21
Carbon, wt-%	85.45	87.08
Hydrogen, wt-%	14.72	12.88
Oxygen, wt-%	0.05	0.07
Sulfur, ppm	130	109
Nitrogen, pm	2	51
Density, g/ml	0.752	0.874
N-paraffins, wt-%	20.56	–
Iso-paraffins, wt-%	12.52	–
Naphthenes, wt-%	61.41	–
Polynaphthenes, wt-%	1.47	–
Aromatics, wt-%	4.03	–
Monoaromatics, wt-%	–	29.3
Diaromatics, wt-%	–	0.6
Polycyclic aromatics, wt-%	–	0.7

Bio-oil hydroprocessing

Hydroprocessing includes a hydrocracking reactor, four fractionation columns to separate fuel gas, naphtha, and diesel range fuels, and flash separators to recover fuel gas. The hydrocracking reactor operates at 675°C and 88 bar. Hydrocracking products are separated into naphtha and diesel range fuels. Fuel gas from the hydrocracker contains unconverted hydrogen which is recycled into the process. A small quantity of fuel gas is bled out of the recycle loop to prevent gas build-up.

Researchers have demonstrated oxygen and nitrogen removal rates of up to 85 wt-%.^{42–45} Related experiments have also shown improvement in the hydrogen to carbon ratio of hydrotreated bio-oil products.⁴⁶

Bio-oil and natural gas reforming

Reforming employs natural gas, fuel gas, or bio-oil to generate a hydrogen-rich gas stream. The reformer is modeled as an equilibrium reactor operating at 850°C and 25 bar. Reforming products are sent to a water-gas-shift (WGS) reactor operating at 290°C and 25 bar. The WGS reactor is a temperature approach stoichiometric reactor where CO and water react to form additional hydrogen and CO₂. Hydrogen at 99.9% purity is recovered with a pressure-swing adsorption (PSA) unit. The remaining flue gas contains mostly CO₂ and has negligible fuel value. The generated hydrogen is sent to the stabilization and hydroprocessing sections. Bio-oil stabilization processes require more hydrogen than the subsequent hydroprocessing process. This model assumes that 80% of the hydrogen goes towards bio-oil stabilization representing 4.29 wt-% of the upgraded bio-oil feed.¹⁰

Process economics

This study estimates the capital and operating costs associated with the conversion of bio-oil to naphtha and diesel range stock fuel via hydroprocessing technologies. Equipment costs are estimated with Aspen Process Economic AnalyzerTM. Project investment costs are based on Peters and Timmerhaus investment factors.⁴⁷ Operating costs and profitability analysis are based on the discounted cash flow rate of return (DCFRROR) method developed by the National Renewable Energy Laboratory (NREL).⁴⁸ Table 4 summarizes the economic assumptions employed in this study.

Table 4. Operating and capital cost assumptions for 1440 tonnes day bio-oil upgrading biorefinery. TPEC: Total Purchased Equipment Cost; TIC: Total Installed Cost; IC: Indirect Cost.

Capital costs		
Total installed cost	3.02	TPEC factor
Indirect cost	3.91	TPEC factor
Project contingency	20	% of TIC + IC
Total fixed capital	4.69	TPEC factor
Working capital	15	% of Total fixed capital
Lang factor	5.24	TPEC factor
Variable operating costs		
Bio-oil	0.94	\$/gal
Natural gas	4.65	\$/1000scf
Hydrogen	1.50	\$/kg
Process water	0.029	\$/tonne
Cooling water	0.032	\$/tonne
Heating oil	0.078	\$/tonne
Fossil carbon emission	0	\$/tonne
Waste water	0.86	\$/tonne
Fixed operating costs		
Labor costs	3.4	\$/MM/year
Overhead	60	% of Labor Costs
Maintenance	2	% of TPI
Insurance & taxes	2	% of TPI

Equipment costs

There is limited data available on the costs of bio-oil upgrading technology. Thus, most cost estimates rely on economic databases procured from vendors. Bio-oil upgrading technology requires pre-engineered technology that is not commonly available in public sources. There are no commercial large-scale implementations of this process. Our equipment costs were estimated based on mass and energy balance calculations from Aspen Plus 7.3TM. We sized major processing units with parameters published by PNNL.¹⁰ The total installed costs factor is 3.02. Project contingency is 20% of total installed and indirect costs. Working capital is 15% of total installed, indirect and contingency costs. The Lang factor is a measure of the total capital cost to the equipment cost of a facility. The Lang factor of this biorefinery cost estimate is 5.24, which is in the higher range of values suggested by Peters and Timmerhaus for chemical plants.⁴⁷

Operating costs

Bio-oil upgrading incurs operating costs that are similar to crude refining processes. The main cost component is feedstock cost, and there are significant contributions from catalyst and hydrogen costs. In this study, bio-oil is priced at \$0.94/gallon bio-oil.³¹ This price is based on bio-oil from a 100 ton per day mobile fast pyrolysis unit using \$50/ton dry poplar wood feedstock. Previous estimates for bio-oil production costs range from \$0.50 to over \$2.00 per gallon.^{49–56}

Feedstock and energy costs for the base case scenario are \$0.16/m³ (\$4.65/1000 scf) natural gas,⁴⁰ \$1.50/kg hydrogen, \$0.064/kWh electricity, and \$0.078/tonne heating oil. Process and cooling water are priced at 2.9 and 3.2 cents per tonne respectively.⁴⁷ Waste-water clean-up costs \$0.86 per tonne, but this cost depends on the extent of processing required to meet environmental conditions. At this moment, there is limited information on the compounds present in waste water from this process. Excess hydrogen is credited at the same price as purchased hydrogen. Labor costs are based on assumptions from NREL.⁵⁷ Overhead is 95% of total salaries. The average salary with benefits is just under \$76 000 per year. Maintenance and insurance are each estimated at 2% of total project investment (TPI).

Catalysts are a major factor in the profitability of refining processes due to the high cost of precious metals, potential for reduced catalytic activity, and challenges in recovering spent catalysts. Capital and annual costs for commercial bio-oil catalysts are unavailable. Therefore, catalyst costs shown here are based on engineering assumptions from existing crude oil refinery estimates. In conventional crude oil refineries, hydrotreating/hydrocracking catalyst capital costs can be as high as \$4000 per barrel per day (bpd) capacity with makeup costs of \$1.5/barrel of feed. Additional information on catalysts costs can be found in petroleum handbooks.⁵⁸ We assume annual catalyst processing losses are 30%, which represents a full replacement rate every 3.33 years. Precious metals in the lost catalyst are refined at a 99% recovery rate with a \$0.11/kg of precious metal recovery price. The annual interest rate on the catalyst alone is 2%. Table 5 shows the price and densities of the catalyst metals.

Biorefineries can be financed with either private or public funding sources and some projects employ a combination of both sources. This study assumes that the biorefinery is

privately financed with 100% equity, which is representative of a mature commercial project.¹¹ The general plant has a depreciation period of seven years and no salvage value after this period. The depreciation method is double declining balance (DDB), which maximizes tax benefits during the depreciation period. The plant construction period is 2.5 years with 50% of full capacity revenues after 6 months, 75% variable costs, and 100% fixed costs (labor, maintenance, insurance). Plant operating capacity is 329 days per year (90% availability). The internal rate of return is 10%, and profits are charged a standard tax rate of 39%.

Response surface model

This study presents an RSM for the costs of naphtha and diesel range blend stock fuel production from bio-oil upgrading. The decision variables consist of the natural gas flow rate, the fraction of bio-oil upgraded or reformed, the purchase cost of bio-oil, natural gas, hydrogen, and the cost of fossil carbon emissions. Table 6 includes a description of the decision variables and the range of values considered. Five data points are generated for each of the decision variables. This represents a total of 5⁹ = 1 953 125 data points. Data points were fit to a second order polynomial surface using JMPTM.

Results

The base case scenario for this biorefinery concept generates 71.8 million gallons of naphtha and diesel range blend stock fuel per year (5193 barrels per day total). Previous studies have estimated the total fuel output to be 58.2,¹¹ and 72.6¹⁰ million gallons per year for a similarly sized biorefinery. Figure 4 shows the material flows between different process areas for the design case where all the requisite hydrogen

Table 5. Catalyst precious metal prices,⁵⁹ densities and modeled loading (wt-%) for hydroprocessing,¹⁹ reactors.

	Price (\$/kg)	Density (kg/m ³)	Loading (wt-%)
Alumina (Al ₂ O ₃)	\$2.50 ^a	8000	82.7
Nickel	\$24.00	8800	0
Cobalt	\$35.00	8746	3
Molybdenum	\$33.00	10 190	14.3

^aConservative estimate based on price of scraped aluminum metals.

Table 6. Response surface model decision variables and value ranges. Five points were generated for each variable (1 953 125 data points).

Variable	Min	Max
Bio-oil upgrading rate (tonne/day)	1150	1440
Natural gas input (tonne/day) ^a	0	180
Bio-oil price (\$/gal)	\$0.7	\$2.00
Natural gas price (\$/tonne) ^b	\$100.00	\$400.00
Hydrogen cost (\$/kg)	\$0.00	\$2.00
Hydrogen credit (\$/kg)	\$0.00	\$2.00
Fixed capital cost (\$MM)	\$121	\$225
Catalyst cost (\$MM/year)	\$9.21	\$27.6
Carbon cost (\$/tonne)	\$0.00	\$100.00

^aAdditional process hydrogen provided as needed.
^bNatural gas prices correspond to \$0.0798 and \$0.320 US dollars per m³.

is generated from natural gas reforming. Figure 5 includes overall system mass and energy balances of the major processing flows. The fuel conversion efficiency depends on the bio-oil and natural gas input rates as shown in Figure 6.

The following sections discuss the economic analysis results, response surface model, and the application of the RSM to a biorefinery emissions optimization problem. The Aspen Plus 7.3TM model file, detailed equipment listing, and

an example spreadsheet implementation of the RSM are available as supporting online information.

Bio-oil upgrading economic analysis

The 71.8 million gallons of blend stock fuel output corresponds to a yield of 109.2 gallons per dry ton of biomass (2000 tonne/day biomass input equivalent). This yield can be adjusted to a 100% renewable basis by assuming that there is no external natural gas or hydrogen input. In the case of bio-oil derived hydrogen, the fuel yield is estimated at 88.0 gal per dry ton of biomass. This compares with PNNL's estimate of 100 and 65 gallons per ton yields for non-renewable and adjusted fuel yields.¹⁰ Differences in the adjusted fuel yields relate to the level of integration of hydrogen sources (bio-oil separation, reactor fuel gas recycle, reformer performance, hydrogen separation efficiency...). For the scenario of solely relying on hydrogen from bio-oil reforming, about a third of available bio-oil is required to upgrade the remaining fuel.^{10,11}

A summary of the economic costs for gasoline and diesel production via bio-oil upgrading is shown in Table 7. Our estimates indicate that this bio-oil upgrading biorefinery concept could produce gasoline and diesel at a minimum fuel selling price (MFSP) of \$2.48 per gallon. The total project investment (TPI) for this upgrading biorefinery is \$171.5 million for 1440 tonnes of bio-oil feed capacity (7535

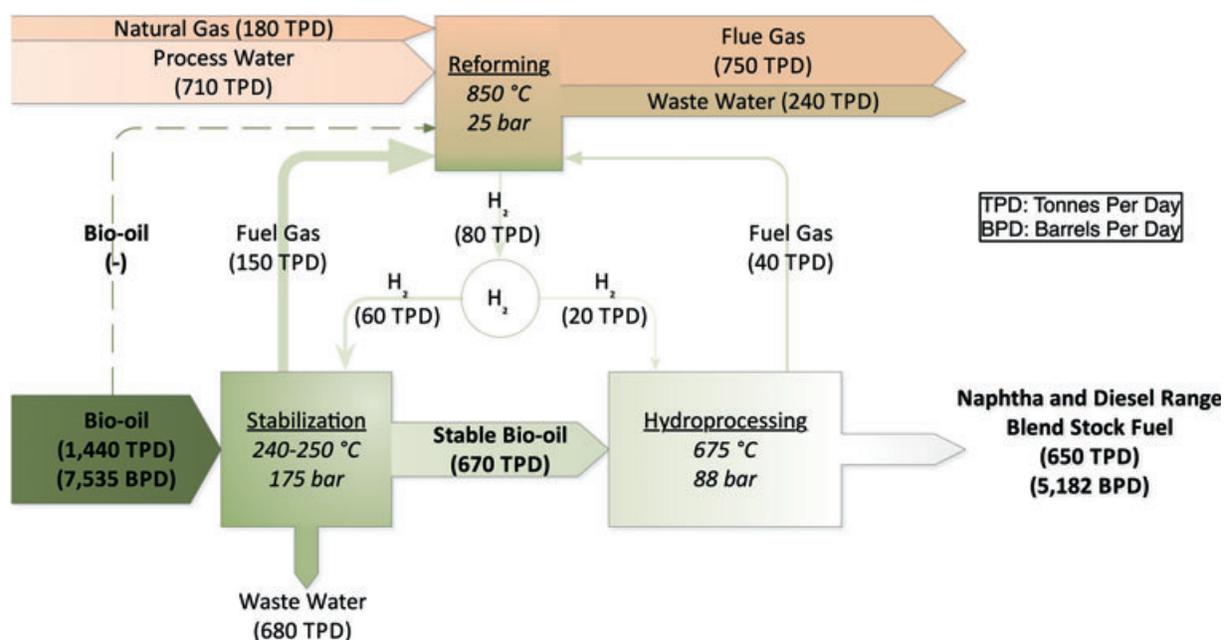


Figure 4. Bio-oil upgrading to naphtha and diesel range blend stock fuel material flows between process areas.

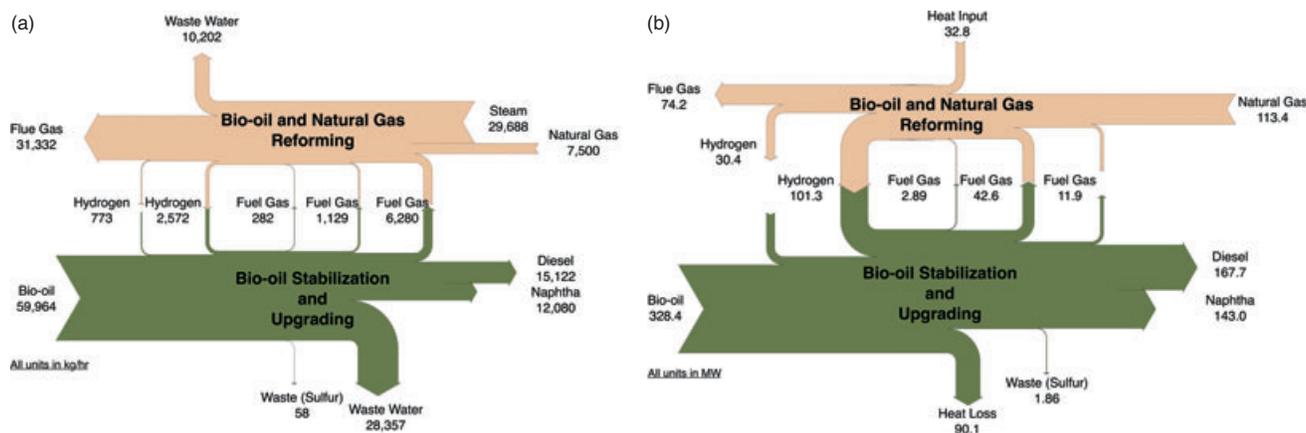


Figure 5. Mass (a) and energy (b) -HHV basis, Sankey diagrams of bio-oil upgrading to naphtha and diesel fuels.

barrels per day input). This cost is equivalent to \$34 400 per barrel per day of output capacity and twice as expensive as conventional oil refineries, which average \$15 000 per barrel per day (BPD) of capacity.⁶⁰ The average conventional oil refinery capacity is above 126 000 BPD,¹ which results in lower per unit capital costs due to economies of scale.

Bio-oil upgrading RSM

Equation 4, with the coefficient values in Table 8 and given assumptions, can estimate the MFSP. A spreadsheet

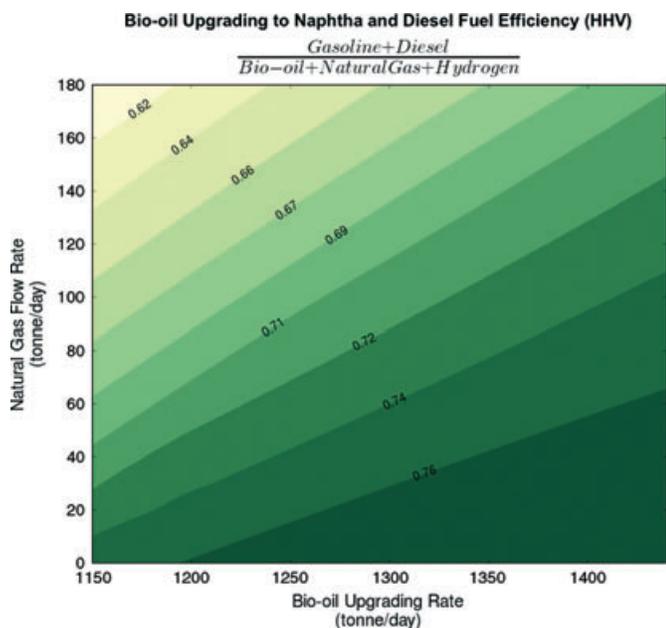


Figure 6. Biofuel conversion fuel efficiency (HHV basis) based on bio-oil, natural gas, and hydrogen input. Excess heat and other energy products not included.

Table 7. Bio-oil upgrading to naphtha and diesel process model summary, capital, and operating costs.	
Process summary	
Bio-oil input capacity (tonne/day)	1440
Naphtha-range fuel output (MMGPY)	34.5
Diesel-range fuel output (MMGPY)	37.3
Fuel yield (gal/ton dry biomass equiv.)	109.2
Adjusted fuel yield (gal/ton dry biomass)	88.0
Capital costs	
Upgrading	\$31 600 000
Separations	\$22 600 000
Reforming	\$38 300 000
Total installed equipment cost	\$92 500 000
Indirect Costs	\$27 300 000
Project Contingency	\$24 000 000
Total project investment	\$171 500 000
(\$/gal of capacity)	\$2.34
(\$/barrel per day)	\$34 400
Operating costs (cents/gal)	
Bio-oil	136.2
Electricity	4.0
Process water	0.1
Catalyst	25.6
Natural gas	14.3
Hydrogen	0.0
Cooling water	1.4
Heating oil	0.4
Fossil carbon emissions	0.0
Process waste water	0.3
Fixed costs	17.5
Co-product credits	0.0
Capital depreciation	12.1
Average income tax	9.7
Average return on investment	25.9
Total	247.6
Minimum fuel selling price (\$/gal)	\$2.48

Table 8. Response surface model coefficients to estimate the minimum fuel selling price of naphtha and diesel range blend stock fuel via bio-oil upgrading										
Coefficients (α_i, β_j)	Bio-oil upgrading rate	Natural gas rate	Bio-oil price	Natural gas price	Catalyst cost	Carbon price	Capital costs	Hydrogen price	Hydrogen credit	Linear coeff. (β_j)
Bio-oil upgrading rate	2.24655E-06	-4.58150E-06	-9.55537E-04	-2.31226E-07	-9.17822E-12	-5.88121E-08	-2.02503E-12	3.03195E-04	2.69191E-04	6.02088E-05
Natural gas rate	-	7.38800E-06	-5.24908E-04	4.91938E-06	-5.04157E-12	1.25124E-06	-1.11095E-12	-5.60581E-04	-4.80792E-04	-2.24142E-03
Bio-oil price	-	-	3.03860E-02	7.09686E-08	2.39428E-12	1.80399E-08	-1.90076E-12	5.18621E-06	-1.06833E-05	1.63421E+00
Natural gas price	-	-	-	5.67923E-07	4.82157E-16	5.47726E-12	-3.84631E-16	3.65333E-10	-2.40552E-09	5.41715E-04
Catalyst cost	-	-	-	-	1.50813E-16	1.23879E-16	-1.32665E-20	3.98706E-14	-6.75249E-14	1.72227E-08
Carbon price	-	-	-	-	-	5.11121E-06	-9.74542E-17	9.28476E-11	-6.08360E-10	2.78232E-04
Capital cost	-	-	-	-	-	-	4.73060E-18	-3.02912E-14	5.89182E-14	3.92899E-09
Hydrogen price	-	-	-	-	-	-	-	2.04466E-03	-1.11653E-07	3.92905E-02
Hydrogen credit	-	-	-	-	-	-	-	-	2.04465E-03	-1.31982E-01
MFSP0	-	-	-	-	-	-	-	-	-	-
Center point (\bar{x}_i)	1295.22	90.0	1.35	250.00	1.84E+07	50.00	1.73E+08	1.50	1.50	-
Minimum value	1150	0	0.70	100.00	9.21E+06	0.00	105.79E+06	0.00	0.00	-
Maximum value	1440	180	2.00	400.00	27.62E+06	100.00	196.47E+06	5.00	5.00	-
Units	tonne/day	tonne/day	\$/gal	\$/tonne	\$	\$/tonne	\$	\$/kg	\$/kg	-

implementation of this model is available in the supporting information or upon request.

$$MFSP = \sum_{i=1}^9 \sum_{j=i}^9 \alpha_{i,j} \times (x_i - \bar{x}_i) \times (y_j - \bar{y}_j) + \sum_{i=1}^9 \beta_i \times x_i + MFSP_0 \tag{4}$$

JMPTM determined a response surface model that fits the data at a statistically significant level (R-square 0.999) with a mean response of 3.10 and root mean square error of 0.091. An ANOVA table is provided in the appendix.

Equation 5 can estimate process hydrogen input, utility use, and total fuel output based on the bio-oil and natural gas input flow rates. Coefficients for these process results are shown in Table 9. These process results constitute part of the carbon and energy footprint of the bio-oil upgrading process.

$$Output = \sum_{i=1}^2 \sum_{j=i}^2 \alpha_{i,j} \times (x_i - \bar{x}_i) \times (y_j - \bar{y}_j) + \sum_{i=1}^2 \beta_i \times x_i + Output_0 \tag{5}$$

Figure 7 shows the impact of bio-oil upgrading rate and natural gas input on MFSP. We assume that biorefineries reform bio-oil to generate hydrogen for bio-fuel production. At bio-oil upgrading rates of 80%, bio-oil and fuel gas reforming generates enough hydrogen to convert the upgraded bio-oil to liquid fuels. However, the biorefineries requires natural gas, or fuel gas from a nearby source,

to maximize biofuel output. Some assumptions for bio-oil upgrading rate and natural gas input yield excess hydrogen, which is factored in as a by-product.

Figure 7 suggests that there is an optimum bio-oil upgrading rate at different bio-oil prices. At bio-oil prices of \$0.70 per gallon, the optimum bio-oil upgrading flow rate is 1270 tonnes per day (88% of total bio-oil capacity) with the remaining bio-oil sent to the reformer for hydrogen generation. The optimum bio-oil upgrading rate at bio-oil prices of \$0.94 per gallon is 1330 tonnes per day (92% of bio-oil capacity). Finally, at a bio-oil price of \$1.37 per gallon, the process is most profitable when almost all the available bio-oil is converted to naphtha and diesel. These trends suggest that at expensive bio-oil prices, biorefineries would need to maximize fuel production in order to reduce costs. At lower bio-oil prices, process profitability may improve by operating below the maximum bio-oil upgrading flow rate depending on the local availability of hydrogen sources.

Figure 8 shows the relationship of bio-oil upgrading rate and several decision variables to the MFSP. The hydrogen credit price range of \$0.00 to \$5.00 returns the widest range of fuel selling prices (\$2.61–£3.30 per gallon). Carbon emission costs of up to \$100.00 per tonne do not significantly impact the biofuel price. Decision variables that exhibit a strong non-linear relationship with the MFSP are typically associated with either natural gas or hydrogen. Catalyst price and capital costs show less variation in the plots, but

Table 9. Response surface model coefficients for bio-oil upgrading (x_1) and natural gas (x_2) flow rates in metric tonnes per day to estimate hydrogen input, utility rates, and total fuel output.

	Electricity	Hydrogen input	Cooling water	Fuel oil	Steam	Biofuel output
x_1	6.903E+03	6.465E-02	-8.090E+01	-7.723E+00	-1.644E-01	3.594E-01
x_2	-2.995E+03	-1.145E-01	2.042E+02	3.053E+01	3.407E-01	1.661E-01
$(x_1 - \bar{x}_1) \times (x_1 - \bar{x}_1)$	6.458E+00	1.840E-04	2.185E-02	2.921E-02	-1.703E-06	1.757E-04
$(x_1 - \bar{x}_1) \times (x_2 - \bar{x}_2)$	-5.110E+01	-8.733E-04	-1.314E-01	-1.421E-01	-2.909E-06	-8.718E-04
$(x_2 - \bar{x}_2) \times (x_2 - \bar{x}_2)$	-3.534E+00	7.184E-04	3.909E-02	1.175E-01	1.207E-06	6.777E-04
Intercept	-2.586E+06	-7.083E+01	1.813E+05	1.989E+04	6.630E+02	1.077E+02
Units	Watt	tonne/day	tonne/day	tonne/day	tonne/day	tonne/day
R ²	0.578	0.975	0.995	0.979	1.000	0.998
R ² Adjusted	0.578	0.975	0.995	0.979	1.000	0.998
Root mean square error	684991.003	1.861	1135.548	343.655	0.012	1.823
Mean of response	6137831.011	7.418	95249.259	13409.737	480.701	592.812

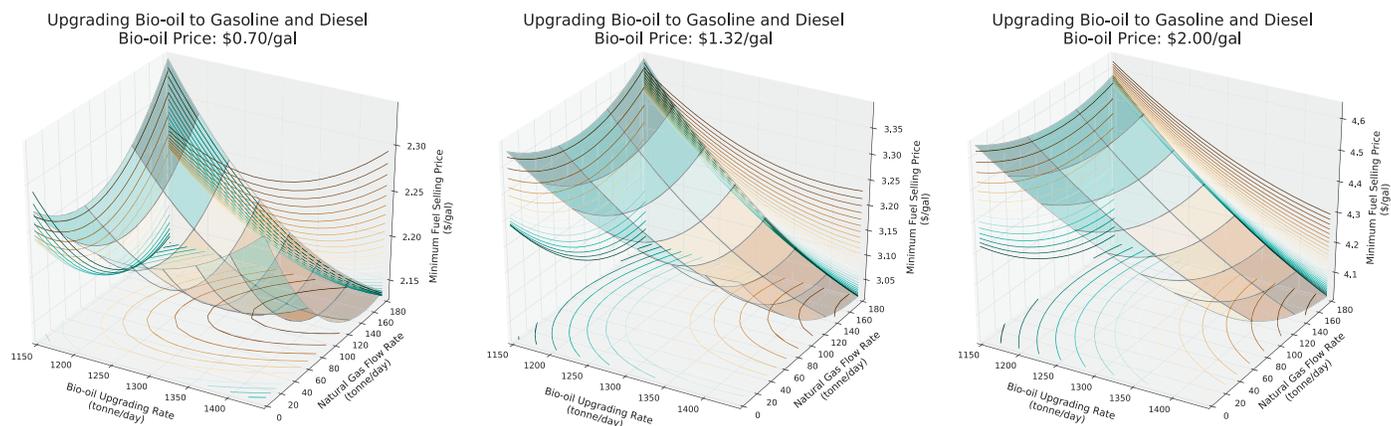


Figure 7. Surface plots of the minimum fuel selling price of naphtha and diesel range fuel based on low (\$0.70/gal), mid (\$1.32/gal), and high (\$2.00/gal) bio-oil prices vs. bio-oil upgrading rate and natural gas flow rate. Natural gas price of \$234/tonne and hydrogen price of \$1.50/kg.

in reality their relation to profitability is complex. Further study is needed to understand the impact of catalyst performance and capital cost on the MFSP.

A biorefinery emissions optimization application of the RSM

The US Renewable Fuels Standard (RFS2) requires minimum levels of emission reductions compared to petroleum-based gasoline for biofuels to qualify under the blending mandates. This requirement constrains the amount of fossil fuel that can be employed to increase biofuel yields. Here, we illustrate a constrained optimization problem using the response surface to determine the lowest MFSP that meets the RFS emissions mandate. The constrained optimization formulation can be formally described by Eqn (6).

minimize $MFSP(x_i)$

subject to

$$\frac{\alpha x_2}{\gamma \text{biofuel}(x_1, x_2)} + \text{biomass}_{emissions} \leq (1 - \beta) \text{gasoline}_{emissions} \quad (1)$$

$$\text{hydrogen}_{input}(x_1, x_2) = 0 \quad (2)$$

$$LB_i \leq x_i \leq UB_i \quad \forall x_i \in \Omega \quad (3)$$

$$\text{var } x_i \quad i \in (1, 2) \quad (6)$$

where MFSP is the minimum fuel selling price as determined by the RSM; α is a factor for kg of $\text{CO}_{2,eq}$ per tonne of natural gas (2,750 kg/tonne); β is the minimum percent reduction in emissions (assumed 80% in this example; the RFS2 constraint is 60% for advanced cellulosic biofuels); γ is a conversion factor of 41.26 GJ per tonne of liquid fuel; LB

and UB are lower and upper bounds for each model variable; Ω is the set of variables included in the response surface model; and x_1 and x_2 are the bio-oil upgrading and natural gas input rates. The formulation constrains hydrogen input to zero to focus on the use of natural gas within the biorefinery. Economic variables are fixed, and the solver routine can only vary bio-oil upgrading and natural gas flow rates. We employed the function `fmin_slsqp`, a Sequential Least Squares Programming implementation found in SciPy v 0.10*, to determine the optimal solution. This RSM model may be subject to local minima that could make convergence difficult; therefore care must be taken to make reasonable initial guesses or employ robust optimization packages.

The biofuel emissions and hydrogen inputs are the respective functions described in Eqn (9). Input variables are bounded to avoid extrapolations, which could result in inaccurate results. Biomass emissions are based on the fossil fuel emissions embedded in the use of biomass (cultivation, harvesting, transportation. . .) estimated by Argonne National Laboratory for the 2011 GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) model.⁶¹ We assume that the biorefinery corresponds with a fuel gas/natural gas refinery scenario using forest residue. For this scenario, embedded biomass emissions are about 6,400 grams of $\text{CO}_{2,eq}$ per mMBTU of biofuel (6.1 kg $\text{CO}_{2,eq}$ per GJ of fuel). Petroleum gasoline emissions are almost 100 000 grams of $\text{CO}_{2,eq}$ per mMBTU (94.6 kg $\text{CO}_{2,eq}$ per GJ).

*Available online <http://www.scipy.org>

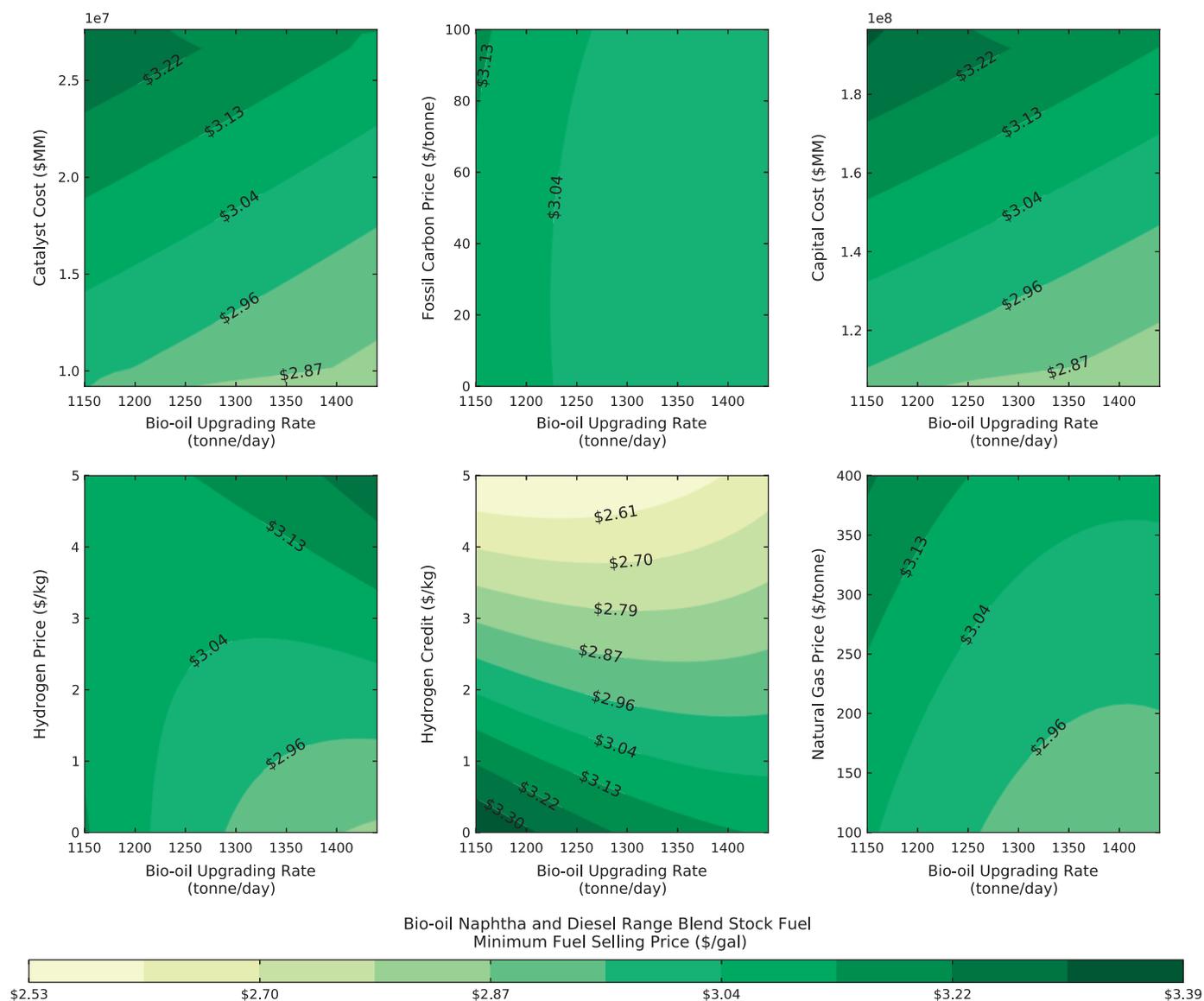


Figure 8. Contour plots for the naphtha and diesel fuel minimum fuel selling price as a function of capital cost, hydrogen, catalyst, carbon, and natural gas prices, and bio-oil upgrading rate.

Figure 9 shows a graphical representation of the optimization solution. In order to meet the constraints, this biorefinery concept would only be able to upgrade 1288 tonnes per day of available bio-oil while employing 113.6 tonnes per day of natural gas. This result suggests that under similar conditions, biorefineries would only be able to upgrade 89.7% of available bio-oil before meeting the an 80% emission reduction constraint. The MFSP for this case is \$2.66 per gallon.

In order to increase biofuel production, the biorefinery could seek alternative hydrogen sources with reduced emissions. In this alternative scenario, constraint (2) in Eqn (6) could be

relaxed to allow for hydrogen input from a renewable source (hydrogen from water electrolysis using wind or solar power for example). For this scenario, we assume a conservative hydrogen cost of \$3.0 per kg. The optimal result has a slightly higher upgrading rate of 1366 tonnes per day and 119.0 tonnes per day of natural gas input. The difference in MFSP (\$2.64 per gallon) is negligible compared to the previous scenario.

This optimization example illustrates a benefit of the RSM. To determine the final solution, the optimization algorithm required 74 iterations. Aspen Plus 7.3TM models can take several minutes to converge making multivariate optimizations

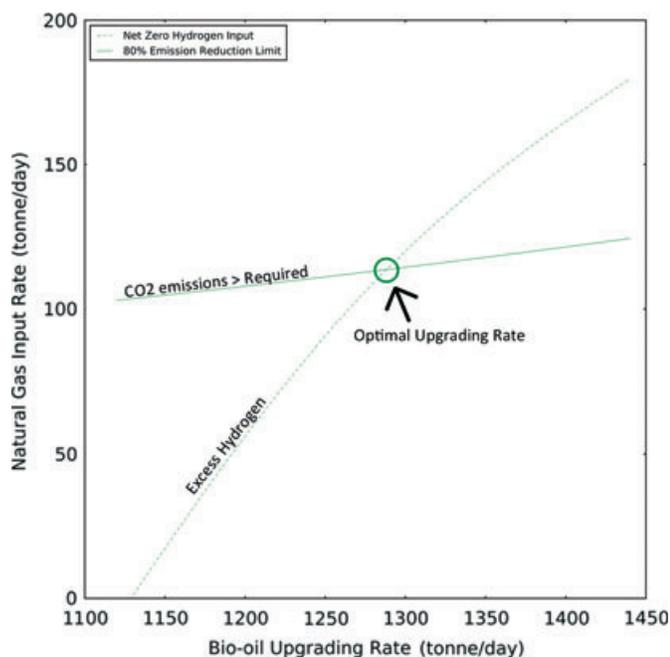


Figure 9. Bio-oil upgrading and natural gas input rates constraint lines for net zero hydrogen input and 80% emission reductions compared to petroleum gasoline. The intersection of these curves is the optimal solution to reducing emissions without alternative hydrogen sources.

time consuming. Aspen PlusTM includes built-in optimization tools optimized for process assessment, but these are not designed to tackle formulations for macro-scale policy and environment impact analysis.

Conclusions

The purpose of this study is to develop a response surface model for bio-oil upgrading to drop-in transportation fuels. Bio-oil upgrading requires hydroprocessing reactions to stabilize and convert its organic compounds to naphtha and diesel range blend stock fuel. Large quantities of hydrogen are required to upgrade bio-oil. Therefore, bio-oil upgrading concepts have explored several options for procuring the needed hydrogen. This study presents an RSM model for bio-oil upgrading with natural gas and merchant hydrogen. The RSM model employs 9 decision variables to estimate the minimum fuel selling price (MFSP) of drop-in transportation fuels from bio-oil.

Economic results from this study estimate that a 1440 tonnes per day bio-oil upgrading facility could generate up

to 71.8 million gallons of naphtha and diesel range stock fuel (5182 barrels per day). The total project investment for this plant is \$171.5 million. The MFSP is calculated as \$2.48 per gallon. This MFSP is similar to what is reported in the literature (\$1.74–\$3.09 per gallon)^{10,11} for bio-oil hydroprocessing biorefineries.

Inspection of surfaces generated with the RSMs suggest optimization opportunities for bio-oil based fuel production. The shape of the MFSP cost curve was found to be sensitive to the bio-oil price. The optimum bio-oil upgrading flow rate for zero natural gas input varied from 1250 to 1440 tonnes per day for bio-oil prices of \$0.94 to \$1.37 per gallon. At high bio-oil prices, biorefineries should maximize biofuel production to improve profitability. However, a portion of the bio-oil can be converted to hydrogen if the cost is less expensive than reforming natural gas and justifies the lost revenue from the reduced biofuel output.

This study investigated the potential impact of fossil carbon emission constraints as an example application of the RSM. Carbon emission constraints limiting the use of natural gas for biofuels, such as those in the RFS2, could reduce the amount of bio-oil upgraded to transportation fuels to less than 90% depending on process performance and market conditions. This result underscores the importance of considering policy impacts on biorefinery operation and performance.

Supporting information

Supporting information may be found in the online version of this article.

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