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Natural Gas and Cellulosic Biomass: A Clean Fuel Combination? Determining the Natural Gas Blending Wall in Biofuel Production

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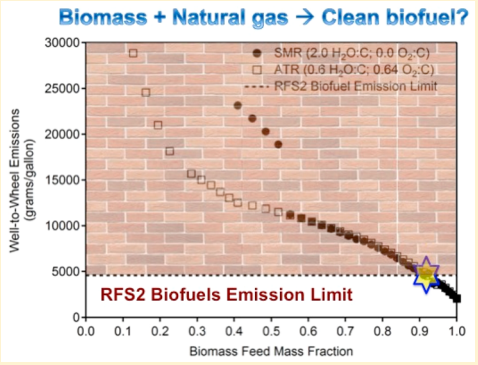
Supporting Information

ABSTRACT: Natural gas has the potential to increase the biofuel production output by combining gas- and biomass-to-liquids (GBTL) processes followed by naphtha and diesel fuel synthesis via Fischer−Tropsch (FT). This study reflects on the use of commercial-ready configurations of GBTL technologies and the environmental impact of enhancing biofuels with natural gas. The autothermal and steam-methane reforming processes for natural gas conversion and the gasification of biomass for FT fuel synthesis are modeled to estimate system well-to-wheel emissions and compare them to limits established by U.S. renewable fuel mandates. We show that natural gas can enhance FT biofuel production by reducing the need for water−gas shift (WGS) of biomass-derived syngas to achieve appropriate H_2/CO ratios. Specifically, fuel yields are increased from less than 60 gallons per ton to over 100 gallons per ton with increasing natural gas input. However, GBTL facilities would need to limit natural gas use to less than 19.1% on a LHV energy basis (7.83 wt %) to avoid exceeding the emissions limits established by the Renewable Fuels Standard (RFS2) for clean, advanced biofuels. This effectively constitutes a *blending* limit that constrains the use of natural gas for enhancing the biomass-to-liquids (BTL) process.



1. INTRODUCTION

There is growing interest to convert natural gas into transportation fuels due to the discovery of large nonconventional gas resources across the world. According to the U.S. Energy Information Administration (EIA), proven reserves of natural gas in the U.S. increased from 191 743 to 283 879 standard billion cubic feet. These discoveries have precipitated a decline in U.S. average natural gas prices from a 2008 high of $13.07 per 1000 standard cubic feet (scf) ($462/m^3) to an average of $4.72 per 1000 scf in May, 2014.[1] The historically low ratio of natural gas to crude oil price encourages the use of natural gas in traditional oil markets, such as the transportation fuels sector.

Gas-to-liquids (GTL) technology has been under development for decades but has only recently achieved commercial success.[2] On the other hand, biomass-to-liquids (BTL) technology has yet to achieve commercial success. In 2011, the United States Environmental Protection Agency (EPA) revised the Renewable Fuels Standard (RFS2) annual target for advanced cellulosic biofuel production from 250 million gallons to 25.5 million gallons based on projected industrial capacity.[3] The EPA revised mandates for this category by greater than 90% in subsequent years. Under the current RFS2 regulation, gasoline and diesel fuels derived from natural gas do not qualify for credits.

Concept designs for advanced, cellulosic biofuels are typically based on stand-alone biorefineries that limit the use of fossil fuels for process heat or feed. Gasoline emission reductions for these concepts range between 70% and 90%.[4] The large emission reduction provides room for the use of some amount of natural gas (or other fossil fuel) in the biofuel production process while keeping emissions at a level that would meet RFS2 regulations. As shown in Table 1, natural gas is commonly considered as a heat source in thermochemical biomass conversion processes where there is insufficient excess fuel gas or biomass for process heat. Combined gas- and biomass-to-liquids (GBTL) facilities have the potential to increase the production of clean fuels that meet the EPA's emission and blend market targets. Several studies have evaluated the merits of hybrid fossil and biomass conversion technologies that integrate both feeds through the production of synthesis gas (syngas), a mixture of hydrogen and carbon monoxide.[5−7] Both natural gas and biomass-derived syngas are suitable for the production of drop-in transportation fuels via the methanol-to-gasoline (MTG)[8] or the Fischer−Tropsch

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Table 1. Biomass and Natural Gas Use and Well-to-Wheel Emissions in Biofuel Production Processes

process/product	biomass input (ton/day)	natural gas input (ton/day)	yield (gal/ton *biomass*)	well-to-wheels emissions (grams $CO_{2,eq}$/mmbtu)
petroleum refining/diesel[16]	–[a]	–[a]	–[a]	98 000[17]
fermentation/ethanol[18]	2000	128	99.7	23 000[17]
gasification/FT fuels[12]	2000	867[b]	117	25 000[17]
bio-oil upgrading/gasoline[13,19]	2000	154.2[b]	81.4	12 000[17,20]
bio-oil upgrading/gasoline[14]	2000	187.2	100	39 000[17,20]

[a]Not available. [b]Based on 0.317 kg H_2/kg CH_4 steam reforming yield.

(FT)[9] upgrading process. However, common FT catalysts employ a syngas mixture with a 2:1 H_2/CO molar ratio to generate the optimal distribution of fuel products, and both natural gas and biomass generate syngas streams with H_2/CO ratios far away from this optimal ratio. Consequently, further processing is required to meet the desired H_2/CO specification. Natural gas typically yields a syngas with a H_2/CO ratio close to 3.7, requiring two-step reforming to separate the excess H_2. Conversely, biomass gasification yields syngas with a range of H_2/CO ratios typically in the order of ca. 0.57 due to its lower H_2 content relative to natural gas, and the water–gas shift (WGS) reaction is typically used to increase the H_2/CO ratio to a value closer to 2. Unfortunately, the WGS reaction consumes CO, thereby lowering the overall carbon yields of the resulting biofuel.

In a GBTL facility, natural gas and biomass-derived syngas can be mixed at varying ratios and conditioned using conventional processes to meet the target syngas composition for FT synthesis with considerably higher feed-to-fuel yields than BTL processes alone (*vide infra*). The two common technologies for natural gas in this scenario are steam methane reforming (SMR) and autothermal reforming (ATR). These technologies involve process and environmental trade-offs, some of which are investigated in this study. The syngas from natural gas is fossil in origin, and the SMR process is typically driven by burning additional natural gas. As such, the use of natural gas to balance the final H_2/CO ratio becomes an additional source of greenhouse gas emissions. These emissions must be taken into account in the life cycle analysis to confirm that the biofuel produced is compliant with the RFS2 standard. Alternatively, an ATR converts natural gas into syngas with lower CO_2 emissions compared to a SMR but generates a syngas stream with a lower H_2/CO ratio, thus necessitating significant water–gas shift of CO to CO_2 to achieve the 2:1 H_2/CO ratio required by the FT unit. Although there is considerable research on the technical and environmental performance of GTL and BTL technologies,[7,10] environmental assessments for the combined GBTL process are scarce. Notably, complete well-to-wheels analyses are nonexistent. Given that the conversion of natural gas to liquid fuel contributes to greenhouse gas emissions, it is imperative to develop high-fidelity process and environmental models to assess the feasibility for emission reductions by *blending* the natural gas to liquids process with biofuel production for the transportation sector.

Here, we show a well-to-wheels analysis that provides metrics for the production of clean, sustainable transportation fuels from a biomass-to-liquids process enhanced by natural gas that meets the emission reduction requirements set forth by the Environmental Protection Agency (EPA) as part of the 2007 Energy Independence and Security Act (EISA).[11] Specifically, we model how FT biofuel production yields are improved by the use of natural gas, which provides the required H_2 to achieve appropriate H_2/CO ratios for optimal fuel synthesis. We then quantify the resulting greenhouse gas emissions and demonstrate that a blending limit exists in GBTL processes given that the production of biofuels in GBTL facilities is inherently constrained by the RFS2 transportation fuel emission requirements. A sensitivity analysis details how this constraint restricts the use of natural gas to a specific range, which varies according to the choice of technology and operation conditions. Effectively, this work constitutes the first report of a comprehensive RFS2 blend limit wells-to-wheels emissions analysis for a combined GBTL production process.

2. BROADER CONTEXT

Natural gas plays a role in almost all fuel synthesis applications either directly as a reacting agent or indirectly as a process fuel. Several gas-to-liquids schemes have been developed and some have achieved commercial success. The MTG and FT processes can utilize natural gas as the primary feedstock for liquid fuel synthesis.[10] Similarly, natural gas plays an important role in biofuel production given that modern ethanol biorefineries employ natural gas for heat generation. Recent studies discuss the possibility of adding natural gas-derived syngas or hydrogen for fuel production in biomass gasification[12] and pyrolysis biorefineries.[13,14] Life-cycle analyses of biomass gasification and pyrolysis processes have estimated that advanced cellulosic biofuel emissions meet the 60% reduction mandated by the RFS2.[4,15] On the other hand, exclusive use of natural gas for fuel production (GTL) via FT synthesis results in emissions (116.89 $kgCO_{2,eq}$/mmbtu)[16] that exceed the 60% emission reduction limit. Therefore, biomass addition is required for compliance. Recent studies have focused on stoichiometric addition of natural gas to the biofuel production process.[12−14] In these studies, the natural gas input rate is dictated by the hydrogen input required by the chemical reaction. However, some configurations fail to meet the EPA emission reduction mandates. It is highly important to identify how much natural gas can be added to produce clean, advanced biofuels as defined by the RFS2. This study seeks to address this question in the context of the GBTL platform in a manner that can be extended to other biofuel production processes.

3. METHODOLOGY

This study combines an Aspen Plus process model of the combined gas- and biomass-to-liquids process (GBTL) with well-to-wheels emission analysis based on the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model (GREET) developed by Argonne National Laboratory.[16] A GBTL facility converts natural gas and biomass into synthetic liquid fuels via the MTG or FT synthesis process. While several GBTL technologies that produce transportation fuels compatible with existing vehicle and fuel infrastructure have been proposed,[10] this study focuses on the FT synthesis pathway to naphtha- and diesel-range blend stock fuels.

3.1. Process Description. *3.1.1. Reactor Design.* Our GBTL process model is based on the baseline flowsheet model developed by Field and Brasington[21] and subsequently enhanced by Field and Brasington at MIT. The flowsheet

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was adapted to combined biomass and natural gas conversion to syngas and subsequent catalytic synthesis to FT liquids followed by upgrading to naphtha and diesel range blend stock fuels. Figure 1 summarizes the key processing steps for the

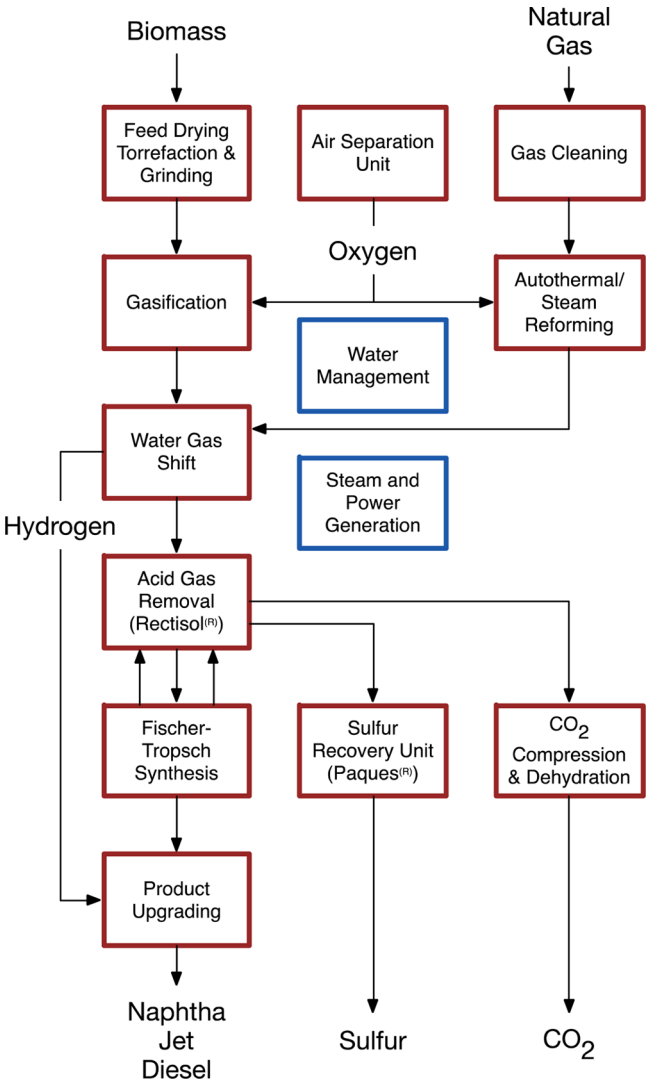

Figure 1. Natural gas- and biomass-to-liquids via Fischer–Tropsch synthesis process block diagram.

GBTL concept and highlights the intermediate conversion steps and auxiliary facilities. The key enabling technologies are biomass gasification and natural gas reforming (autothermal or steam). The facility capacity in this study varies with the biomass to natural gas feed rates with a representative case of 1992 and 168 tons per day of biomass and natural gas, respectively.

This study employs an entrained flow gasifier to convert biomass into syngas with a low impurity content and high energy value. There are several commercial entrained flow gasifiers[22] that operate at elevated temperatures (≥1200 °C) to enable high conversion efficiency and tar destruction. However, there is limited commercial experience of processing biomass with entrained flow reactors.

Our process employs either an autothermal or steam methane reforming reactor to convert natural gas to synthesis gas.[10] These reactors differ by the heat delivery method and optimal $H_2O/O_2/C$ ratios. Autothermal reactors generate requisite heat by partial combustion of natural gas within the front-end of the reactor; steam-methane reforming relies on indirect heat delivered from an external furnace. The autothermal reformer commonly employs a lower H_2O/C (0.6:1) molar ratio than the ratio employed in the steam-methane reformer (2:1). Finally, the autothermal reformer employs a 0.25:1 O_2/C molar ratio whereas there is no O_2 input in the steam-methane configuration. An alternative to both systems is the partial oxidation reformer (POX), which employs O_2 without steam to generate syngas with a 1.8:1 H_2/CO molar ratio but suffers from safety concerns.[10] These reactors can be operated over a wide range of conditions. We varied temperature, pressure, steam to carbon ratio, and oxygen to carbon ratio in the sensitivity analysis.

Steam-methane reforming reactions are described by eqs 1a, representing the SMR operation, and 1b, representing the autothermal reactor. At temperatures of 200 to 350 °C, the water–gas shift reaction 1c increases the final H_2/CO ratio. Steam reforming generates an exit gas with a H_2/CO ratio of 3.7 or higher depending on the steam input rate and operating conditions. Autothermal reforming (ATR) yields a H_2/CO molar ratio that approaches the Fischer–Tropsch synthesis requirement of 2.0.

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad (1a)$$

$$4CH_4 + O_2 + 2H_2O \leftrightarrow 10H_2 + 4CO \quad (1b)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (1c)$$

This study assumes that the entrained flow gasifier operates at 1400 °C and 45 bar pressure. The gasification feed includes a steam input based on a 0.16 steam to carbon molar ratio. Heat is generated within the reactor with a variable oxygen input sufficient to maintain the reactor temperature (calculated 0.37 O_2/C molar ratio). The autothermal reactor operates at 950 °C and 25 bar with 0.6 steam to carbon and 0.64 oxygen to carbon molar ratios.[10] The steam-methane reformer operates at 950 °C and 25 bar with a 2.0 steam to carbon ratio and zero oxygen input. The heat for steam reforming is provided by combusting natural gas with air in a dedicated furnace. Table 2 summarizes the reactor operating conditions.

Table 2. Biomass Gasification and Natural Gas Reforming Reactor Technology and Operating Conditions

	entrained flow gasifier (EFG)	autothermal reformer (ATR)	steam-methane reformer (SMR)
temperature (°C)	1400	950	950
pressure (bar)	45	25	25
H_2O/C molar ratio	0.16	0.6	2
O_2/C molar ratio	0.37[a]	0.64	0
heat delivery	direct	direct	indirect

[a]Adjusted for adiabatic operation.

Table 3 describes the properties of delivered willow and natural gas (pipeline quality) at the facility gate. The facility receives willow with a 50 wt % moisture content and pressurized natural gas via pipeline. The natural gas composition shown here is representative of the North American market.[23]

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Table 3. Pipeline Quality Natural Gas and Delivered Willow Composition and Properties

natural gas[23]		willow (dry basis)	
methane (vol %)	93.42	carbon (wt %)	49.32
ethane (vol %)	5.54	hydrogen (wt %)	5.94
N_2 (vol %)	0.55	nitrogen (wt %)	0.63
CO_2 (vol %)	<0.47	sulfur (wt %)	0.07
H_2S (vol %)	0.01	oxygen (wt %)	42.54
–	–	ash (wt %)	1.5
moisture (wt % as received)	0.01		50
lower heating value (MJ/kg dry)	48.7		17.55[23]

3.1.2. Process Design. The overall process model includes distinct blocks representing the various process and auxiliary units of the GBTL plant. The process units include biomass feedstock preparation, air separation, gasification, natural gas reforming, water–gas shift, acid gas removal, CO_2 recovery, sulfur recovery, Fischer–Tropsch (FT) synthesis, hydrogen recovery, and product upgrading.

The auxiliary units are steam and power generation and water management systems. The model also estimates utility requirements of various process and auxiliary units such as electricity, cooling water, and low-, medium-, and high-pressure saturated steam (LP, MP, HP). Figure 1 is a simplified block flow diagram of the process design depicting the key process steps and auxiliary units of the GBTL plant.

As received biomass, consisting of forest residue (willow chips) collected as a byproduct of logging or forestry activities, is shredded and dried to a 10–15 wt % moisture level. Hot air, generated using LP steam from downstream processes, is used to dry biomass. The dried biomass is then sent to the torrefaction unit. The torrefaction process lowers the biomass moisture to less than 2 wt % and releases 25 wt % volatile matter. This process takes place with temperatures ranging from 200 to 300 °C in a reducing environment, improving the heating value and grindability of biomass. The heat required for torrefaction is supplied using superheated HP steam from downstream units. Subsequently, the torrefied biomass is ground to particles 100 μm in diameter to meet feeding requirements of the entrained flow gasifiers. The gaseous product of the torrefaction process (torrefaction gas) is dehydrated (by cooling) and sent to the steam island to be used as fuel gas. Electricity and steam requirements for shredding, drying, and grinding units are estimated using prepackaged models built into Aspen Plus and modified based on literature data.· Torrefaction performance is based on work by Bates and Ghoniem.[24] The ground torrefied biomass is fed into the gasifier at pressure using CO_2 recovered from the Rectisol process. The gasifier converts biomass into raw syngas while operating at 45 bar and 1400 °C. Syngas compositions are determined using an equilibrium approach (Gibbs). The high operating temperature of the entrained-flow gasifier ensures nearly complete conversion of biomass to syngas. The raw syngas is quenched with water, removing particulates, tar, and some other impurities. The quench process also provides steam needed by the downstream water–gas shift unit to provide the desired H_2/CO ratio.

Natural gas undergoes preheating and sulfur removal before being fed into the reforming reactor (either SMR or ATR). The reformer syngas composition is estimated with a Gibbs equilibrium model and a 15 °C equilibrium temperature approach. A cryogenic distillation process within the air separation unit generates the requisite oxygen for reforming and biomass gasification. Syngas streams from the gasification and reforming processes are mixed in the conditioning section where they undergo water–gas shift reactions if the H_2/CO is below 2.0. Excess hydrogen is recovered and sent to the product upgrading section for hydrocracking of large hydrocarbons. The tail gas from the Pressure Swing Adsorption (PSA) unit is used as fuel gas in the steam island for steam generation and/or superheating. The shifted syngas is cooled at different stages using a combination of steam generation, air, and water cooling units. The cooled syngas, which contains 2.0 mol of H_2 per mole of CO, is fed into the acid gas removal (Rectisol) unit, which selectively removes H_2S and CO_2 components from the syngas. The acid gas removal process reduces the CO_2 and H_2S contents of syngas to 2 vol % and 100 ppb_{vol}, respectively. The treated syngas from the acid gas removal unit enters the FT synthesis reactors. The CO_2 and H_2S fractions from acid gas removal are sent to CO_2 and sulfur recovery units, respectively. This study assumes that the CO_2 is eventually released to the atmosphere instead of being sequestered which would present an alternative scenario for further reducing emissions. The H_2S fraction is processed in the Paques process and is converted to elemental sulfur that can be sold as a byproduct.[25]

In addition to H_2 and CO, the FT synthesis feed contains compounds (such as CO_2, CH_4, N_2, and Ar) that are inert during the FT conversion process. However, buildup of these compounds can have adverse effects on catalyst performance, product distribution, and equipment size requirements. The FT synthesis loop includes a high temperature autothermal reformer for unconverted light gases and a purge stream that maintains a level of all inert components combined below 10 vol % of the feed stream. The reformed light gas stream (recycle gas) is sent to another acid gas removal absorption column for CO_2 removal (reduced to 2 vol %) and mixed with

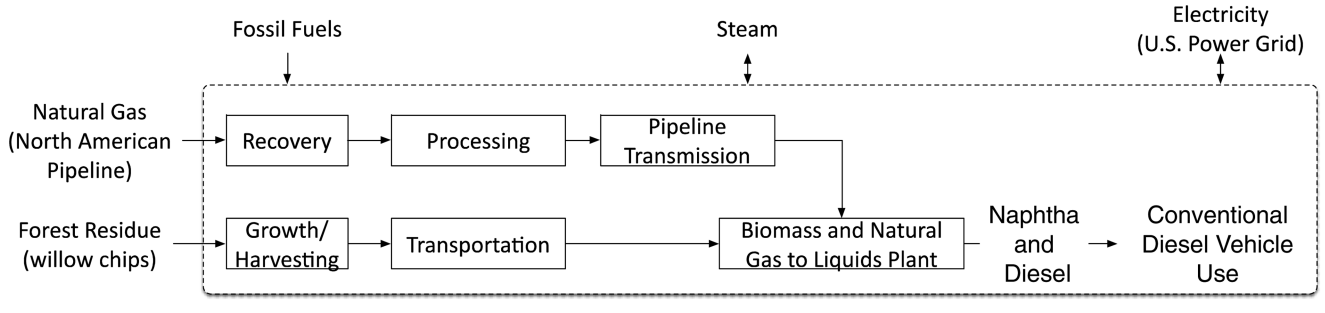

Figure 2. Well-to-wheels (WTW) gas- and biomass-to-liquids system boundary.

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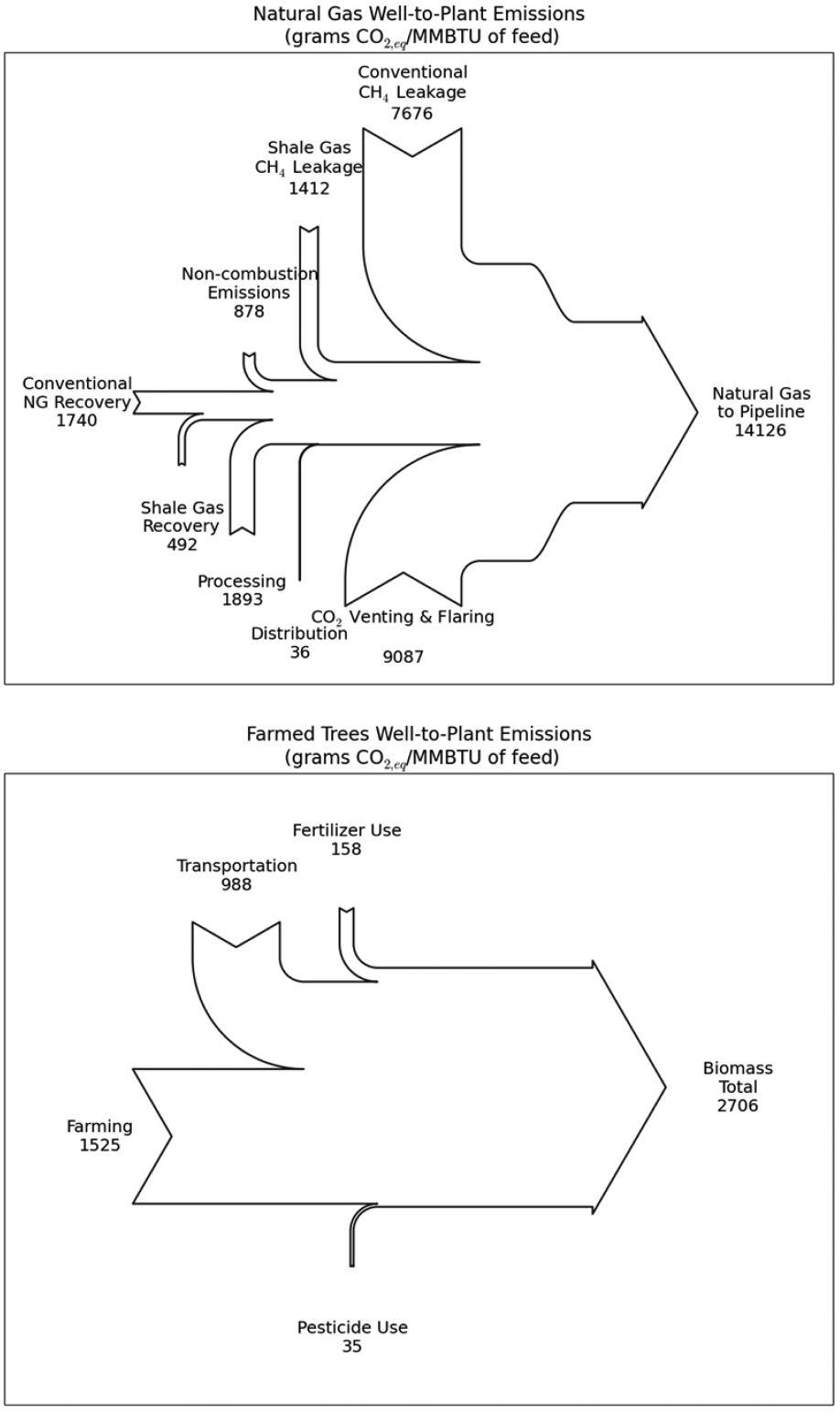

Figure 3. U.S. conventional natural gas, shale gas, and forest residue well-to-plant (WTP) emissions.

fresh treated syngas and sent to the FT reactor. The FT reactor consists of a fixed bed with a cobalt-based catalyst. Finally, the FT products are hydrocracked and separated into naphtha and diesel range blend stock fuels in the product upgrading unit of the GBTL plant. Although the naphtha and diesel products are considered finished blend fuels, they may undergo further processing to meet market specifications with minimal impact to the life-cycle emissions of the fuel. FT light gases and heavy waxes are either reformed or released as a waste product and receive no emission allocations. The steam and power unit of the plant balances steam generation and consumption within the GBTL plant for three types of steam: LP, MP, and HP at 5, 17, and 60 bar, respectively. Steam turbines consume any excess steam to supplement power input to the plant. The remaining power requirement of the GBTL plant is assumed to be imported from the U.S. national grid. The water management

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unit is a model section that tracks water consumption, as well as water generation, within different units and provides the water balance for the GBTL plant. Although commercial natural gas facilities can operate on a 100% natural gas input, these configurations are not considered in this study since they will not meet the RFS2 emissions threshold.

3.2. System Description. Figure 2 describes the system boundaries of this study. Our analysis envelops the collection, conversion, and eventual use of GBTL biofuel in conventional diesel vehicles. This concept model captures the major energy use and emission factors in line with similar environmental studies and methodology employed by the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model (GREET) by Argonne National Laboratory.[16]

The system input material streams are North American (NA) natural gas and forest residue (willow chips). Feedstock emission allocations are based on the displacement method meaning that residue emissions are calculated from the additional economic activity of utilizing the residue. Emissions associated with the cultivation and growth of the trees are attributed to their primary economic purpose which may include consumer products and energy applications. We assume a 77/23% split of conventional and shale gas recovery. The raw gas is processed at a gas processing facility before pipeline transmission to the GBTL plant. Raw biomass is transported to the GBTL facility with minimal processing. However, there are important logistical challenges for delivering biomass to a large GBTL facility that are beyond the scope of this study. At the GBTL facility, both feeds undergo a thermochemical conversion to syngas, which is catalytically processed into liquid transportation fuels. The finished product is delivered to pumping stations for blending and vehicle use. Each of these steps incurs energy penalties, material losses, and greenhouse gas emissions.

Figure 3 illustrates the emission flows for collection and transportation of NA conventional natural gas and shale gas and willow chips. These are also known as the well-to-plant (WTP) emissions. The values shown are based on calculations by the GREET model and include various assumptions regarding plant growth, crop management, and direct and indirect land use emissions.[16] As shown, natural gas WTP greenhouse gas (GHG) emissions are dominated by methane leakages through various steps in the supply chain. Recent studies have attempted to estimate methane leakage at gas wells.[26−28] Natural gas recovery results in emissions primarily from both conventional and shale gas well CH_4 leakage. Once recovered, venting and flaring by well equipment and processing incur additional emissions. Forest residue WTP emissions are primarily from farming and transportation activities. These include tree planting, branch and trunk cutting, and collection. Assuming that the harvested trees are replanted, biomass embedded carbon emissions are recovered during the growth process resulting in a closed biomass-carbon cycle.[16] We model the FT liquids in GREET as a combined product without separate allocation methods for the naphtha and diesel range hydrocarbons.

GBTL facility emissions are calculated using the equations provided in the Supporting Information. The process model estimates the process efficiency, carbon conversion, fuel yield, electricity, and steam use or export at the facility.

Process efficiency is the ratio of naphtha, diesel, and steam to the natural gas and biomass energy input. Carbon conversion is defined as the ratio of carbon in naphtha and diesel to the carbon in the total feed. Fuel yield is calculated as the volume of transportation fuel produced per dry ton of feed. A biomass-only fuel yield is provided for comparison purposes. Finally, steam input is accounted for with natural gas combustion whereas export steam displaces natural gas use as a fuel.

Plant-to-wheels (PTW) emissions are based on FT liquids transportation to U.S. pump stations and consumption in conventional diesel engine vehicles. Fuel transportation results in transmission energy losses and emissions. Vehicle performance is based on a conventional diesel engine with a 28.1 mile per gallon rating. We employ a 100-year global warming potential (GWP) method for climate forcing compounds.

4. RESULTS AND DISCUSSION

Biomass use can reduce emissions of the combined gas and biomass to liquids (GBTL) process below the RFS2 emission reduction requirements as shown in Figure 4. The amount of biomass required to comply with existing regulations for advanced, cellulosic biofuels is process dependent. The compliant blend case SMR scenario has a natural gas blending limit of 8.91 wt % (21.3% LHV energy basis) whereas the ATR scenario can process 7.83 wt % natural gas (19.1% LHV energy basis) before exceeding the minimum emission reduction mandates. A key consideration from these results is that, although the FT liquid fuel could qualify as an advanced biofuel under these conditions, the natural gas contribution may not qualify for RFS2 credits. Figure 4 shows how WTW emissions vary with biomass fraction in the feed. The RFS2 mandates a 60% reduction of vehicle emissions compared to conventional liquid fuels (98 000 g $CO_{2,eq}$/mmbtu), which is represented by the dashed line at 40 950 g $CO_{2,eq}$/mmbtu (4594 g $CO_{2,eq}$/gallon) or an equivalent 163.6 g $CO_{2,eq}$/mile.

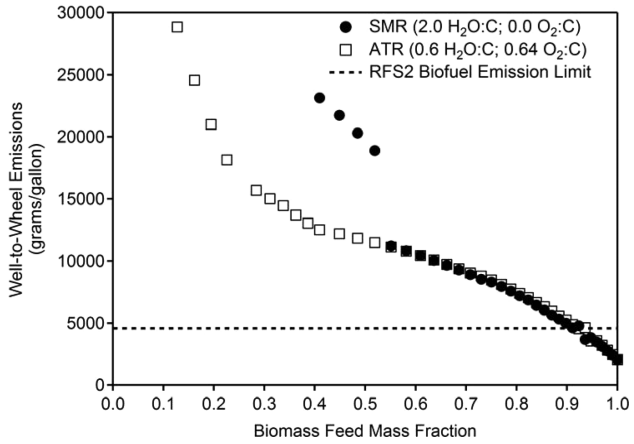

Figure 4. Autothermal (ATR) and Steam-Methane (SMR) reforming well-to-wheels (WTW) emissions vs fraction of biomass in process feed. The SMR and ATR are operated at 950 °C and 25 bar. The RFS2 mandates a 60% emission reduction compared to fossil fuels equaling 409 g $CO_{2,eq}$/vehicle mile traveled or 40 950 g/mmbtu (4594 g/gallon) of fuel consumed.

As discussed previously, these reactors can operate over a wide range of conditions thereby drastically impacting the process performance. The following sections describe the main material and energetic components related to process performance and emissions and the sensitivity to reactor operating conditions.

4.1. Gas and Biomass to Liquids Performance. The ATR configuration has some technical advantages compared to

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the SMR. For Fischer−Tropsch liquids (FTL), the ATR can operate over a wider range of biomass feed fractions than the SMR, as shown in Figures 4 and 5. The ATR scenario achieves

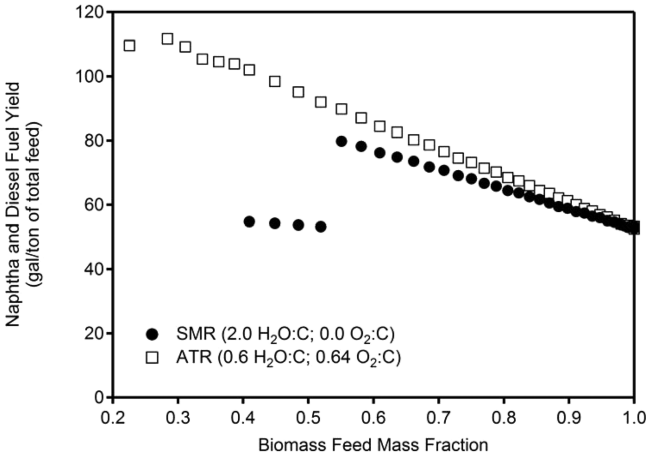

Figure 5. Autothermal reforming (ATR) and steam-methane reforming (SMR) naphtha and diesel yields vs fraction of biomass in process feed. The SMR and ATR are operated at 950 °C and 25 bar.

feed-to-fuel yields of up to 110 gallons per ton of feed with ca. 30 wt % biomass in the feed. In fact, the ATR configuration can operate solely on natural gas with operation and process modifications.[10]

The SMR process design in this study requires more than 55% biomass mass feed to prevent a H_2 build-up in the FT process. Below 55%, the SMR suffers a drastic drop in fuel yield and an increase in emissions as represented by the discontinuities in Figures 4 and 5 (circles). Thus, the SMR design cannot produce FT fuel efficiently at low biomass input fractions without extensive process modifications beyond the scope of this study. Furthermore, an industrial ATR would operate under higher pressures than a SMR, resulting in higher methane conversion efficiencies. We define efficiency as the ratio of energy outputs (FT fuel, power, steam) to energy input (natural gas, biomass, and process fuel).

The SMR and ATR configurations achieve similar fuel yields of 80 to 90 gallons per ton of feed for biomass feed fractions greater than 55 wt %. However, the ATR system is slightly more efficient. For example, at an 85 wt % biomass feed fraction, the SMR yields 63 gallons per ton with an efficiency of 43%. The ATR under similar conditions yields 65 gallons per ton with an efficiency of 45%.

Figure 6 compares the material, energy, and carbon flows of the two configurations. Under the blend case conditions, the ATR and SMR have similar flow diagrams. However, minor differences are noticeable: the SMR generates slightly more steam but results in higher energy losses than the ATR. The ATR achieves a higher carbon conversion to transportation fuels (34.1%) when compared to that achieved with the SMR (32.8%). These results are subject to operating conditions as discussed in the Sensitivity Analysis section.

4.2. Sensitivity Analysis. Figures 7 and 8 compare the sensitivity of fuel yield, process efficiency, energy use, and system emissions to variations in reforming temperature, pressure, and H_2O/C at the reactor inlet. Fuel yield is the primary contributor to overall efficiency. For example, for both the ATR and SMR scenarios, we see a greater increase in fuel yield than efficiency between reformer temperatures of 700 and 800 °C. High reactor temperatures have decreasing benefits in terms of fuel yield and can even result in lower yields. This can occur because higher reformer temperatures decrease the H_2/CO ratio entering the WGS unit and increase the amount of carbon, steam, and heat required to meet the requisite 2:1 H_2/CO ratio. Furthermore, high reactor temperatures require additional energy to raise natural gas and steam feed temperatures. Although some of this energy can be recovered by cooling the reactor gas effluent, in general, this results in energy penalties. The ATR achieves a higher efficiency and fuel yield under all conditions considered in this study. The worst-case scenarios are when the ATR and SMR operate below 800 °C or when the SMR operates with a 0.6 H_2O/C ratio. Low

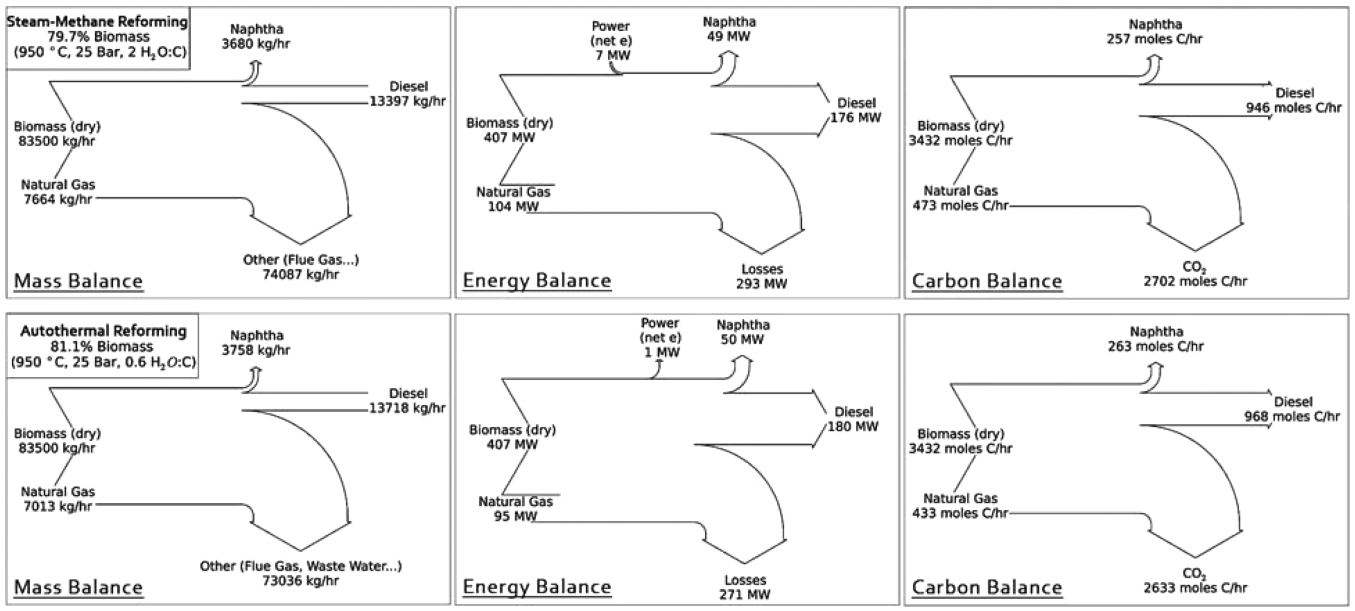

Figure 6. Material, energy, and carbon flows of key system flows for the steam-methane and autothermal reforming of natural gas and gasification of biomass to Fischer−Tropsch liquids.

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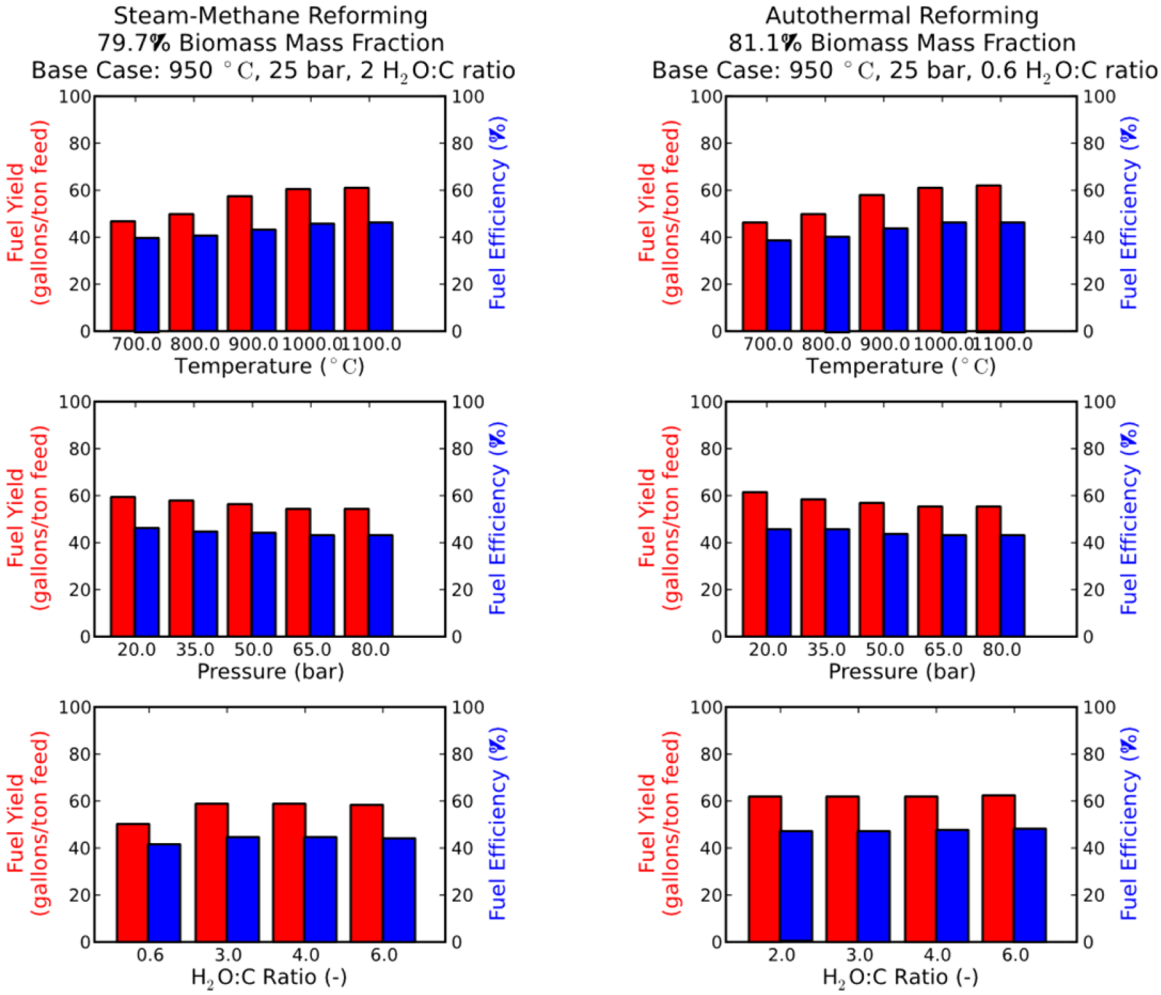

Figure 7. Sensitivity analysis of autothermal reforming (ATR) and steam-methane reforming (SMR) naphtha and diesel yields (left) and efficiency (right) based on reformer temperature (700−1100 °C), pressure (20−100 bar), and H_2O/C (0.6−6) molar ratio.

H_2O/C ratios increase the potential for coking, which deactivate and potentially damage the reactor catalyst.

Energy use is, by definition, inversely related to process efficiency. Energy use is the amount of energy that leaves the system as an undesirable product (heat losses, unrecoverable energy, low value products). In this case study, energy use is the amount of energy input that is not recovered as transportation fuel or steam. Fossil fuel use is defined as the amount of fossil fuel that a process losses to the environment as heat or unconverted fuel.

Energy use has a more complex relation with system emissions. Typically, higher energy use corresponds to increased emissions because it is related to higher carbon losses. However, not all energy losses result in carbon emissions. For example, unconverted char would increase process energy use but may reduce system emissions if it is sequestered through soil fixation. In order to minimize release of fossil carbon CO2, and so qualify, it is essential that the GBTL facility use its natural gas efficiently. From this perspective, efficient use of carbon from biomass is less essential, though it is quite important for the process economics.

The SMR scenario exhibits an increase in energy use when changing the H_2O/C ratio from 3 to 4. A higher H_2O/C increases the natural gas derived syngas H_2/CO ratio, which in turn increases the fuel yield at this high biomass feed fraction.

However, the higher H_2O/C requires an increase in natural gas combustion to maintain the reactor temperature. Therefore, H_2O/C should be optimized for a given system but is fixed in this study.

There are several additional variables that could impact the WTW emissions of the GBTL process. These include feedstock choice, natural gas source, and conversion pathway. These parameters were beyond the scope of this study.

4.3. Resource Use and Sustainability. Biomass is a renewable energy source that can lower the environmental impact of the transportation sector. Unfortunately, biomass conversion to drop-in transportation fuels has proven difficult to scale up. Commercial natural gas conversion processes have been developed; however, natural gas is a finite resource, and it could only replace petroleum use for a limited duration. There are mutual benefits for improving the resource use and sustainability of both pathways.

For example, according to the U.S. Bureau of Transportation Statistics (BTS), the U.S. transportation sector consumed 27.51 quadrillion (10^{15}) BTUs in 2010.[29] If 100% of U.S. transportation energy demand were to be met by a GTL process with 60% efficiency, and consuming only US gas as its feed, all the current estimated reserves of U.S. gas would be consumed

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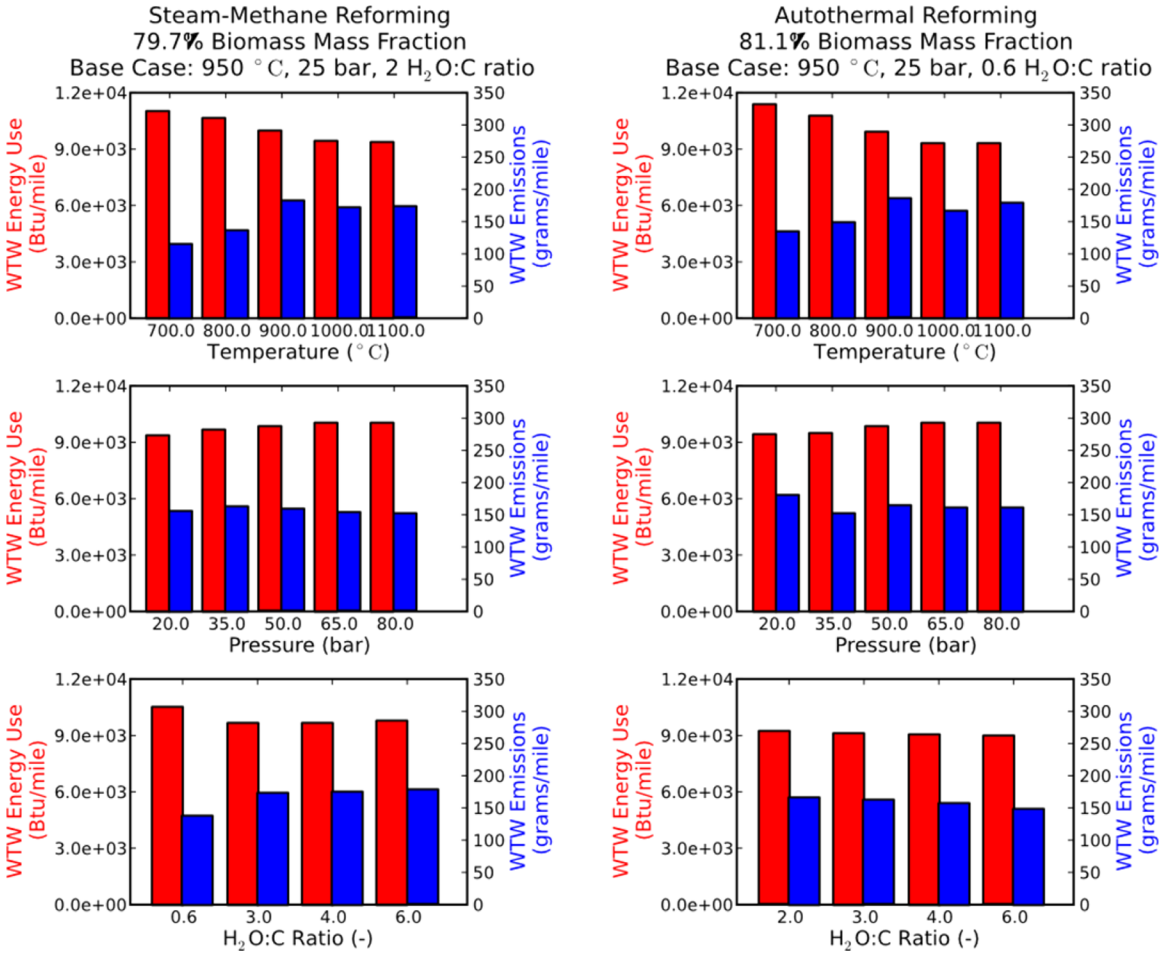

Figure 8. Sensitivity analysis of autothermal reforming (ATR) and steam-methane reforming (SMR) naphtha and diesel energy use (left) and emissions (right) based on reformer temperature (700−1100 °C), pressure (20−100 bar), and H_2O/C (0.6−6) molar ratio.

in less than 7 years. However, GBTL facilities supplying 1/3 of current transportation fuel production in the USA, using 80% (by energy) biomass as feed, would drastically extend the lifetime of natural gas use while still satisfying the RFS2 mandates.

Natural gas contributions to the U.S. transportation sector could increase following the discovery of large reserves of natural gas and, consequently, lower gas prices. One pathway to clean transportation fuel production is the combination of natural gas with biomass in GBTL facilities. However, our analysis indicates that natural gas use in GBTL facilities would be limited by emission reduction requirements in order to qualify as clean, advanced biofuels under the RFS2. This study compared the technical and environmental performance of combining SMR and ATR technology with a high temperature, entrained-flow gasifier for FT naphtha and diesel synthesis. Our results indicate that natural gas can enhance FT biofuel production by reducing the need for WGS of biomass-derived syngas. Fuel yields increase from less than 60 gallons per ton to over 100 gallons per ton with increasing natural gas input. The ATR can operate over a wider range of natural gas to biomass feed fractions because of its relative greater ability to meet the proper H_2/CO ratio, and it achieves a higher efficiency.

GBTL facilities would need to limit natural gas use to less than 19.1% on a LHV energy basis in order to qualify as clean, advanced biofuels. This natural gas blending limit is subject to technology choice and operation. Sensitivity analysis shows that efficiency, fuel yield, energy use, and emissions vary with reforming temperature, pressure, and reactor inlet H_2O/C. These conclusions are subject to uncertainties in the quantified GHG emissions and should be revised as information on these technologies emerges. The commercialization potential for GBTL technologies is subject to many technical, economic, and policy factors. This study focused on the challenges of compliance with RFS2 emission reduction requirements for a specific GBTL design. Design modifications would require evaluation of system life cycle emissions. Future work would need to consider the impact of technical innovation, economic conditions, and alternative policies on the market potential for GBTL technologies.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00060.

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Notes

The authors declare no competing financial interest.

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