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Synergistic Combination of Natural Gas and Biomass in Gasification-based Systems for Chemicals and Fuels Production

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Abstract

Synthesis gas or syngas is a fuel gas mixture consisting primarily of hydrogen (H_2) and carbon monoxide (CO). Syngas can be used directly for power generation or to synthesize a wide variety of chemicals and fuels such as naphtha, diesel, liquefied petroleum gas (LPG), dimethyl ether (DME), gasoline, synthetic or substitute natural gas (SNG), hydrogen, and ammonia (NH_3). Three major approaches to generation of syngas from natural gas are practiced in industry; steam methane reforming (SMR), autothermal reforming (ATR), and partial oxidation (POx). Main markets for these H_2 -rich syngas production routes include ammonia synthesis and petroleum refining. Syngas can also be produced through thermochemical conversion (e.g., gasification) of carbonaceous feedstocks such as coal and biomass. Gases from these solid feedstocks tend to be rich in CO and often require additional processing prior to utilization, particularly for biomass-derived syngas and the need to reform tars and remove multiple contaminants.

This paper explores the combination of biomass and natural gas for the production of biofuels, which have become in recent years a growing component of the U.S. transportation fuel supply, particularly for gasoline-powered vehicles. Advanced processes are being developed to utilize biomass resources to realize three major imperatives: (1) the need for oxygenates in gasoline to enhance octane and reduce smog-forming reactions, (2) the need to reduce greenhouse gas (GHG) emissions, and (3) the desire to replace imported petroleum with domestically produced fuel. However, with biomass alone, it may not be practical to achieve economies of scale, largely because the low bulk density of biomass challenges its collection and transportation to a centrally located biorefinery. For natural gas, current and projected prices, owing to the shale gas boom in recent years, have revived interest in gas-to-liquids (GTL) initiatives. However, with natural gas alone, the GTL route does not confer any significant GHG reduction and thus would not help meet government-mandated environmental targets. Besides addressing these two key hurdles, the coupling of these two widely differing feedstocks has strong technical merits provided by synergies between the CO-rich syngas from oxygen/steam gasification of biomass and H_2 -rich syngas from NG conversion, making it possible to produce high-quality syngas and with flexible H_2 -to-CO ratios, more readily amenable to meet the needs of various syngas conversion technologies.

The paper explains the complementary chemistries of biomass and natural gas and considers major integration and process intensification options, including close-coupling of the O_2 -steam biomass gasifier with a non-catalytic POx reactor and co-conversion of both feedstocks in a single, compact reactor. Key advantages are outlined for biomass gasification and downstream syngas processing (tar reforming in particular), as well as for the production of liquid hydrocarbons (i.e., gasoline via TIGAS and biodiesel through Fischer-Tropsch synthesis). Costs and environmental benefits are evaluated in detail for one selected case to show that overall performance can be significantly improved as a result of synergistically combining natural gas and biomass, through enhanced syngas quality, higher yields, and much reduced downstream processing including CO_2 capture requirements.

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Introduction

Biofuels are a growing component of the U.S. transportation fuel supply, particularly for gasoline-powered vehicles. The growth in biofuels has been driven by three major imperatives: the need for oxygenates in gasoline to enhance octane and reduce smog-forming emissions, the need to reduce greenhouse gas emissions, and the desire to replace imported petroleum with domestically produced fuel, embodied in the 2004 Energy Independence and Security Act (EISA) and the related Renewable Fuel Standard (RFS).

Advanced processes are needed to produce not only alcohols but also hydrocarbons from cellulosic biomass and wastes that do not have a competing application as food. Though under development, and in the national interest, advanced, second-generation biorefineries have struggled to attract the investment needed to move into commercial demonstration. Important barriers, which are intrinsic to the use of a low-density feedstock that depends on natural processes, include:

- Economy of scale
- Feedstock security, logistics, and capacity factor
- Process complexity

Concurrently, advances in natural gas drilling and production have provided energy markets with new supplies of natural gas from shale deposits. These technologies have reduced the cost of natural gas by a factor of 2 to 3, depending on location. This in turn has revived interest in gas-to-liquids (GTL) initiatives. However, conversion of natural gas to liquid transportation fuels does not confer any significant greenhouse gas reduction and thus would not help meet the EISA targets.

In our view, these convergent developments can be reconciled to overcome barriers listed above by integrating biomass and natural gas into a flexible hybrid system based on thermochemical gasification. Because the respective chemistries of biomass and natural gas are complementary, this integration is equivalent to adding a “virtual GTL plant” to the biorefinery at zero added capital cost. We forecast a productivity increase that can reduce the lifetime production cost of gasoline by up to 20 percent, in addition to hedging the risks of feedstock supply and cost.

Relevant GTI Experience and Capabilities

Over the years GTI has performed significant large pilot-scale gasification testing of numerous biomass fuels, partial oxidation of natural gas, syngas treatment (including catalytic methane and tars reforming), and conversion of conditioned and purified syngas into valuable liquid hydrocarbon fuels. Biomass gasification has been tested at GTI during numerous test campaigns as part of developing commercial design data for two biofuel programs since 2008, one to produce biodiesel from forest residues¹ and the other to produce green gasoline from woody biomass.² In this latter program, GTI, in collaboration with its partners Haldor Topsøe, Andritz/Carbona, UPM, Phillips 66, and the U.S. Department of Energy, has successfully conducted pilot-scale testing of its integrated biorefinery (IBR, Figure 1 and Figure 2) for the production of gasoline from biomass. The facility consists of three major pilot plants and is designed to process approximately 21 tonnes of biomass per day to produce approximately 22.5 barrels of gasoline blendstock. The first pilot plant, so-called Gasification Section, is comprised of a fluidized-bed gasifier (up to 6 MWth input); a hot gas candle filter; a catalytic

reformer for reforming benzene, tars, methane and other light hydrocarbons, and for destroying ammonia; and a syngas direct cooler. The second pilot-plant, Acid Gas Removal Section, is comprised of a syngas compressor and a gas-liquid contactor using a physical solvent (Morphysorb®) for removing CO₂ and H₂S to the specifications required by downstream syngas conversion units. The third pilot plant is Topsøe's Improved Gasoline Synthesis (TIGAS) process for highly integrated purification of the treated syngas, DME/methanol synthesis, subsequent conversion of these intermediate oxygenates into high-octane gasoline, and product/by-product separation.

To support the long-term operation of these facilities as an integrated unit in test campaigns lasting up to 30 days, GTI has developed and implemented practical analytical approaches, equipping key sections of the IBR facility with innovative sampling and monitoring systems. Carefully designed and planned combinations of online monitoring field instruments and off-line analyses in GTI's analytical laboratory enable comprehensive process performance assessment. In a typical test campaign, complete characterization of the biomass-derived syngas, including speciation of tars and other contaminants, and performance assessment of the catalytic reformer, hot syngas candle filter, and syngas direct cooler are provided. Data necessary for environmental characterization of by-product solids and liquids are also developed, thus providing complete data packages to support commercial design efforts. A unique micro-GC based approach has been developed and implemented to support essentially unattended monitoring of the AGR Section, a key syngas cleanup and conditioning component in the IBR facility. An extensive system has been developed for the syngas conversion facility, TIGAS Section, to permit performance assessment of the purification stage, the gasoline synthesis loop, and the products/by-products separation section. These systems also enable regular sampling of the gasoline product for subsequent stabilization and analysis to determine key quality metrics (octane number, Reid vapor pressure, bromine number). Customized protocols have been developed to provide for rapid determination of MeOH, trace oxygenates, and other compounds in wastewater from the process to monitor catalyst aging and assess effluent overall quality and suitability for disposal.

Efficient natural gas conversion has also been successfully demonstrated in a non-catalytic POx reactor based on Aerojet Rocketdyne's Advanced Gasifier design. The feasibility of the AR technology, and the anticipated benefits, have been validated in over 700 hours of testing at 16.3 tonnes/day coal feed rate in the gasifier pilot plant facility at GTI.³ Using the same rapid mix injector modified for natural gas feeding in place of coal, AR is developing a compact, high-pressure POx reactor for a low cost gas-to-liquids (GTL) process.⁴ The injector burns natural gas in a short residence time (< 100 millisecond) POx reactor with oxygen and minimal amounts of steam to produce a synthesis gas containing H₂ and CO at an H₂/CO molar ratio near 2. The POx injector has been operated for over 60 hours of highly successful testing at about 8.2 tons/day natural gas feed mounted on the existing coal gasifier and water spray quench vessel.

Therefore, the commercially-relevant experience at GTI processing biomass and natural gas separately for production of liquid transportation fuels has led us to evaluate the potential synergies for a combination of these feeds.

Benefits of Combining Biomass and Natural Gas

Hydrogen Source

A full understanding of the complementarity of biomass and natural gas chemistry requires a discussion of how hydrogen is supplied to the process.

Biomass is hydrogen-poor compared to gasoline or diesel, typically having a H:C atomic ratio of 1.4, compared to 1.8 needed for motor fuel. For this reason, to produce hydrocarbon fuels hydrogen in syngas is typically supplemented from added steam, through its reaction with carbon as a reductant, producing H₂ and CO in the required ratio. Natural gas, in contrast, is hydrogen-rich compared to gasoline or diesel, with a H:C atomic ratio close to 4.0.

This suggests a synergy between biomass and natural gas that can minimize the steam requirement for conversion of natural gas into hydrocarbon fuels, and thus save energy, water, and water purification costs. And it can minimize any waste of surplus hydrogen from natural gas.

Theoretically, only 9 wt% natural gas could supply all the hydrogen needed to bring the combined H:C to the desired ratio of 1.8. The full process chemistry is, of course, more complex, but this illustrates that the addition of a small amount of natural gas can have a large impact on the conversion chemistry. As mentioned above, providing hydrogen from natural gas reduces operating expenses by reducing steam requirement for gasification. Heat recovery in a HRSG upstream of acid gas removal (AGR) would still be required, but would simply produce steam with more superheat for on-site power generation.

Besides the potential for natural gas to donate hydrogen to the biomass for raising the H:C ratio as needed to produce gasoline, the use of natural gas creates another opportunity. Natural gas can facilitate reaction pathways where a major fraction of the carbon in biomass feed is converted to liquid fuels by forming H₂O instead of CO₂.

Why is this advantageous? As an example, for the production of gasoline from biomass alone, a preferred chemistry is to produce dimethyl ether (DME, chemical formula CH₃OCH₃) as an intermediate by using a syngas with H₂/CO ratio of ~1.0, via the reaction:



However, if the syngas has a H₂/CO ratio of ~2.0, we can produce water instead of CO₂, thus:



Lower CO₂ formation translates to a smaller AGR unit and greater incorporation of feedstock carbon into the product. In certain process configurations which are discussed later, the higher steam content provides other advantages in preventing carbon deposition. In summary, better carbon efficiency, lower water consumption, and smaller gas processing units are excellent potential outcomes of the natural synergy between biomass and natural gas.

Economy of Scale

Biomass availability radius is generally considered to be 48.3 to 128.8 km, depending on type of biomass, terrain, and other factors.⁵ For the base case developed under an integrated biorefinery project just completed by Haldor Topsøe, GTI, Andritz-Carbona, and UPM, gasoline and LPG are produced from woody biomass. A prospective first commercial site is the UPM mill

in Grand Rapids, Minnesota. According to a 2013 study, that location has an availability of 2 million green tonnes per year in a 120.7-km radius. This translates to 2,722 bone-dry tonnes per day, producing 1.3 million bbl/yr of gasoline. GTI has calculated that a gasoline output of 2.0 million bbl/yr would achieve a *biomass-only* gasoline production cost of \$0.63/liter (\$2.38/gallon) over a 15-year project lifetime.* The capital cost per barrel of product per day is \$134,000/bbl/day. A smaller capacity would result in higher production cost.

One way to improve the economics is to augment the biomass input with natural gas, as has been suggested and proposed by others.^{6,7,8} Naturally, this reduces the renewable content of the product, but the facility can still be designed to meet the U.S. EPA definition of a Cellulosic Biofuel (D3 RIN)⁹, because the life cycle analysis (LCA) of the TIGAS biorefinery shows a 91.7% GHG reduction. To qualify for a D3 RIN, a product must show 60% GHG reduction. Because natural gas is already 25% lower than gasoline in GHG burden on an energy basis, the blended feedstock may comprise as much as 21 wt% natural gas (48% by energy content) and still meet that target.

In that hybrid case, the biorefinery could be scaled up to as much as 2.9 million bbl/yr, reducing the production cost by up to 20%, depending on the capital cost impact of adding natural gas, bringing the capital efficiency in line with world-scale GTL projects. This could make the difference between a go and a no-go for prospective investors.

To support this conclusion, we conducted a preliminary analysis of the impact of natural gas input on gasoline production, steam requirement, and GHG reduction for a range of natural gas fractions, using published estimates of carbon conversion in GTL plants, which ranges from 58% to 77%. Reducing the gasifier steam requirement, as explained above, may also result in additional energy savings, which could further increase the overall gasoline yield or generate surplus power.

The results in Figure 3 show that, based on published estimates of carbon conversion, natural gas has the potential to increase gasoline output by between 79% (a) and 112% (b) while keeping avoided GHG emissions above 60%. The analysis also shows that about 16 wt% natural gas can essentially eliminate the need for steam to the gasifier to supply hydrogen. Fluidization requirements in the gasifier which are typically provided by steam can be substituted by a combination of recycled tail gas and CO₂ recovered from the acid gas plant. Steam would still be generated to recover heat upstream of syngas compression and that steam would be available for power generation as well as other plant needs.

To estimate the impact of natural gas on the gasoline production cost, we considered the baseline commercial biorefinery described above with added natural gas input ranging from zero to 20 wt% (1.47 million Nm³/d). The natural gas conversion was held at 67.5% [midpoint between cases (a) and (b) in Figure 3] for this calculation.[†]

* Reference case: integrated biorefinery feeding 4040 tonne/day wood chips at 20 wt% moisture to a fluidized-bed oxygen-blown pressurized gasifier and demonstrated cleanup system including acid gas removal. No shift step is needed. The gasification plant feeds syngas to a TIGAS plant for gasoline synthesis. All on-site power is generated from unreacted syngas components, on-site water treatment provides 100% of water needs, and CO₂ is partially recycled to gasifier and other on-site functions. Construction begins in 2018, startup in 2019, first full year of production in 2020. Debt/equity ratio = 0.50, interest rate = 8.0%, term of loan = 15 years, production cost and byproduct credits expressed in 2019 dollars.

† Natural gas price from EIA 2011 forecast for industrial users, indexed to inflation at 2.4%. Electricity price from IEA 2013 forecast for the state of Indiana, similarly indexed to inflation. Biomass purchase

As shown in Figure 4, the levelized production cost of gasoline over the 15-year lifetime of the plant decreased from \$0.63/liter (\$2.38/gal) to \$0.51/liter (\$1.94/gal), which is an 18.5% decrease. As expected, the impact of natural gas addition on production cost is highest with the first increment and gradually diminishes as more is added. This will facilitate staying within the cellulosic biofuel RIN limit without greatly impacting the production cost as feedstock properties change.

Note that this cost analysis also assumes that other key parameters such as capital cost and availability are not changed by the addition of natural gas to the system. To dig deeper into this assumption, we calculated sensitivities of the gasoline production cost to the following:

- Facility capital cost
- Plant availability
- Biomass delivered price
- Natural gas delivered price
- Electricity purchase price
- Natural gas conversion to product
- Debt/equity ratio (DER)

Price assumptions are \$55.1/tonne for wood (20% moisture chips) and \$0.61/MJ for natural gas, both in the startup year of 2019.

Results are shown in Figure 5 (a) through (e). For the biomass-only case, plant availability and capital cost are the leading factors, followed closely by the price of biomass. DER is far less important, as is the purchase price of electricity. Of course, with no natural gas, the conversion and price of natural gas is of no consequence in this case.

As the fraction of natural gas added to the feedstock increases, as noted above, the forecasted baseline cost of gasoline drops from \$0.63/liter (\$2.38/gal) to \$0.51/liter (\$1.94/gal). Moreover, the impact of capacity factor and capital cost shrinks while the impact of natural gas price and conversion grow. At the highest natural gas fraction studied, the degree of natural gas conversion overtakes plant availability and the natural gas price becomes more important than the capital cost, but all four of these are similar in magnitude.

This is significant because, for example, the gasoline production cost impact if plant availability should drop by 15% is +\$0.07/liter (+\$0.25/gal) for the 100% biomass case, but only +\$0.03/liter (+\$0.13/gal) for the 20 wt% natural gas case. Given the fact that natural gas should reduce the risk of downtime due to biomass supply disruptions, the economic benefits should be further magnified.

Similarly, the capital investment would have a smaller impact on the investment risk with natural gas enhancement because the effect of a 15% growth in installed cost would only increase the gasoline production cost by +\$0.03/liter (+\$0.10/gal) for the maximized natural gas case, compared to an increase of +\$0.05/liter (+\$0.19/gal) for the biomass-only case. This is particularly meaningful for risk minimization because the capital cost impact of adding natural gas is uncertain at this point.

price from UPM (private communication). All costs and selling prices are at plant gate. Production cost is levelized cost over 15-year plant/loan lifetime, based on 2019 dollars.

Feedstock Security, Logistics, and Capacity Factor

While biomass is abundant and ubiquitous, it is still subject to risks related to weather, pests, pathogens, and other ecological factors. Competition for supply, since the resource is constrained by logistics to be so localized, can upset prices. These risks can result in fluctuations in supply, price, or both. Even when supply of fresh biomass is unimpeded, storage can be problematic due to potential degradation from insects, mold, and mechanical breakdown in the presence of temperature and humidity fluctuations. Among strategies for reducing those risks are densification via pelletization and/or torrefaction to enable long-term storage.^{10,11} Feedstock flexibility to utilize a wide range of biomass types, including wood wastes, agricultural wastes, and dedicated energy crops, can also mitigate fluctuations in the availability of a given feedstock.

Integrating natural gas into the process design, particularly with flexibility in the biomass/natural gas ratio, can also mitigate the feedstock logistics risk for the producer.¹² Access to a natural gas pipeline with the capacity needed for the biorefinery would provide a convenient hedge against feedstock supply interruptions.

The same risks cited above may also impede the biorefinery's ability to maintain capacity to meet production targets. Besides resulting in lower revenue, this can also incur penalties under long-term contract if offtake targets for customers cannot be met. Even if biomass availability meets targets, variations in biomass quality (ash, moisture, physical properties) can affect throughput for a variety of reasons, and thus the capacity factor. Pipeline gas provides a hedge against that eventuality.

The impact of plant availability (capacity factor) on gasoline production cost was shown in each of the Figure 5 diagrams. The impact of biomass delivered price, which also could be influenced by natural and market events, was also shown in Figure 5. Hedging the fuel supply with natural gas minimizes the risk associated with these factors, just like biomass provides a hedge against natural gas price excursions which would engender risk for a pure GTL plant. Figure 5 shows how the impact of natural gas price on gasoline cost is lower as the biomass fraction increases.

Process Complexity and Efficiency

It is widely understood that process complexity can incur costs in the form of reduced availability and higher maintenance. There is also a relationship between complexity and energy efficiency in that maximum heat recovery may require more unit operations to squeeze out the most available waste heat. It is vital to understand and make the right decisions on the inherent trade-offs.

In a thermochemical biorefinery, product yield is directly affected by thermal efficiency because process heat is derived from combustion of feedstock and/or syngas components, and so production cost is quite sensitive to product yield. Figure 6 shows how the gasoline production cost would vary for two cases (100% biomass, 80% biomass/20% natural gas[‡]) when the gasoline yield varies by ± 15 percent.

[‡] Maximum natural gas input by mass that can still meet the Cellulosic Biofuel standard of 60% GHG reduction. This case assumes 67.5% natural gas carbon conversion to gasoline carbon.

Process improvements that can both improve energy efficiency and reduce complexity are beneficial. One process step that can consume valuable syngas components for internal energy needs is tar destruction. Biomass gasification plants, whether direct or indirect, must contend with unwanted byproduct tars¹³ that can foul process hardware and poison catalysts. Two approaches that have been applied for eliminating tars are oil scrubbing (e.g., OLGA)¹⁴ and catalytic tar reforming (CTR)¹⁵ using either *in-situ* steam or externally generated steam. Scrubbing systems are complex and require that tars be either re-injected or disposed of outside the process. Tar reforming generally requires catalysts and large vessels to achieve adequate residence time at high temperature.

An alternative to CTR in the bio-syngas environment is thermal tar destruction with heat provided by partial oxidation of natural gas. With the availability of oxygen, steam, and CO₂ in the biorefinery, those reactants can be employed to get optimal operation to avoid soot formation, control temperature, and control the H₂:CO ratio as desired. In this way, the application combines features of both partial oxidation (POx) and autothermal reforming (ATR).

Figure 6 shows this concept, where natural gas is fired with oxygen at partial oxidation conditions to provide thermal reforming of higher hydrocarbons in the syngas. The partial oxidation reformer (POR) exit temperature is about 1205°C, which promotes efficient heat recovery in a HRSG before cooling and compression of the syngas for AGR treatment.

There are two key advantages that come from substituting a POR for a CTR reactor. First, the POR vessel will be smaller and less capital-intensive than a CTR unit because of higher temperature, greatly reduced residence time, and simplicity of construction. Second, the POR will avoid the need for catalysts that must be replaced or regenerated. The additional heat requirement for the higher temperature is, as mentioned above, almost entirely recoverable for steam and power generation.

Figure 7 also shows optional streams as dashed lines: natural gas to the gasifier and optional steam to the POR unit, as needed to avoid carbon deposition and maximize tar reforming. The benefit of the high temperature available from natural gas firing is a reduction in vessel size compared to a large catalytic tar reformer, as well as avoidance of the need to combust valuable syngas components to raise the syngas temperature sufficiently for tar and light hydrocarbon reforming.

Summary and Recommendations

Significant technical and economic benefits can be realized through incorporation of natural gas into biofuels production from biomass. Co-processing of these two fuels can increase process scale to lower CAPEX per unit production, increase process efficiency to lower OPEX per unit production, stabilize OPEX and production costs, supply hydrogen to make higher quality products, simplify or eliminate process steps (intensification), and supply heat to permit maximum renewable content in liquids. GTI's analysis indicates multiple advantages for the combined feeds can occur in the gasifier, or through closely coupling the biomass gasifier with a natural gas POx unit. Further testing and analysis is needed to investigate how best to implement hybridization, provide data on the effectiveness of different options, and support a commercial biorefinery design effort.

Figures



Figure 1. GTI's Flexible, Feed-to-Product Platform for Integrated Pilot-scale Demonstration of Energy Conversion Technologies

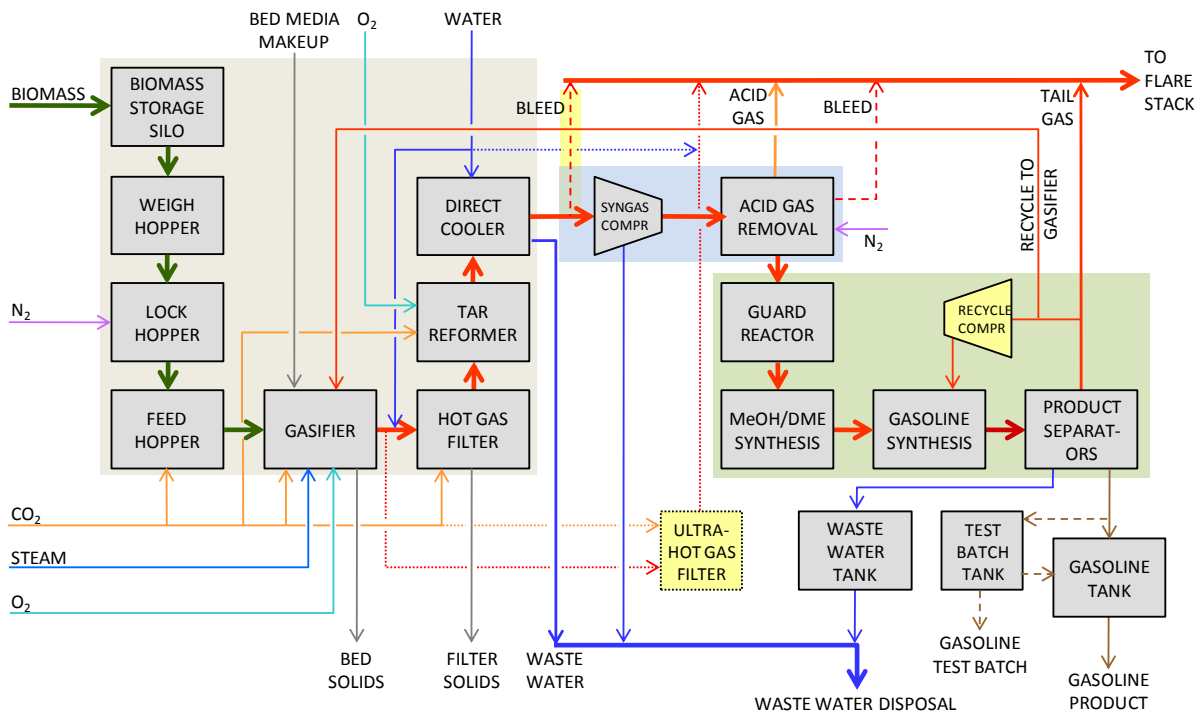


Figure 2. Pilot Integrated Biorefinery Block Flow Diagram

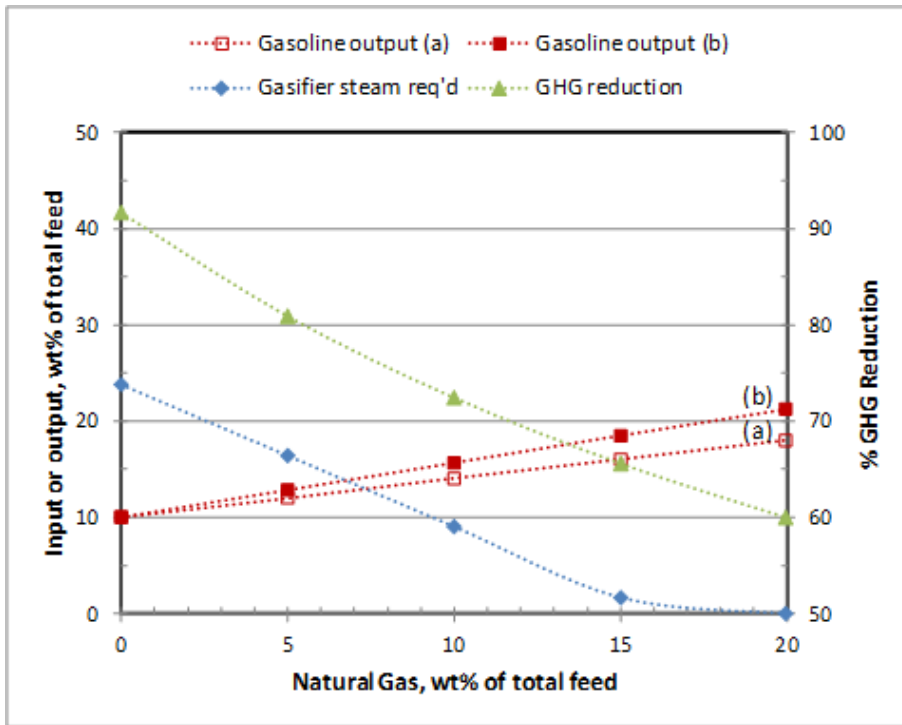


Figure 3. Impact of Natural Gas Addition on Key Biorefinery Metrics (a) = 58% methane conversion; (b) = 77% methane conversion

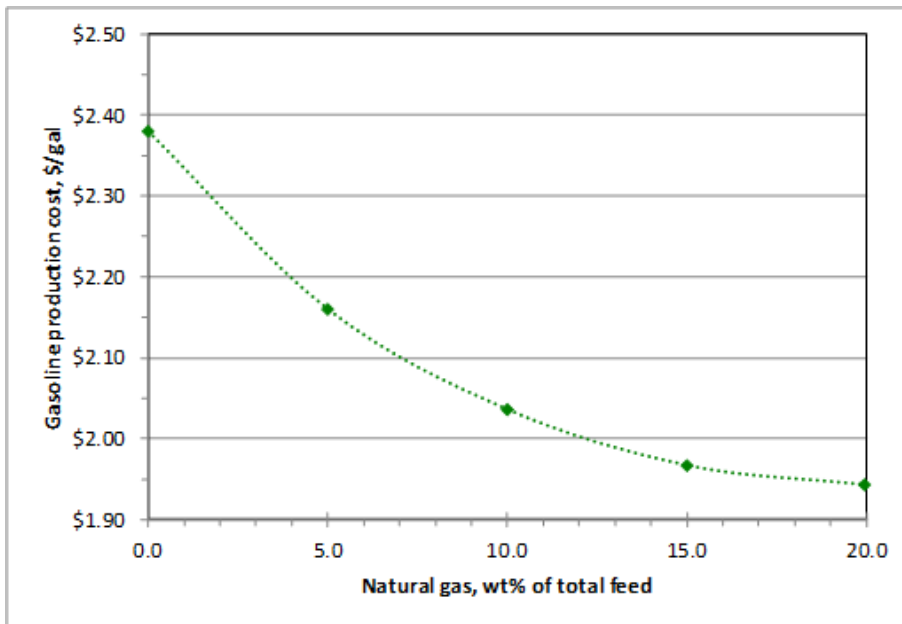


Figure 4. Gasoline Production Cost as a Function of Natural Gas Fraction to the Biorefinery

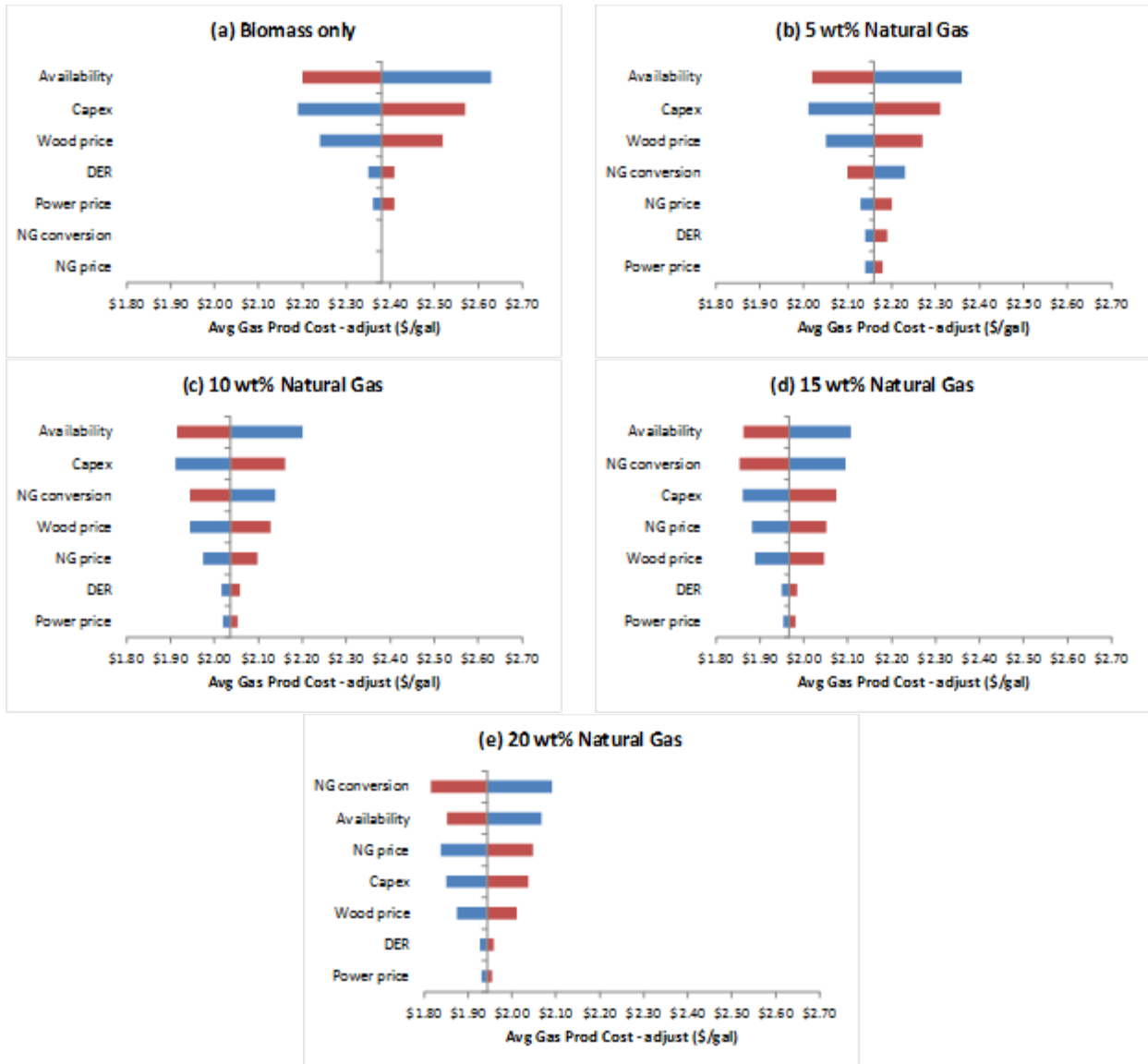


Figure 5. Sensitivity of Gasoline Production Cost to $\pm 15\%$ Variations in Key Parameters

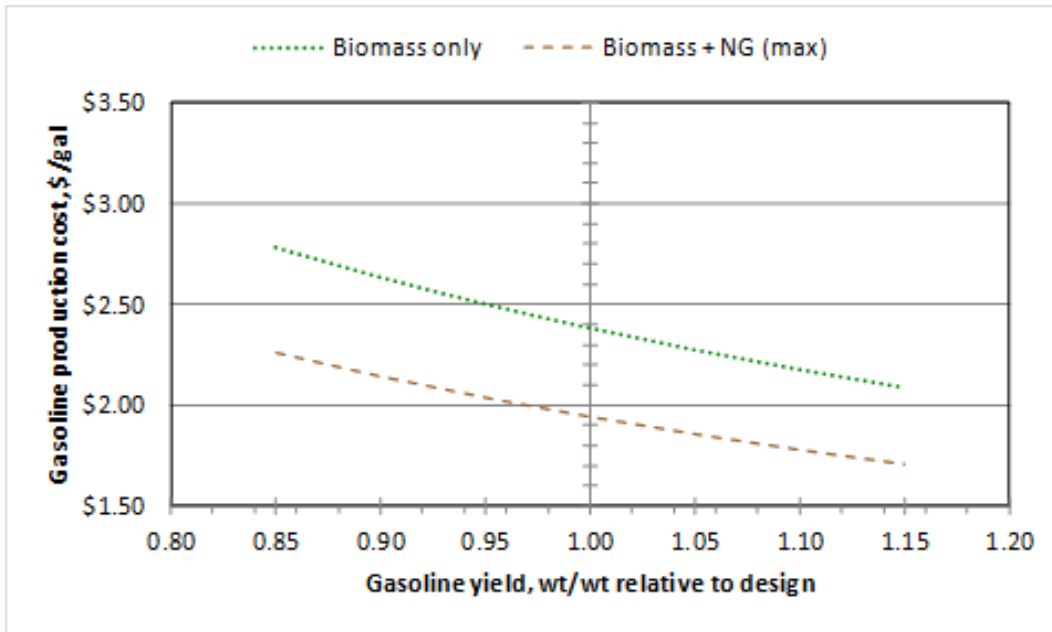


Figure 6. Effect of Gasoline Yield on Gasoline Production Cost (Levelized cost over 15-year lifetime in 2019 dollars)

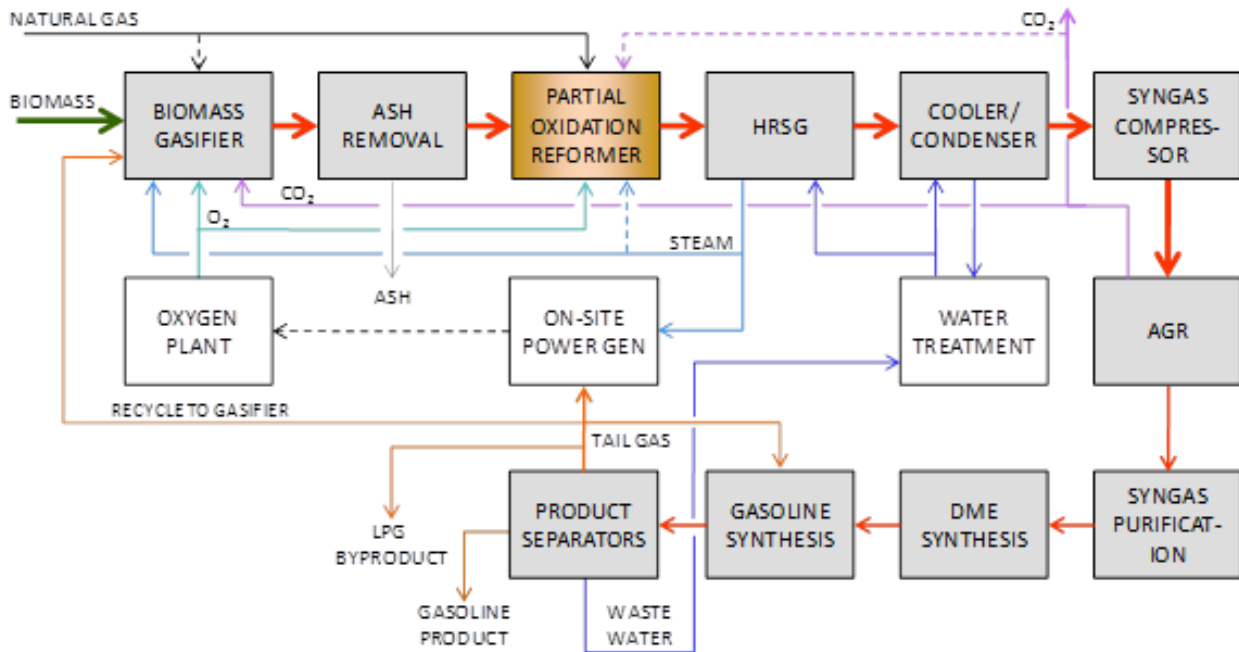


Figure 7. Commercial Biorefinery with Natural Gas Firing a POx Tar Reformer

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