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Conceptual process design and economics for the production of high-octane gasoline blendstock via indirect liquefaction of biomass through methanol/dimethyl ether intermediates

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Abstract: This work describes in detail one potential conversion process for the production of high-octane gasoline blendstock via indirect liquefaction of biomass. The processing steps of this pathway include the conversion of biomass to synthesis gas via indirect gasification, gas clean-up via reforming of tars and other hydrocarbons, catalytic conversion of syngas to methanol, methanol dehydration to dimethyl ether (DME), and the homologation of DME over a zeolite catalyst to high-octane gasoline-range hydrocarbon products. The current process configuration has similarities to conventional methanol-to-gasoline (MTG) technologies, but there are key distinctions, specifically regarding the product slate, catalysts, and reactor conditions. A techno-economic analysis is performed to investigate the production of high-octane gasoline blendstock. The design features a processing daily capacity of 2000 tonnes (2205 short tons) of dry biomass. The process yields 271 liters of liquid fuel per dry tonne of biomass (65 gal/dry ton), for an annual fuel production rate of 178 million liters (47 MM gal) at 90% on-stream time. The estimated total capital investment for an nth-plant is $438 million. The resulting minimum fuel selling price (MFSP) is $0.86 per liter or $3.25 per gallon in 2011 US dollars. A rigorous sensitivity analysis captures uncertainties in costs and plant performance. Sustainability metrics for the conversion process are quantified and assessed. The potential premium value of the high-octane gasoline blendstock is examined and found to be at least as competitive as fossil-derived blendstocks.

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A simple blending strategy is proposed to demonstrate the potential for blending the biomass-derived blendstock with petroleum-derived intermediates. Published 2015. This article is a U.S. Government work and is in the public domain in the USA. Biofuels, Bioproducts and Biorefining published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

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

Keywords: biomass; thermochemical conversion; indirect gasification; dimethyl ether homologation; high-octane gasoline; process design; techno-economic analysis; sustainability

Introduction

There is a current emphasis on the conversion of biomass to cost-competitive, liquid hydrocarbon fuels via direct and indirect liquefaction pathways. The US Department of Energy's Bioenergy Technologies Office (BETO) is enabling the development of technologies for the production of infrastructure-compatible, cost-competitive liquid hydrocarbon fuels from lignocellulosic biomass feedstocks.[1] This work describes process design and techno-economic analysis of making high-octane gasoline blendstock from a blended biomass. The processing steps of this pathway include the conversion of biomass to synthesis gas (syngas) via indirect gasification, gas clean-up, catalytic conversion of syngas to methanol, methanol dehydration to dimethyl ether (DME), and catalytic conversion of DME to a high-octane, gasoline-range hydrocarbon blendstock product. The conversion process configuration leverages technologies previously advanced by research funded by BETO and demonstrated in 2012 with the production of mixed alcohols from biomass.[2] Biomass-derived syngas clean-up via reforming of tars and other hydrocarbons is one of the key technology advancements realized as part of this prior research and 2012 demonstrations. The process described in this work evaluates a new technology area for the downstream utilization of clean biomass-derived syngas for the production of high-octane hydrocarbon products through methanol and DME intermediates, which is subsequently converted via homologation reactions to high-octane, gasoline-range hydrocarbon products.

While the current conceptual process configuration possesses similarities to conventional methanol-to-gasoline (MTG) processes,[3,4] it differs from the conventional MTG process in two key aspects: the quality of the hydrocarbon products and the severity of hydrocarbon synthesis process conditions (Table 1).

Hydrocarbon products

The conventional MTG process produces a mix of gasoline-range, hydrocarbon compounds with a high concentration of aromatics, as well as byproducts such as durene (1,2,4,5-tetramethylbenzene), light hydrocarbons, and coke. The gasoline product mixture has a motor octane number (MON) of ~83, a research octane number (RON) of ~92, and an average octane number ((RON+MON)/2) of approximately 87.[5] Fuel standards are changing to limit the amount of aromatic compounds allowed in gasoline,[6] which means a highly aromatic bio-gasoline blendstock could experience limited blending potential and lower relative product values. The chemistry proposed herein produces a low-aromatic, branched-paraffin product that has a MON of 90+, a RON of 95+, and an expected average octane number ((RON+MON)/2) of greater than 93.[7] In addition, decreased selectivity toward hexamethylbenzene (a coke precursor) has been observed during experiments;[8] some coke formation is expected given the chemistry and the assumption of multi-year catalyst cycles for the process design. The reduced coking potential relative to conventional MTG can result in higher yields. With biomass feedstock being the single most expensive component of the process, higher yields per ton of biomass can have a significant positive impact on the process economics.

Hydrocarbon synthesis process conditions

The hydrocarbon-producing reactor in the traditional MTG process operates in the range 650°F–950°F (343°C–510°C) and the yield is limited by reactor configuration. Operations are limited to lower per-pass conversions to prevent runaways in a fixed-bed shell and tube exchange reactor or fluidized bed reactors are specified in the process design for efficient heat management to allow high single-pass conversions.[3,4] Conversely, for the process configuration presented in this design report, the

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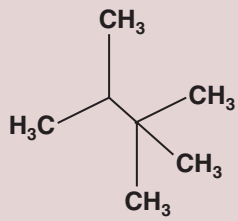
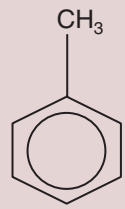
Table 1. Comparative summary of the characteristics of the pathway from woody biomass to high-octane gasoline blendstock relative to those of the traditional methanol-to-gasoline (MTG) process.

Process Attribute	High-Octane Gasoline Pathway	Methanol to Gasoline (MTG)	Impact on Techno-Economic Analysis
Molecular structures favored in synthesis reactions	Branched paraffins 	Aromatics 	High-octane product rich in branched paraffins, similar to a refinery alkylate. H-saturation decreases density, increasing product volume.
Example Compound Specific Gravity	Triptane 0.70	Toluene 0.87	
Hydrocarbon synthesis catalyst	Beta-Zeolite (12-membered rings)	ZSM-5 (10-membered rings)	Different pore sizes and structures result in different compound selectivities.
Octane number of gasoline-range product	RON: 95+ MON: 90+	RON: 92 MON: 83	Octane number increases value of product as a finished fuel blendstock.
Selectivity of C_5+ product	C_5+ product only (67.1 Gal / Ton)	~ 85% C_5+ (55.1 Gal / Ton)	High selectivity to primary (premium quality) product maximizes overall product value.
Severity of synthesis operating conditions	350 – 450 Deg. F 130 PSIA	650 – 950 Deg. F 315 PSIA	The lower severity operating conditions result in lower capital and operating costs relative to MTG.
Coke formation	Coke formation is minimized by hydrogen addition and selectivity to branched paraffins rather than aromatics.	High propensity for coke formation due to aromatic coke precursors.	Minimizing coke formation helps to maximize product yield / carbon efficiency and maximizes catalyst regeneration and replacement cycles.

reactions occur at 350°F–450°F (177°C–232°C) and can be operated at high per-pass conversions using reactors with inter-stage cooling. Additionally, by operating at the lower temperature, coke formation is reduced, resulting in less frequent catalyst bed regenerations and the potential for reduced capital and operating costs.

In order to assess the economic viability and potential of this conversion process, we have developed a conceptual process model with economic projections to estimate the minimum fuel selling price (MFSP). The MFSP can be used by policymakers and BETO to help refine research objectives and associated performance targets that will be necessary to produce cost-competitive fuels from biomass. Techno-economic analysis (TEA) also facilitates direct biomass conversion research by examining the sensitivity of the MFSP to process alternatives and projected research advances, as well as to track research progress via state of technology assessments. The analysis presented here also includes consideration of the life-cycle implications of the baseline process model, by tracking sustainability metrics for the modeled biorefinery, including greenhouse gas emissions, non-renewable energy or fossil energy consumption, and consumptive water use.

Methods and assumptions

Economic assumptions

The techno-economic analysis reported here uses n^{th}-plant economics. The key assumption associated with n^{th}-plant economics is that a successful industry has been established with many operating plants using similar process technologies. It is prudent for n^{th}-plant analysis to ignore artificial inflation of project costs associated with risk financing, delayed start-ups, equipment overdesign, and other costs associated with pioneer plants. A summary of the nth-plant assumptions applied in this analysis is provided in Table 2.

Process description and assumptions

A simplified flow diagram for the process is shown in Fig. 1. The diagram depicts the major processing steps for the conversion of woody biomass to syngas via indirect steam gasification, syngas clean-up, and sequentially synthesis of methanol, dimethyl ether, and high-octane hydrocarbons. Each process area in the design is described below. Major design and capital cost basis parameters are summarized in the Supporting Information (Tables S1-S8).

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Table 2. Assumptions for nth-plant techno-economic analysis.

Description of Assumption	Assumed Value
Internal rate of return (IRR)	10%
Plant financing by equity/debt	40%/60% of total capital investment
Plant life	30 years
Income tax rate	35%
Interest rate for debt financing	8.0% annually
Term for debt financing	10 years
Working capital cost	5.0% of fixed capital investment (excluding land purchase cost)
Depreciation schedule	7-year MACRS schedule[1]
Construction period (spending schedule)	3 years (8% Y1, 60% Y2, 32% Y3)
Plant salvage value	No value
Start-up time	6 months
Revenue and costs during startup	Revenue = 50% of normal Variable costs = 75% of normal Fixed costs = 100% of normal
On-stream percentage after startup	90% (7,884 operating hours per year)

[1]Capital depreciation is computed according to the IRS Modified Accelerated Cost Recovery System (MACRS). Because the plant described here is not a net exporter of electricity, the steam plant and power generation equipment is not depreciated over a 20-year recovery period, according to the IRS. The whole plant capital is depreciated over a 7-year recovery period.

Table 3. Analysis of wood feedstock.

Component	Weight % (Dry Basis)	
Carbon	50.94	
Hydrogen	6.04	
Nitrogen	0.17	
Sulfur	0.03	
Oxygen	41.9	
Ash	0.92	
	BTU/lb	MJ/kg
Higher heating value[a] (HHV)	8,601	20.01
Lower heating value[a] (LHV)	7,996	18.60

[a]Calculated using the Aspen Plus Boie correlation.

Feed handling and preparation

The modeled biomass feedstock has an ultimate analysis shown in Table 3. The assumed moisture content is 10 wt%, with an ash content of <1% and nominally sized to 2 mm for the gasifier. A cross-flow dryer is included in the system to allow pre-heating of the feed prior to feeding in to the reactor, using process waste heat. This also allows for contingencies during wet weather when additional feed drying may be necessary. The feedstock is delivered at $88 per dry tonne. Table 4 shows the unit operation costs for the supply of blended woody biomass to a gasification process. All values are presented in units of 2011 US dollars per dry tonne.

Gasification

Biomass is indirectly gasified.[12] Heat for the gasification reactions is supplied by circulating synthetic olivine sand that is pre-heated in a char combustor and fed to the gasifier. Conveyors and hoppers feed biomass to the low-pressure (18 psig/0.124 MPa) entrained flow gasifier. Steam is injected into the gasifier to stabilize the flow of biomass and olivine through the gasifier. Within the gasifier, biomass thermally deconstructs at 1598°F (870°C) to a

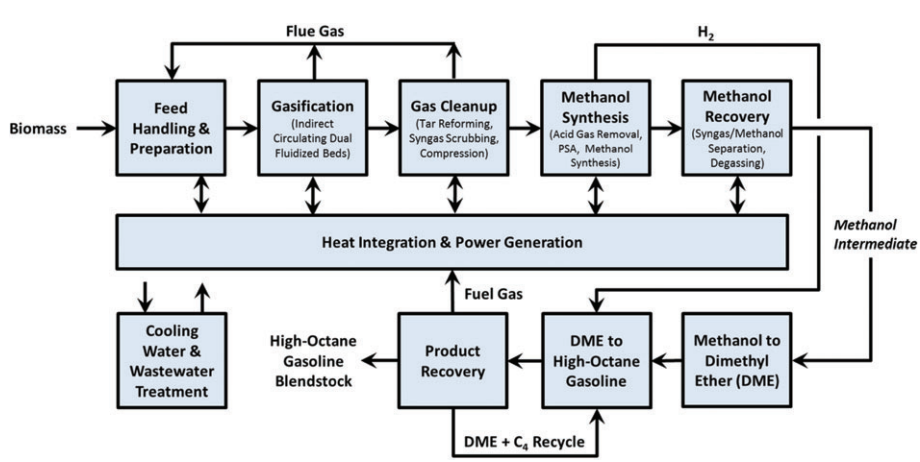

Figure 1. Simplified process flow diagram.

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Table 4. Unit Cost Breakdown for Woody Biomass Feedstock (in 2011 dollars).[11]

Cost Element	Pulpwood	Wood Residues	Switchgrass	Construction and Demolition Waste	Blend
Formulation Contribution	*45%*	*32%*	*3%*	*20%*	
Grower payment/access cost	27.56	29.05	21.68	8.98	24.14
Harvest and collection	24.52	0.00	16.99	0.00	11.54
Landing Preprocessing	13.42	9.62	0.00	10.86	11.29
Transportation	12.00	3.67	4.96	7.57	8.29
Preprocessing	26.42	26.42	21.72	31.00	27.19
Storage	3.56	3.56	6.06	3.56	3.64
Handling	2.09	2.09	2.09	2.09	2.09
Total Delivered Feedstock Cost, $/dry tonne	109.67	74.42	73.50	64.07	88.18

mixture of syngas components (such as CO, H_2, CO_2, and CH_4), tars, and solid char containing residual carbon from the biomass and coke deposited on olivine. Cyclones at the exit of the gasifier separate the char and olivine from the syngas. The solids flow to the char combustor where the char is burned in air in a fluidized bed, resulting in olivine temperatures greater than 1800°F (982°C). The hot olivine and residual ash are carried out of the combustor by the combustion gases and separated using a pair of cyclones. The first cyclone captures olivine while the second cyclone captures ash and olivine fines. Hot olivine flows back into the gasifier, completing the gasification loop. The hot flue gas from the char combustor is utilized for heat recovery and feedstock preheating. Ash and olivine fines are cooled, moistened to minimize dust, and removed as waste.[13]

Synthesis gas clean-up and syngas compression

Syngas clean-up in this design includes reforming of tars, methane, and other hydrocarbons followed by cooling, quenching, and scrubbing of the syngas for downstream operations. The water-gas shift reaction also occurs in the reformer. Tars, methane, and light hydrocarbons are reformed to syngas in a circulating, fluidized, solid catalyst system, complete with reforming and regeneration operations in separate beds. In the Aspen Plus simulation, the conversion of each compound is set to match targets that have been demonstrated.[2,14–16] Raw syngas is reacted with the tar reforming catalyst (Ni/Mg/K supported on alumina[17]) in an entrained flow reactor at (1670°F/910°C) and at a gas hourly space velocity of approximately 2500 h^{-1}. The catalyst is then separated from the effluent syngas in a cyclone. From the cyclone, the spent catalyst flows to the catalyst regenerator vessel where residual coke from the reforming reactions is removed from the catalyst by combustion. The hot catalyst is separated from the combustion flue gas in the regenerator cyclone and flows back to the tar reformer reactor to provide the energy necessary for the reforming reactions. Additional syngas and unreacted gases from the methanol synthesis reactor are also combusted in the regenerator to provide all the heat necessary for the endothermic reforming reactions. The hot reformed syngas is cooled through heat exchange with other process streams and scrubbed with water to remove persistent impurities like particulates, ammonia, halides, and recalcitrant tars. Scrubber water is purged and treated continuously at an on-site waste-water treatment facility. After heat recovery, the remaining low-quality heat in the flue gas from the catalyst regenerator is utilized for feedstock preheating. After quenching and removing any condensable material and solids, the low-pressure cooled scrubbed syngas is compressed using a three-stage centrifugal compressor with inter-stage cooling where the pressure is increased to approximately 430 psia (2.96 MPa).[13]

Acid gas removal and methanol synthesis

The compressed fresh syngas enters an amine-based acid gas enrichment unit and a Merichem LO-CAT sulfur recovery unit for removal of the CO_2 and H_2S. The recovered H_2S-rich acid gas stream is routed to the Merichem LO-CAT sulfur recovery unit where H_2S is converted to elemental sulfur and stored for disposal. The remaining CO_2 is vented to the atmosphere. After the acid gas removal step, the cleaned syngas is then split into two streams. The smaller stream of the cleaned syngas (about 6%) is sent to a pressure swing adsorption (PSA) system where hydrogen is separated for hydrocarbon synthesis in the methanol to high-octane gasoline area. The majority of the cleaned and conditioned syngas is further compressed to 735 psia (5.07 MPa) for methanol synthesis; the

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syngas is converted to methanol in a tubular, fixed-bed reactor containing a copper/zinc oxide/alumina catalyst. The vapor-phase product from the methanol synthesis reactor must be cooled to recover the methanol and to allow unconverted syngas and any inert gaseous species (CO_2, CH_4) to be recycled or purged. This is accomplished with a series of heat exchangers, including air cooling and water cooling. The mixture of methanol and unconverted syngas is cooled through heat-exchange with the steam cycle and other process streams. The methanol is separated by condensing it away from the unconverted syngas. Unconverted syngas is recycled back to the methanol synthesis reactor inlet. Heat must be removed from the methanol synthesis reactors because the synthesis reaction is exothermic. Temperature control and heat removal from the exothermic reactor is accomplished by steam production on the shell-side of the tubular reactor. The steam temperature and pressure can be maintained and controlled by back-pressure control at the outlet of the steam drum.

Methanol conditioning

The methanol leaving the reactor has been condensed at elevated pressure and has absorbed a sizeable quantity of gas (mostly CO_2). Once the crude methanol stream is reduced to lower temperature (110 °F/43 °C) and pressure (98 psia/0.68 MPa), it is sent to a distillation column to de-gas the methanol. The methanol intermediate is sent to storage for upgrading to gasoline.

Methanol to high-octane gasoline synthesis

This area of the process includes the conversion of methanol to dimethyl ether (DME) and the subsequent conversion of DME to high-octane hydrocarbons, as depicted in Fig. 2. Methanol dehydration to DME takes place in an adiabatic packed bed reactor with commercially available gamma alumina (γ-Al_2O_3) catalyst at 482°F (250°C) and 140 psia (0.965 MPa). Among various alumina-based catalysts, the γ-Al_2O_3 catalyst generally exhibits the best catalytic performance and hydrothermal stability for vapor-phase dehydration of methanol to DME.[18] The catalytic vapor-phase dehydration of methanol to DME is an exothermic reaction. The reactor heat is recovered with an intercooler for steam generation to allow for the adiabatic temperature rise with a targeted maximum reactor temperature of 482°F (250°C). DME is assumed to exit the methanol-to-DME reactor in equilibrium with methanol at the reactor exit temperature (88.5% conversion of methanol).

Hydrocarbon formation from DME is accomplished in two four-stage packed bed reactors containing NREL's in-house developed metal modified beta-zeolite (H-BEA) catalyst.[8] The yields from the process are heavily weighted toward branched C_7 molecules, with octane ratings greater than 100. High-octane gasoline is subsequently produced by the combination of acid-catalyzed homologation of DME and methylation of olefins. It has been demonstrated that the H-BEA catalyst exhibits some of the highest productivities and selectivities among zeolites studied

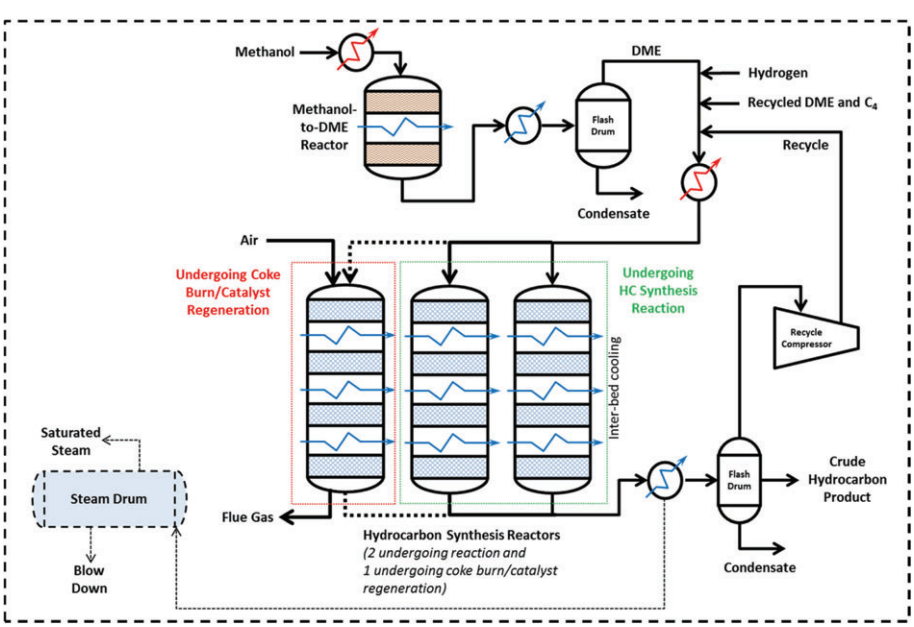

Figure 2. Simplified process flow diagram of methanol-to-hydrocarbons synthesis area.

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for the homologation of DME to branched paraffins and olefins.[7,19,20] DME is preferentially converted to C_4 and C_7 hydrocarbons. The predominant isomers for isobutyl species are isobutane and isobutene. Triptyl species (2,2,3-trimethylbutane and 2,2,3-trimethyl-but-1-ene) make up about 75% of all C_7 species. Rates increase but selectivities transition to an aromatic-dominated product with increasing temperature (especially above 250°C). In this model, DME is converted to gasoline-range hydrocarbons at a maximum temperature of 450°F (232°C). In the Aspen Plus simulation, the selectivity and conversion of each compound is set to match targets that are believed to be attainable through near-term research efforts (Table S6). With the current metal modified beta-zeolite catalyst, the C_4 products are recycled to the reactors for methylation of olefins to larger hydrocarbons. Unconverted DME is also recycled to the reactors for additional homologation. The single-pass conversion of DME is about 40% and the resulting overall DME conversion (including recycle) is 92.5%. Hydrogen addition is considered for the current target process assessment and has the purpose of reducing aromatic byproducts. Hexamethylbenzene (HMB) is used as a proxy for coke and heavy aromatic deposits on the catalyst in this analysis, given the literature precedent for its formation in this process.[19] The inclusion of HMB is also used to satisfy the overall stoichiometry of the reactions.

Temperature control and heat removal from the hydrocarbon synthesis reactors is accomplished by using multiple adiabatic reactors in series with inter-stage cooling. The heat is recovered as low pressure steam. It is assumed that while two reactors are in DME-to-hydrocarbons service, the other reactor is in coke-burn/catalyst regeneration. The catalyst regenerator burns carbon (coke) deposits off the catalyst particles, regenerating the catalyst activity and providing heat for steam generation. Future pilot-scale experiments will demonstrate and validate the conceptual hydrocarbon synthesis reactor system configuration.

Product recovery

The separation step of the high-octane gasoline mixture is relatively simple compared to that used in refinery operations for gasoline recovery.[21] This process area consists of just two distillation columns. The water-free crude hydrocarbon product is first sent to the first distillation column where liquid C_{4+} and gasoline-range hydrocarbons are separated from the light ends (C_{3-}) and unconverted DME. DME is recycled to the hydrocarbon synthesis reactor and the light gas stream (i.e., C_{3-} or fuel gas) is sent to the fuel combustor in the synthesis gas clean-up area. The bottom product is subsequently sent to the second column where C_4 is separated from gasoline-range hydrocarbons. The overhead of the second column is then recycled to the hydrocarbon synthesis reactors. The bottoms of the second column are the high-octane hydrocarbons which are cooled and then stored for sale as high-octane gasoline.

Heat and power generation

A conventional steam cycle produces steam for direct injection into the gasifier and reformer. Indirect steam is used for heating associated with distillation and the acid gas strippers in the acid gas removal system. Electricity is generated using three steam turbines, with intermediate reheat, to meet the demands of the plant. As mentioned earlier in the methanol synthesis section, additional electricity is generated by sending a portion of the pressurized unreacted gases from the methanol synthesis reactor through a turbo-expander. The majority of electricity is used for syngas compression. The steam cycle is integrated with the biomass conversion process. Preheaters, steam generators, and super-heaters are integrated within the process design to generate the steam from boiler feed water. Process condensate is recycled to the steam cycle, de-gassed, treated, and combined with make-up water.

Cooling water and other utilities

A cooling water system is included in the Aspen Plus model to determine the requirements of each cooling water heat exchanger within the biomass conversion process as well as make-up water and power requirements. The design also includes additional water optimization; process condensate is treated and combined with the cooling water make-up to reduce fresh water consumption.

Heat integration

Recovery and utilization of waste heat from the high temperature streams is imperative to maximize the overall efficiency of the plant design. Therefore, a pinch analysis was performed and a heat exchanger network was designed for this high-octane gasoline production process. The design of the heat integration network resulted in significant energy savings and corresponding increases in product yields. Detailed design specifications can be found in the full report.[13]

Sustainability metrics

Key sustainability metrics for the conceptual process are presented to quantify environmental impacts. Direct

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biorefinery emissions (i.e., CO_2, NO_2 and SO_2), water consumption, and other process-related metrics were derived from the conversion process model already described. The boundary for all metrics is the biorefinery (or the fuel production stage) which was the focus of this research. Upstream processes (i.e., feedstock production and transportation) and downstream processes (i.e., fuel distribution and vehicle operation) are not incorporated in the quantification of the metrics. Embodied emissions and resource consumption from the biorefinery related to construction and maintenance, material and energy inputs, and emission/consumption credits associated with co-products were also included.

For life-cycle assessment, SimaPro v.8.0.2 software[22] was used to develop and link units quantifying life cycle impacts. All process input/output inventory estimates were derived from Ecoinvent v.2.2[23] and the US Life Cycle Inventory (LCI)[24] processes to fill the data gaps. The Ecoinvent processes were modified to reflect US conditions and the US LCI processes were adapted to account for embodied emissions and fossil energy usage. The material and energy flows of the conversion step capture the impacts of input raw materials, and outputs, such as emissions, wastes, and coproducts as predicted by the process model (Table S9).

Results and discussion

Process performance

The final composition of the high-octane gasoline from the current methanol to hydrocarbons process is compared with those from a typical conventional gasoline and the reported composition for MTG gasoline,[21] as presented in Fig. 3. Gasoline produced from this design contains only paraffins (87 wt%) and olefins (13 wt%). While coke and heavy aromatics are produced during DME homologation, they are assumed to deposit on the catalyst surface and are subsequently removed during catalyst regeneration. The high-octane number (> 92) of the gasoline blendstock is attributed to its high concentration of branched paraffins (99% of the total paraffins). Furthermore, as opposed to MTG, no durene is formed in this high-octane gasoline process. In this design, hydrogen is added to suppress formation of coke and aromatic byproducts (coke precursors). Recent study reveals that a Cu-modified H-BEA catalyst is able to incorporate hydrogen from gas-phase H_2 co-fed with DME into the desired branched alkane products while maintaining the high C_4 and C_7 carbon selectivity of the parent H-BEA.[8] This hydrogen incorporation is achieved through the combination of metallic Cu nanoparticles present on the external surface of the zeolite (which perform H_2 activation and olefin hydrogenation) and Lewis acidic ion-exchanged cationic Cu present within the H-BEA pores (which promotes hydrogen transfer). A comparative summary of the characteristics of the pathway from biomass feedstock to high-octane gasoline blendstock relative to those of the traditional MTG process is presented in Table 1.

Table 5 presents a brief summary of high-octane gasoline yield, which represent the overall process performance. The annual production rate is 47 million gallons, equaling to 45 gallon gasoline equivalent (GGE) or 170 liter gasoline equivalent (LGE) per year. Similarly, the corresponding product yield is 65 gallons or 62 GGE per dry US ton (258 LGE/dry tonne). The distribution of the total energy content in dry biomass (LHV basis) is shown in Fig. 4. The total energy in the dry portion of the biomass feed (0% moisture) is approximately 1470 MMBtu/hr (1550 GJ/hr). Approximately 45% of the LHV is recovered in gasoline range product. A significant amount (31%) is lost through air-cooled exchangers, and the rest (24%) is lost because of moisture in the feed and other water input to the process, as well as electrical and thermal losses.

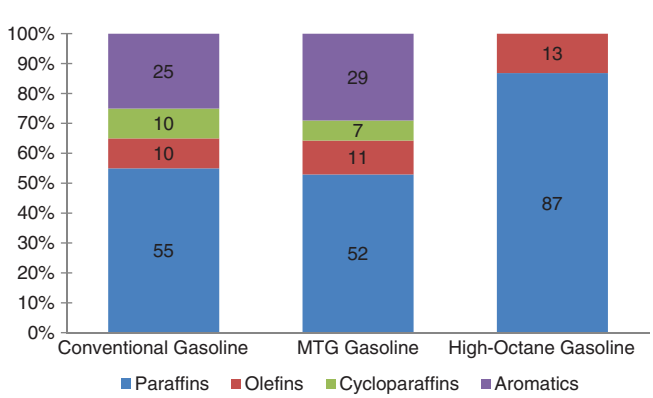

Figure 3. Comparison of gasoline composition (in wt%).

Table 5. Production rates and yields at plant operating capacity.

Production rates		
MM (gal/yr)	MM (GGE/yr)	MM (LGE/yr)
47	45	170
Product yields		
gal/dry U.S. ton	GGE/dry U.S. ton	LGE/dry tonne
65	62	258

GGE: gallon gasoline equivalent
LGE: liter gasoline equivalent

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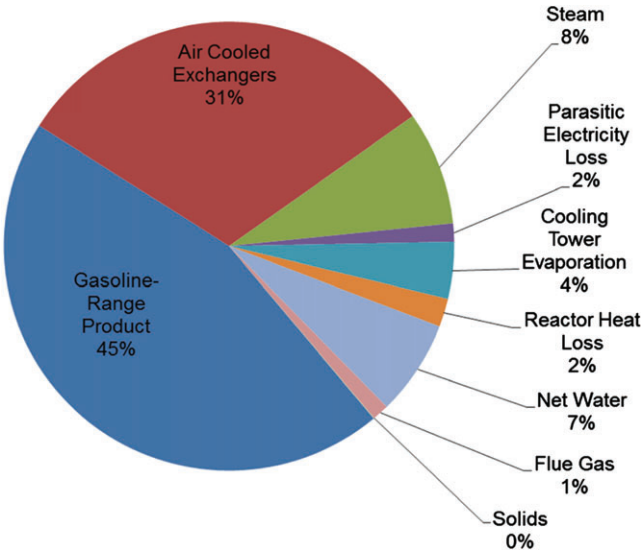

Figure 4. Overall energy analysis (dry biomass LHV basis).

Total capital investment

The capital costs for each plant area are based on data from various sources including NREL design reports, technology licensors, industry equipment suppliers, cost estimates from Harris Group Inc., published literature, and Aspen Icarus Process Evaluator 2006.5 cost estimating software. The purchased costs for the equipment and installation factors are used to determine the installed equipment cost. Table 6 presents a summary of total purchased equipment costs (TPEC), installation factors ($f_{installation}$), and total installed costs (TIC) for each area of the plant.

The indirect costs (non-manufacturing fixed-capital investment costs) are estimated using factors based on the total direct cost (TDC). The factors are summarized in Table 7 as percentages of TPEC, total direct cost (TDC), and fixed capital investment (FCI), which is equal to the sum of TDC and total indirect costs. With the calculated total installed cost and assumptions for indirect costs and working capital, the FCI and TCI are calculated. Table 8 presents a summary of these calculations.

Operating costs

Operating costs, including labor costs, materials and feedstock costs, utility costs, and disposal costs, were evaluated for the 2000 dry metric tonne/day facility. Table 9 demonstrates the breakdown of these operating costs and their contribution to the total production cost. Variable operating costs are determined based on raw materials, waste-handling charges, and by-product credits incurred only during the process operation. Table 10 summarizes the variable operating costs, including the annualized costs for catalysts, olivine, and disposal. The total variable operating cost for the plant is 37.1 cents per LGE or $62.93 million per year. Fixed operating costs are generally incurred in full whether or not the plant is producing at full capacity. These costs include labor and various overhead items. Many of the assumptions on fixed operating costs follow NREL's

Table 6. Summary of capital cost estimates per process area (2011 U.S. dollars).

Area	Process description	TPEC (MM$)	$f_{Installation}$	TIC (MM$)	Percent of total TIC
100	Feed handling and preparation*	0.1	2.00	0.2	0.1
200	Gasification	21.8	2.32	50.5	20.1
300	Synthesis gas cleanup and syngas compression	36.4	1.94	70.7	28.1
400	Acid gas removal and methanol synthesis	16.4	2.28	37.3	14.8
500	Methanol conditioning	1.3	2.65	3.4	1.4
600	Steam system and power generation	22.8	1.68	38.1	15.2
700	Cooling water and other utilities	3.1	2.25	7.0	2.8
1400	Methanol to high-octane gasoline synthesis	18.0	2.15	38.7	15.4
1500	Product recovery	2.4	2.23	5.4	2.2
Areas 100-400, 1400-1500: Inside Battery Limits (ISBL)		**96.3**	**2.14**	**206.1**	**82.1**
Areas 600-700: Outside Battery Limits (OSBL)		**25.8**	**1.74**	**45.1**	**17.9**
Total		**122.2**	**2.06**	**251.2**	**100.0**

*Equipment costs shown for this area are for the cross-flow dryer only. Capital investment costs associated with feed handing and preparation are included in the pre-unit blended biomass feedstock price.

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earlier reports[12,13] and Peters and Timmerhaus.[25] General overhead equals to 90% of total salaries, maintenance equals to 3% of fixed capital investment (FCI), and insurance and taxes equal to 0.7% FCI. As shown in Table 9, the total fixed operating costs are 11.6 cents per liter of fuel produced (12.2 cents/LGE) or $20.65 million per year.

Minimum fuel selling price

Once the capital and operating costs are determined, a discounted cash flow rate of return (DCFROR) calculation was performed to determine the minimum fuel selling price (MFSP) that meets the economic parameter using the general methodology[12,21,26,27] and the economic parameters summarized in Table 2. The MFSP value represents the minimum selling price of high-octane gasoline assuming a 30-year plant life and 40% equity financing with 10% internal rate of return and the remaining 60% debt financed at 8% interest. The resulting MFSP for high-octane gasoline is determined to be $3.25 per gallon of gasoline blendstock, equaling to $3.41/GGE or $0.90/LGE, in 2011 US dollars. Note that the baseline used in the GGE and LGE calculations is obtained from GREET, lower heating value (LHV) of 116,090 BTU/gal (32.36 MJ/L) for gasoline blendstock;[28] the LHV for the high-octane gasoline produced in this work is 110,754 BTU/gal (30.87 MJ/L). A summary of the costs contributing to the MFSP is presented in Fig. 5. The cost contributions to the MFSP are divided into the capital, variable, and fixed operating costs. Feedstock cost is the largest single contributor to the MFSP and represents essentially all (92%) of the variable operating cost. The cost contribution chart shows coproduct credits from the methanol synthesis area, for electricity from the syngas expansion, and for electricity from the steam system and power generation area. However, the process was adjusted so that

Table 7. Cost factors for indirect costs.

Indirect Costs	% of TPEC	% of TDC*	% of FCI*
Prorated expenses	21.2	10.0	6.3
Home office and construction fees	42.5	20.0	12.5
Field expenses	21.2	10.0	6.3
Project contingency	21.2	10.0	6.3
Other costs (start-up and permits)	21.2	10.0	6.3
Total indirect costs	**127.4**	**60.0**	**37.5**
Working capital			**5.0**

*Percentages of TDC and FCI exclude land purchase cost.

Table 8. Project cost worksheet (2011 U.S. dollars).

Total purchased equipment cost (TPEC)		**$122,169,000**
Installation factor		2.056
Total installed cost (TIC)		**$251,234,000**
Other direct costs		
Site development	4.0% of ISBL	$8,246,000
Total direct costs (TDC)		**$259,480,000**
Indirect costs	% of TDC (ex Land)	
Prorated expenses	10.0%	$25,948,000
Home office and construction fees	20.0%	$51,896,000
Field expenses	10.0%	$25,948,000
Project contingency	10.0%	$25,948,000
Other costs (start-up and permits)	10.0%	$25,948,000
Total indirect costs	**60.0%**	**$155,688,000**
Fixed capital investment (FCI)		**$415,168,000**
Land (not depreciated)		$1,610,000
Working capital	5.0% of FCI (ex Land)	$20,759,000
Total capital investment (TCI)		**$437,537,000**
TCI / TPEC		3.581
FCI Lang Factor = FCI / ISBL TPEC		4.310
TCI Lang Factor = TCI / ISBL TPEC		4.542

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Table 9. Breakdown of operating cost contribution (2011 U.S. dollars).

	cents/GJ of products (cents/MMBtu of products)	cents/LGE of products (cents/GGE of products)	Contribution (%)
Feedstock	1054.6 (1112.6)	34.1 (129.2)	37.9
Natural gas	0 (0)	0 (0)	0.0
Catalysts	45.9 (48.5)	1.5 (5.6)	1.7
Olivine	9.7 (10.3)	0.3 (1.2)	0.3
Other raw materials	25 (26.4)	0.8 (3.1)	0.9
Waste disposal	10.2 (10.8)	0.3 (1.3)	0.4
Electricity transfer	0 (0)	0 (0)	0.0
Electricity	0 (0)	0 (0)	0.0
Fixed costs	375.8 (396.5)	12.2 (46)	13.5
Coproduct credits	0 (0)	0 (0)	0.0
Capital depreciation	251.2 (265)	8.1 (30.8)	9.0
Average income tax	148.4 (156.5)	4.8 (18.2)	5.3
Net annual profit (after tax)	859.5 (906.8)	27.8 (105.3)	30.9
Total	2780.3 (2933.4)	90 (340.5)	

the electricity generated is balanced by the electricity required by all other areas, and thus there is no net credit for electricity generation.

Sensitivity analyses

A sensitivity analysis was performed to examine the variability of the MFSP of high-octane gasoline as a function of changes in various process parameters, raw material costs, and financial assumptions. The results of the sensitivity analysis are summarized in Fig. 6. The data are organized by potential impact of parameter deviation on MFSP value (highest to lowest). The sensitivity scenarios represent a deviation in a single project parameter with all other parameters remaining constant at base case values. The case numbers in the text refer to the numbers shown in the labels of Fig. 6.

Deviation from base case financial and market parameters can have significant impacts on the MFSP. The base case financial assumptions are shown in Table 2. Case 1 in Fig. 6 shows the possible savings realized by economies of scale from changes to the plant size. It is assumed in the plant size sensitivity scenario that the same technology is utilized for all plant sizes. A major constraint to larger plant sizes will be significantly higher feedstock logistics costs. However, the economies of scale can potentially be enabled by an advanced logistic supply system.[29] An increase in required internal rate of return (IRR) for the project from 10% to 20% (Case 2) would increase the MFSP from \$0.90 to \$1.16 per LGE (an increase of 28.5%).

Although the plant design basis specifies blended biomass feedstock with mostly woody biomass from pulpwood and forest residues, there is potential for other feedstocks to be introduced as feed, based on future biomass availability. The high ash, low carbon, and high oxygen content in corn stover results in a 20.4% increase in the MFSP (Case 3). The negative impacts of higher ash and high moisture contents are quantified in Cases 6 and 8, respectively. Product yields decrease for higher moisture feedstocks because more energy is used for drying, resulting in higher MFSP; an increase in moisture content from 10% to 20% results in a 9.2% increase in the MFSP. Similarly, an increase in the ash content from 1% to 8% raises the MFSP by 11.7%. The impacts of changes in the feedstock cost are shown in Case 7.

The impact of biomass particle size on the MFSP is not considered here. It has been reported that char formation increases with increasing particle size, but decreases with increasing temperature.[30] However, at gasification temperatures above 1472°F (800°C), particle size exhibited little impact on char formation. As the gasifier of the current design operates at 1,617°F (880°C), the amount of char produced is expected to be similar with different particle sizes. Furthermore, with little variation in char production, the heat generated from char combustion remains unaffected. Consequently, the particle size is expected to have little impact on the process economics.

The yield of the high-octane gasoline blendstock exhibits a direct impact on MFSP, as shown in Case 9. An increase

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Table 10. Summary of variable operating costs (2011 U.S. dollars).

Variable	Information and operating cost
Gasifier bed material	Synthetic olivine and MgO. Initial fill then a replacement rate of 0.01 wt% of circulation or 7.2 wt% per day of total inventory. Delivered to site by truck with self-contained pneumatic unloading equipment. Disposal by landfill.
	Olivine price: $275/tonne
	MgO price: $580/tonne
Tar reformer catalyst	To determine the amount of catalyst inventory, the tar reformer was sized for a gas hourly space velocity (GHSV) of 2,476/h based on the operation of the tar reformer at NREL's pilot plant demonstration unit. GHSV is measured at standard temperature and pressure. Initial fill then a replacement rate of 0.15 wt% of catalyst inventory per day.
	Price: $47.70/kg based on NREL calculations using metals pricing and costs for manufacturing processes.
Methanol synthesis catalyst	Initial fill then replaced every 4 years based on expected catalyst lifetime.
	Catalyst inventory based on GHSV of 8,000/h.
	Price: $21.36
DME synthesis catalyst	Initial fill then replaced every 4 years based on expected catalyst lifetime.
	Catalyst inventory based on GHSV of 605/h.
	Price: $22.71/kg
Beta-zeolite catalyst	Initial fill then replaced every 3 years based on expected catalyst lifetime.
	Catalyst inventory based on total gasoline productivity of 0.14 kg/kg-cat/h.
	Price: $67.90/kg based on cost survey from manufacturers.
Zinc oxide catalyst	Initial fill then replaced every 5 years based on expected catalyst lifetime.
	Catalyst inventory based on GHSV of 4,280/h.
	Price: $13.70/kg
Solids disposal	Price: $60.36/tonne
Diesel fuel	Usage: 38 L/h plant-wide use.
	2012 price projection: $22.39/GJ
Water makeup	Price: $0.35/tonne
Chemicals	Boiler feed water chemicals-Price: $6.13/kg
	Cooling tower chemicals-Price: $3.67/kg
	LO-CAT chemicals-Price: $498.98/tonne sulfur produced from NREL/Harris Group Inc. estimates based on other projects.
	Selective amine makeup-Price: $39.81/million kg acid gas removed.
Wastewater	Most wastewater is cleaned using an RO system and recycled. The balance of the wastewater is sent to off-site treatment facility.
	Price: $0.83/tonne

in the yield from the baseline (65 gal/dry US ton or 271 L/dry tonne) to 70 gallons leads to a 7.2% decrease in MFSP. Likewise, decreasing the yield from 65 gallons to 60 gallons per dry US ton results in an increase of 8.1% in the MFSP.

The impact of changes to the capital costs of the gasifier and reformer is shown in Case 16. Variability in TCI can also have a major impact on MFSP. Conceptual designs like this generally result in accuracy of ±10% to 30% for capital investment estimation.[25] Applying a variability range of –10% to +30% to a TCI sensitivity (Case 4) results in an MFSP range of $0.86 to $1.03 per LGE (–4.8% to +14.5%).

An interest rate increase (Case 13) from the base value of 8% to 12% increases MFSP to $0.95 per LGE (an increase of about 5.0%). Successful R&D and demonstration projects would reduce investment and lending risks and ease the expected rate of return to investors and minimize loan interest rates, reducing MFSP toward the base case value.[31]

Extending the hydrocarbon synthesis catalyst lifetime (Case 14) from the base case of two years and reducing the tar reformer catalyst cost from the base case value (Case 28) will also reduce the MFSP. Case 23 shows that decreasing the single-pass DME conversion to high-octane hydrocarbons from 40% to 25% leads to a mere 1.7 % increase in MFSP.

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Increased availability of low cost natural gas facilitates the development of combined biomass and natural gas to liquids technology. Co-conversion of biomass with natural gas can simultaneously increase fuel yields and reduce fuel production costs provided that the lifecycle GHG thresholds specified in Energy Independence and Security Act (EISA) of 2007[32] are not violated. Case 11 shows that co-processing natural gas at the lifecycle GHG threshold limit

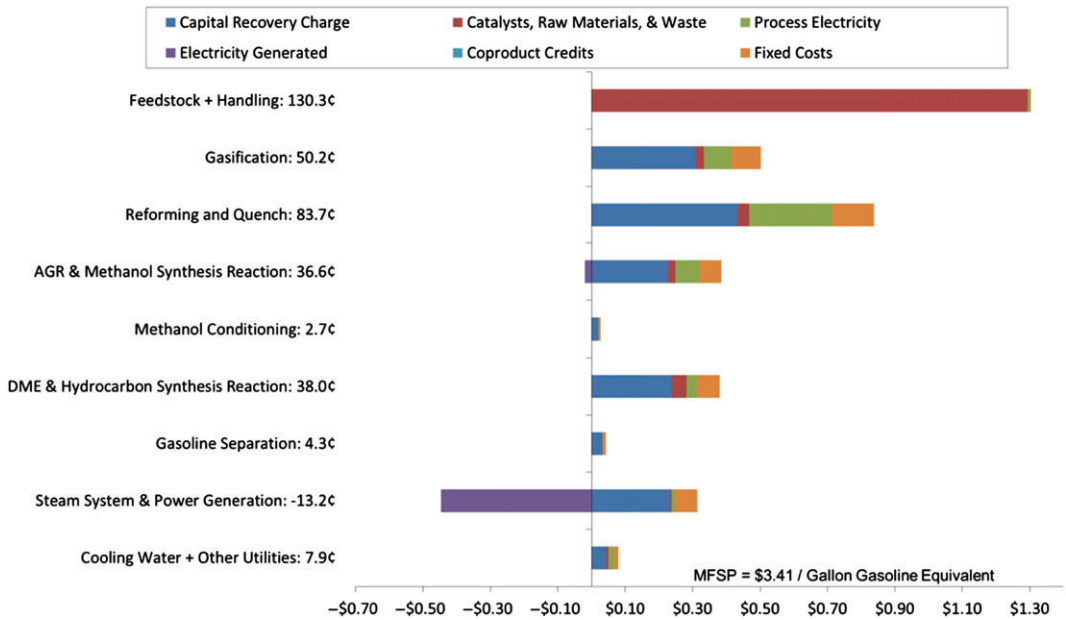

Figure 5. Cost contribution details for high-octane gasoline from each process area.

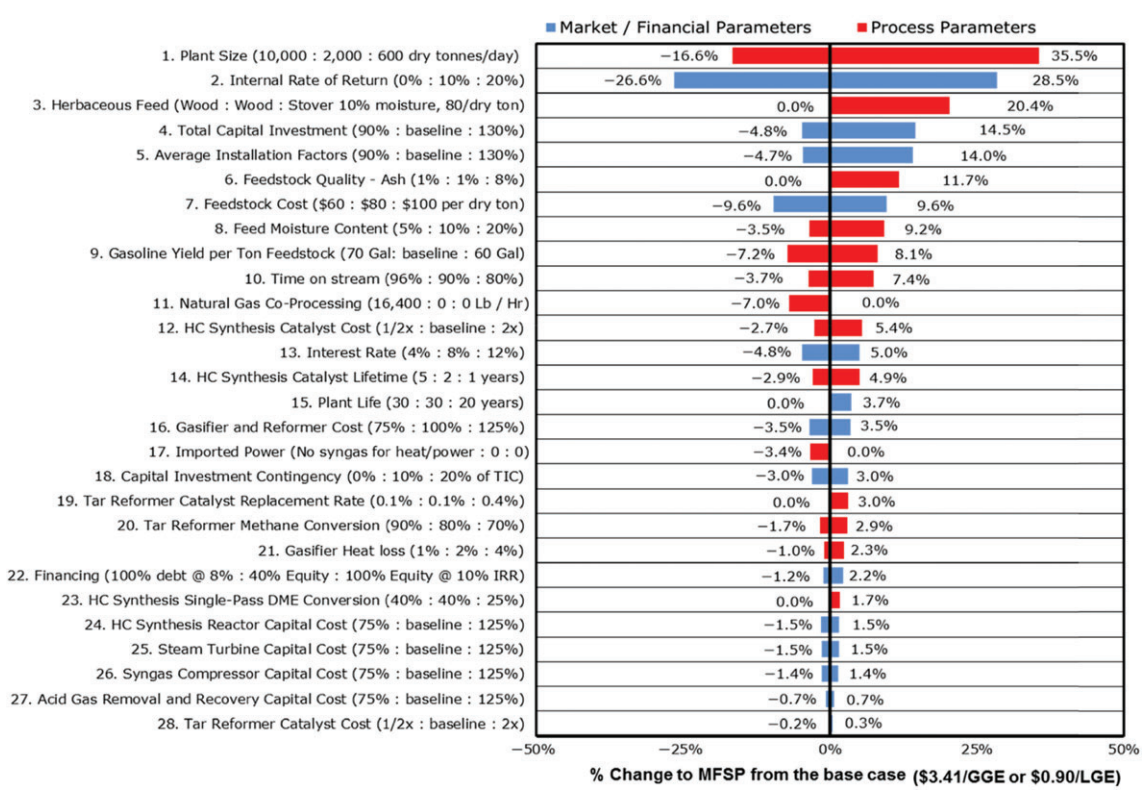

Figure 6. Results of sensitivity analyses.

(i.e., 60% GHG emissions reduction relative to the petroleum baseline) decreases the MFSP by 7% ($0.84/LGE).

Because the heat and power requirements of the process cannot be met through char combustion and combustion of available fuel gas and other process off-gases alone, some raw syngas from the indirect gasifier is diverted from liquid fuel production for heat and power production. Although this option makes the design energy self-sufficient, it also lowers the overall product yield. Case 17 is a sensitivity case without utilizing raw syngas for plant heat and power; electricity import is required. Importing electricity in lieu of combusting syngas improves both fuel yield and carbon-to-fuel efficiency by 7%, leading to lower MFSP, $0.87/LGE, or 3.4% lower than the base case. The corresponding GHG emissions reduction relative to petroleum gasoline benchmark is 82%.

Analysis of premium properties of high-octane gasoline blendstock

The value of a gasoline blendstock is a function of its properties (i.e., octane value). The modeled blendstock is high in branched paraffin content, similar to alkylates from petroleum refineries. The current target compounds have pure-component octane numbers of ~110 and blending octane numbers of 140+. High-octane blendstocks are likely to carry a premium price relative to the finished fuel value. However, the potential premium value of the high-octane gasoline blendstock from the process described in this study is not taken into consideration in MFSP determination. As exhibited in Fig. 7, the estimated octane value (x-axis) and minimum fuel selling price (y-axis) are compared with octane values and wholesale prices of gasoline finished fuel blends and common gasoline blendstocks (with varying octane values).[33,34] There are two data points on the plot representing the high-octane gasoline blendstock. The first data point, labeled 'Product (R+M)/2 (Pure-Component Octane #s)', represents the calculated weighted average octane value (RON+MON)/2, based on the molar composition of the high-octane gasoline blendstock product and published octane values for pure components. The second data point, labeled 'Product (R+M)/2 (Blending Octane #s from Literature)', represents the calculated weighted average blending octane value (RON+MON)/2, based on the molar composition of the high-octane gasoline blendstock product and published octane values for blending pure components.[35,36] The resulting blend octane number is higher than that derived from pure components is due to mixing interactions between various components in the blend. Based on the data in Fig. 7, the high-octane gasoline blendstock is at least cost-competitive with fossil blendstocks of

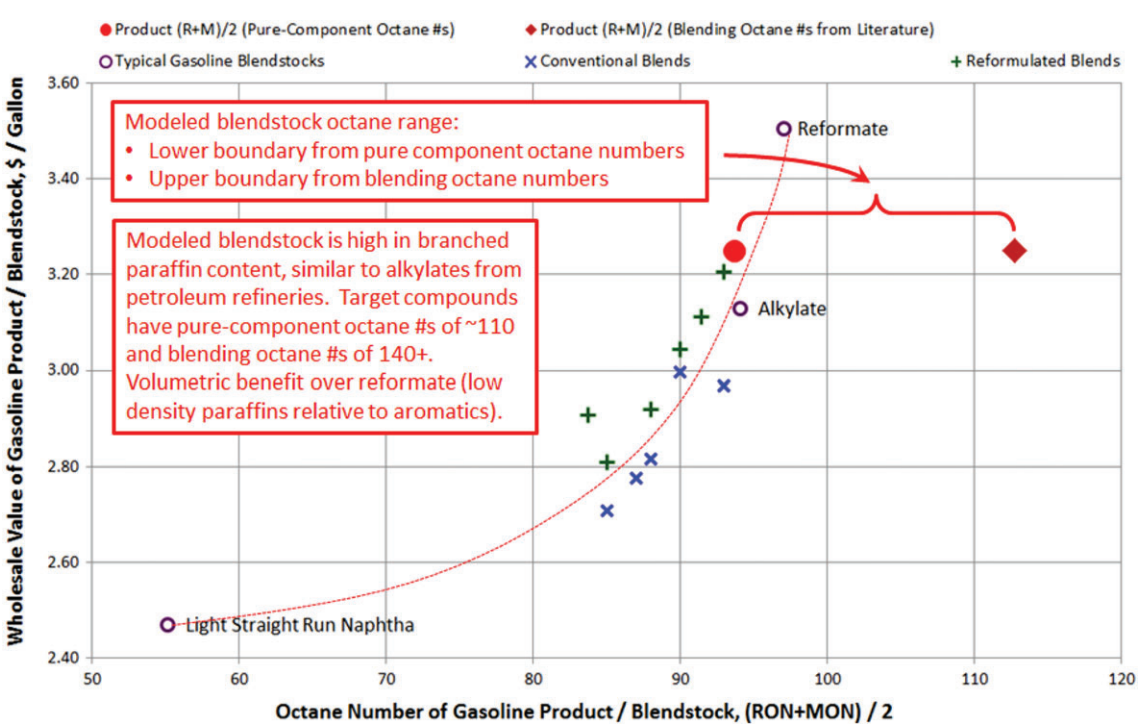

Figure 7. Comparison of octane values and wholesale prices.

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comparable octane numbers at ~92 (RON+MON)/2 and $3.20 per gallon ($0.85/L). In addition, the product has potential to demonstrate higher blended octane benefit, approaching 110 (RON+MON)/2. Analytical testing on actual products and blends with other gasoline components will serve to validate the analysis results and is in progress.

High-octane gasoline blendstock blending strategy

As the biofuels industry continues to expand, it will become critical to understand the means to integrate biomass-derived blendstocks into existing refinery infrastructure and to provide opportunities for refiners to maximize product value. A gasoline blending strategy is typically developed to achieve the combination of cost minimization and value maximization, without violating the fuel-grade gasoline specifications. One of the specifications contained in ASTM D4814 standard specification for gasoline[37] is the distillation class requirements according to ASTM D86.[38] Figure 8 shows the modeled distillation curve for the high-octane gasoline blendstock compared with several seasonal average finished gasoline blends. The plot is intended to identify a simple blending strategy based solely on the distillation curve for the blendstock. Based on this simple analysis, the blending strategy for the blendstock is likely to include two major steps – (1) blend lighter naphtha blendstock to meet the maximum 10 vol % of 158°F (typical front-end volatility) in the finished fuel and (2) blend a heavier naphtha blendstock to meet minimum end point of 300°F (typical tail-end volatility) in the finished fuel. The front-end volatility is adjusted primarily to provide easy cold starting, easy hot starting, and low evaporation and running-loss emissions. The end-point volatility is adjusted largely to provide good fuel economy after engine warm-up, freedom from engine deposits, minimum fuel dilution of crankcase oil, and minimum volatile organic compound exhaust emissions. The sources of quality information utilized for Fig. 8 are Colonial Pipeline Company[39] and Chevron.[40]

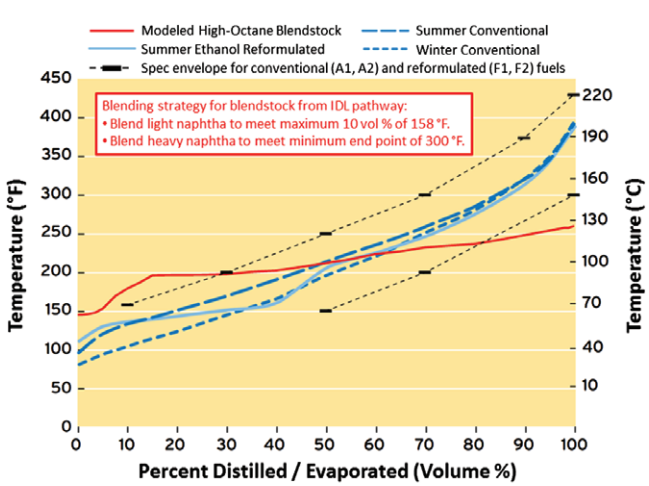

Figure 8. Distillation curve comparison between target blendstock and finished gasolines.

Sustainability metrics

The success of the biofuels industry depends not only on economic viability, but also on environmental sustainability. A biorefinery process that is economically feasible, but suffers from key sustainability drawbacks, is not likely to represent a long-term solution to replace fossil-derived fuels. Overarching concerns like environmental sustainability need to be addressed for biofuels production. Combined TEA and environmental sustainability assessment of emerging pathways helps facilitate biorefinery designs that are both economically feasible and minimally impactful to the environment. Important sustainability metrics for the conversion stage of the biofuel life-cycle are: greenhouse gas (GHG) emissions, fossil energy consumption, fuel yield, biomass carbon-to-fuel efficiency, water consumption, and waste-water generation.

The sustainability metrics are estimated for the high-octane gasoline conversion plant, as shown in Table 11. As the conversion plant is essentially balanced for zero net electricity and does not require natural gas for heat generation, the net GHG emissions and fossil energy consumption associated with the conversion stage are very low, 0.6 g $CO_{2\text{-}e}$/MJ and 6 kJ/MJ, respectively. Direct CO_2 emission from the conversion process is biogenic CO_2 and is not included in GHG emissions quantification per IPCC

Table 11. Summary of sustainability metrics for high-octane gasoline conversion process.

GHGs (g $CO_{2\text{-}e}$/MJ fuel) – (fossil emissions, excluding biogenic CO_2)	0.60
Fossil Energy Consumption (MJ fossil energy/MJ fuel product)	6.0E-03
Total Fuel Yield (L/dry metric ton)	271
Biomass Carbon-to-Fuel Efficiency (C in fuel/C in biomass)	31.2%
Water Consumption (m^3/day; L/LGE)[a]	911; 1.76
Wastewater Generation (m^3/day; L/LGE)	123; 0.24

[a]Water consumption and wastewater generation include only direct use/emissions and do not include water associated with upstream production of materials and energy used at the plant.

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global warming methodology.[41] Consequently, the contributions to GHG at the conversion stage are solely from the associated underlying processes (e.g. material inputs/outputs to and from the facility to support process operations). The analysis was expanded to estimate the full life-cycle GHG emissions for fuels produced from the model feedstock, a blend of pulpwood (45%), wood residues (32%), switchgrass (3%), and constructuction and demolition waste (20%).[11] The full life-cycle GHGs for the high-octane gasoline blendstock from the blended feedstock are estimated at 14.6 g $CO_{2\text{-}e}$/MJ which corresponds to an 84% GHG reduction relative to the 2005 petroleum gasoline baseline GHGs (93.08 g $CO_{2\text{-}e}$/MJ).[32]

The carbon conversion efficiency of the design case is estimated to be 31.2% which is comparable to that achieved by the thermochemical ethanol process (31%),[2] but is noticeably higher than that from the biological conversion of the sugars to hydrocarbons process (26%).[27]

Consumptive water use associated with the high-octane gasoline production consists of make-up water for the steam and cooling systems. Boiler feed water make-up is needed to replace steam consumed in the reformer. Fresh cooling water is needed to make up for losses at the cooling tower (e.g. evaporation and drift) and blowdown for maintenance of the recirculating cooling system. Water consumed for production of materials used at the biorefinery (e.g. catalysts) and for life-cycle stages upstream and downstream of conversion is not included in the analysis. Boiler feed water make-up for steam production is approximately 68% of the total water consumed for the conversion processes. Approximately 12% of the total steam is consumed in the reforming area. Cooling water make-up is approximately 2% of the total water use. It is important to note that steam drum blowdown, cooling tower blowdown, and process water condensate are recycled for use for both steam generation and cooling, significantly reducing raw cooling water make-up. The water consumption for the current high-octane gasoline production is 1.76 L/LGE, which is better than the crude oil refining to gasoline (2.8–6.6 L/LGE).[42]

Conclusions

This paper summarizes the results of a conceptual process design with detailed mass and energy balances in Aspen Plus, economic analysis, and environmental sustainability analysis for the production of high-octane gasoline from biomass via a methanol intermediate. The analysis shows that biomass-derived high-octane gasoline from a thermochemical conversion process has the potential to be cost-competitive with gasoline. The gasoline equivalent price by lower heating value is $3.41 per gallon ($0.90 per liter) with underlying assumptions and catalyst performance targets outlined here. The potential premium value of the high-octane gasoline blendstock from the process described in this study is also assessed. The product is determined to be at least cost-competitive with fossil blendstocks of comparable octane numbers at about 92 and $3.20 per gallon ($0.85/L), with the potential to demonstrate higher blended octane benefit with average octane numbers approaching 110. The sensitivity analysis shows that there is less than ±20% prediction uncertainty in MFSP resulting from a ±30% uncertainty in the total capital cost estimation. While there is always a chance of large escalations in capital costs, acquisition of recent estimates and vendor quotes for most of the equipment reduces the probability of gross over- or under-estimation of costs. Certain unit operations used in the plant design, such as the methanol synthesis reactor, are commercially available. Gasification and tar reforming have been demonstrated in NREL's thermochemical pilot plant. The DME to high-octane hydrocarbons synthesis is the area that is least developed and most in need of further research. The net GHG emissions associated with the conversion stage are very low (0.6 g $CO_{2\text{-}e}$/MJ) because the conversion plant has no net electricity import requirement and does not require any fossil energy input. The overall life-cycle GHG emissions (14.6 g $CO_{2\text{-}e}$/MJ from feedstock production to vehicle operation) reduction exceeds the 60% reduction criteria relative to the 2005 petroleum gasoline baseline (93.08 g $CO_{2\text{-}e}$/MJ). TEA results in this study can serve as the baseline for future comparison and as a basis for comparing this process to other biomass-to-liquid fuel pathways.

Acknowledgments

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References

1. Bioenergy Technologies Office, Multi-Year Program Plan [Internet]. Washington, DC: US Department of Energy; 2013. Available at: https://www1.eere.energy.gov/bioenergy/pdfs/mypp_may_2013.pdf [Accessed February 20, 2015]

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2. Dutta A, Hensley J, Bain R, Magrini K, Tan ECD, Apanel G *et al.,* Technoeconomic analysis for the production of mixed alcohols via indirect gasification of biomass based on demonstration experiments. *Ind Eng Chem Res* **53**(30):12149–12159 (2014).
3. Hindman M, Methanol to Gasoline (MTG) Technology: An Alternative for Liquid Fuel Production. World CTL Conference April 13, Beijing, China (2010).
4. ExxonMobil Research and Engineering, Methanol to Gasoline (MTG): Production of Clean Gasoline from Coal [Online]. Available at: http://www.exxonmobil.com/Apps/RefiningTechnologies/files/sellsheet_09_mtg_brochure.pdf [Accessed October 13, 2015].
5. Mokrani T and Scurrell M, Gas conversion to liquid fuels and chemicals: the methanol route-catalysis and processes development. *Catal Rev* **51**(1):1–145 (2009).
6. US EPA, EPA Regulatory Announcement: Control of hazardous air pollutants from mobile sources: final rule to reduce mobile source air toxics [Online]. Washington, DC: US Environmental Protection Agency, Office of Transportation and Air Quality (2007) p. 5. Report No.: EPA420-F-07-017. Available at: http://www.epa.gov/oms/regs/toxics/420f07017.pdf [Accessed February 20, 2015].
7. Ahn JH, Temel B and Iglesia E, Selective homologation routes to 2,2,3-trimethylbutane on solid acids. *Angew Chem Int Ed Engl* **48**(21):3814–3816 (2006).
8. Schaidle JA, Ruddy DA, Habas SE, Pan M, Zhang G, Miller JT *et al.,* Conversion of dimethyl ether to 2,2,3-trimethylbutane over a Cu/BEA catalyst: Role of Cu Sites in hydrogen incorporation. *ACS Catal* **5**(3):1794–1803 (2015).
9. Craig KR and Mann MK, Cost and performance analysis of biomass-based integrated gasification combined-cycle (BIGCC) power systems [Internet]. Golden, CO: National Renewable Energy Laboratory (1996). Report No.: NREL/TP-430-21657. Available at: http://www.osti.gov/servlets/purl/419974-x2KZhJ/webviewable/ [Accessed February 20, 2015].
10. ECN Phyllis2, Database for biomass and waste [IOnline] (2012). Available at: http://www.ecn.nl/phyllis/single.html February 20, 2015.
11. Jacobson J, Roni MS, Cafferty K, Kenney K, Searcy E and Hansen J, Feedstock and conversion supply system design and analysis – "The feedstock logistics design case" [Online]. Idaho Falls, ID: Idaho National Laboratory (2014). Report No.: INL/EXT-14-33227. Available at: http://www.osti.gov/servlets/purl/1169237/ [Accessed February 20, 2015].
12. Dutta A, Talmadge M, Hensley J, Worley M, Dudgeon D, Barton D *et al.,* Process design and economics for conversion of lignocellulosic biomass to ethanol: thermochemical pathway by indirect gasification and mixed alcohol synthesis [Online]. Golden, CO: National Renewable Energy Laboratory (2011). Report No.: NREL/TP-5100-51400. Available at: http://www.osti.gov/servlets/purl/1015885-Cjy0FT/ [Accessed February 20, 2015].
13. Tan ECD, Talmadge M, Dutta A, Hensley J, Schaidle J, Biddy M *et al*., Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons via indirect liquefaction: thermochemical research pathway to high-octane gasoline blendstock through methanol/dimethyl ether intermediates [Online]. Golden, CO: National Renewable Energy Laboratory (2015). Report No.: NREL/TP-5100-62402. Available at: http://www.nrel.gov/docs/fy15osti/62402.pdf [Accessed June 11, 2015].
14. Dutta A, Syngas mixed alcohol cost validation [Online]. Alexandria, VA: Bioenergy Technologies Office Project Peer Review (2013). Available at: http://www.energy.gov/eere/bioenergy/peer-review-2013 [Accessed February 23, 2015].
15. Carpenter DL, Bain RL, Davis RE, Dutta A, Feik CJ, Gaston KR *et al.*, Pilot-Scale gasification of corn stover, switchgrass, wheat straw, and wood: 1. Parametric study and comparison with literature. *Ind Eng Chem Res* **49**(4):1859–1871 (2010).
16. Magrini-Bair KA, Jablonski WS, Parent YO and Yung MM, Bench- and Pilot-scale studies of reaction and regeneration of Ni–Mg–K/Al2O3 for catalytic conditioning of biomass-derived syngas. *Top Catal* **55**(3-4):209–217 (2012).
17. Yung MM, Magrini-Bair KA, Parent YO, Carpenter DL, Feik CJ, Gaston KR *et al.,* Demonstration and characterization of Ni/Mg/K/AD90 used for pilot-scale conditioning of biomass-derived syngas. *Catal Lett* 1**34**(3-4):242–249 (2009).
18. Mollavali M, Yaripour F, Atashi H and Sahebdelfar S, Intrinsic kinetics study of dimethyl ether synthesis from methanol on γ-Al2O3 catalysts. *Ind Eng Chem Res* **47**(9):3265–3273 (2008).
19. Simonetti DA, Ahn JH and Iglesia E, Mechanistic details of acid-catalyzed reactions and their role in the selective synthesis of triptane and isobutane from dimethyl ether. *J Catal* **277**(2):173–195 (2011).
20. Simonetti DA, Ahn JH and Iglesia E, Catalytic co-homologation of alkanes and dimethyl ether and promotion by adamantane as a hydride transfer co-catalyst. *ChemCatChem* **3**(4):704–718 (2011).
21. Phillips SD, Tarud JK, Biddy MJ and Dutta A, Gasoline from wood via integrated gasification, synthesis, and methanol-to-gasoline technologies [Online]. Golden, CO: National Renewable Energy Laboratory (2011). Report No.: NREL/TP-5100-47594. Available at: http://www.osti.gov/servlets/purl/1004790-PNHiXm/ [Accessed February 20, 2015].
22. SimaPro, Amersfoort, the Netherlands: Product Ecology Consultants (2014).
23. Ecoinvent, Duebendorf, Switzerland: Swiss Center for Life Cycle Inventories (2010).
24. LCI, US Life-Cycle Inventory. Golden, CO: National Renewable Energy Laboratory (2008).
25. Peters M, Timmerhaus K and West R, *Plant Design and Economics for Chemical Engineers*. 5th edition, International Edition. New York, NY: McGraw-Hill (2004).
26. Phillips A, Aden A, Jechura J, Dayton D and Eggeman T, Thermochemical ethanol via indirect gasification and mixed alcohols synthesis of lignocellulosic biomass. [Online]. Golden, CO: National Renewable Energy Laboratory (2007). Report No.: NREL/TP-510-41168. Available at: http://www.nrel.gov/docs/fy07osti/41168.pdf [Accessed February 20, 2015].
27. Davis R, Tao L, Tan ECD, Biddy MJ, Beckham GT, Scarlata C *et al.,* Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons: dilute-acid and enzymatic deconstruction of biomass to sugars and biological conversion of sugars to hydrocarbons [Online]. Golden, CO: National Renewable Energy Laboratory (2013). Report No.: NREL/TP-5100-60223. Available at: http://www.osti.gov/servlets/purl/1107470/ [Accessed February 20, 2015].
28. The Greenhouse Gases, Regulated Emissions, and Energy use in Transportation (GREET) Model [Online]. Argonne National Laboratory (2012). Available at: http://greet.es.anl.gov [Accessed February 20, 2015].

29. Muth DJ, Langholtz MH, Tan ECD, Jacobson JJ, Schwab A, Wu MM *et al.*, Investigation of thermochemical biorefinery sizing and environmental sustainability impacts for conventional supply system and distributed pre-processing supply system designs. *Biofuels Bioprod Bioref* **8**(4):545–567 (2014).
30. Gaston KR, Jarvis MW, Pepiot P, Smith KM, Frederick WJ and Nimlos MR, Biomass pyrolysis and gasification of varying particle sizes in a fluidized-bed reactor. *Energ Fuel* 2**25**(8):3747–3757 (2011).
31. Lamers P, Tan ECD, Searcy EM, Scarlata CJ, Cafferty KG and Jacobson JJ, Strategic supply system design – a holistic evaluation of operational and production cost for a biorefinery supply chain. *Biofuels Bioprod Bioref* Aug 20 (2015).
32. Government Printing Office, Supplemental determination for renewable fuels produced under the final RFS2 program from grain sorghum. *Fed Regist* **77**(242):74592–74607 (2012).
33. US Energy Information Administration, US Refiner Sales for Resale (Average) Prices [Online]. Available at: http://www.eia.gov/dnav/pet/pet_pri_refmg2_d_nus_PWG_dpgal_m.htm [Accessed February 23, 2015].
34. Platts, Oilgram Price Report [Online]. Available at: http://www.platts.com/products/oilgram-price-report [Accessed February 23, 2015].
35. Hobson GD (ed), *Modern Petroleum Technology*. 5th edition. New York, NY: John Wiley & Sons Inc. (1984).
36. Refining Online, FCC Octane MON Versus RON [Online]. Available at: http://www.refiningonline.com/engelhardkb/crep/TCR4_29.htm [Accessed February 23, 2015].
37. ASTM D4814, Standard Specification for Automotive Spark-Ignition Engine Fuel [Internet]. Available at: http://www.astm.org/Standards/D4814.htm [Accessed August 5, 2015].
38. ASTM D86, Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure [Online]. Available at: http://www.astm.org/Standards/D86.htm [Accessed August 5, 2015].
39. Colonial Pipeline Company, Product Codes and Specifications [Online]. Available at: http://www.colpipe.com/docs/default-source/product-specs/product-specifications.pdf
40. Chevron, Motor Gasolines Technical Review [Online]. San Ramon, CA: Chevron Corporation (2009). Available at: http://www.chevron.com/documents/pdf/MotorGasTechReview.pdf [Accessed February 23, 2015].
41. Fischer BS, Nakicenovic N, Alfsen K, Corfee Morlot J, de la Chesnaye F, Hourcade J-Ch *et al.,* Issues related to mitigation in the long term context. *Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Inter-governmental Panel on Climate Change*, ed by Metz B, Davidson OR, Bosch PR, Dave R, and Meyer LA. Cambridge: Cambridge University Press.
42. Wu M, Mintz M, Wang M, and Arora S, Consumptive water use in the production of ethanol and petroleum gasoline. [Internet]. Argonne, IL: Argonne National Laboratory; 2009. Report No.: ANL/ESD/09-1. Available at: http://www.osti.gov/servlets/purl/947085-HEKf3F/ [Accessed February 20, 2015].

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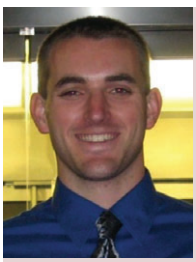

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