Coproduction of Liquid Transportation Fuels and $C_6\_C_8$ Aromatics from Biomass and Natural Gas

Alexander M. Niziolek, Onur Onel, Josephine A. Elia, Richard C. Baliban, and Christodoulos A. Floudas
Dept. of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544

DOI 10.1002/aic.14726

The coproduction of liquid transportation fuels and C_6—C_8 *aromatics from the thermochemical conversion of biomass and natural gas (BGTL+*$C_6\_C_8$*) is investigated in this article. An optimization-based process synthesis framework incorporating multiple synthesis gas conversion technologies, such as Fischer–Tropsch synthesis or methanol conversion, is described. Production of aromatics can proceed through several technologies, such as naphtha reforming and aromatization of hydrocarbons via a metal-promoted H-ZSM-5 catalyst. This is the first article in the literature to incorporate an aromatics complex for the coproduction of liquid fuels and* C_6—C_8 *petrochemicals within a rigorous process synthesis and deterministic global optimization framework. The optimal process topologies across several case studies are discussed and the results indicate that the coproduction of aromatics with liquid fuels can significantly increase the profitability of these refineries.* © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 831–856, 2015
Keywords: Global optimization, Process synthesis, Liquid Transportation Fuels, Aromatics, Biomass and Natural Gas

Introduction

The development of processes that can produce liquid transportation fuels from petroleum alternatives has been the topic of considerable interest. This subject has been brought to the forefront due to the high energy demanded by various sectors of the United States. The majority of U.S. consumption of petroleum-based products is attributable to the U.S. transportation sector, which consumed 13,186 thousand barrels of petroleum-based products per day (kBD) in 2013, or about 70% of the total consumption in the United States.[1] Recent publications have solely focused on the production of liquid fuels so as to address the major challenges facing the U.S. transportation sector, namely (a) satisfying U.S. transportation energy needs through domestically available carbon sources, such as coal, biomass, and natural gas, and (b) mitigating the greenhouse gas (GHG) emissions from the production of these products. However, these studies have not addressed a major aspect associated with the production of liquid fuels. Since petroleum naphtha accounts for 70% of the world's aromatics supply,[2,3] attempts to replace petroleum-based processes with alternative carbon sources must also investigate the production of these high-value chemicals (HVC). Replacement of petroleum-based processes with coal, biomass, and natural gas, three feedstocks that have received interest in recent years, should also address the production of aromatics from these feedstocks as well. Thus, this article seeks to investigate the coproduction of liquid transportation fuels and aromatics from biomass and natural gas.

Aromatics are an indispensable component of chemicals production, representing about one-third of the market for commodity petrochemicals.[4] The main aromatics investigated in this article include benzene, toluene, and the xylenes. Between 2005 and 2008, the world demand for benzene, *para*-xylene, *ortho*-xylene, and *meta*-xylene was approximately 40, 26, 6, and 0.4 million metric tons/year, respectively.[5] Aromatics have a variety of applications in industry. Benzene is used as a precursor to over 250 different products, including polystrene and nylons.[2] Toluene is used in some solvent applications, but is mostly converted into benzene or the xylenes.[2] *Ortho*-xylene is used to produce phthalic anhydride, which is used in the production of plasticizer, while *meta*-xylene is converted into isophthalic acid, an important additive in polyester.[6] The most valuable xylene isomer, *para*-xylene, is used to produce polyethyleneterephtalate fibers, resins, and films.[7]

The two feedstocks, biomass and natural gas, examined in this article both possess advantages over the third major feedstock considered in recent years, coal. Despite lower delivered costs for coal (\$2.0–\$2.5/MM Btu) than biomass (\$4.0–\$9.0/MM Btu) or natural gas (\$4.8–\$5.8/MM Btu),[8] capital costs for coal gasification are generally much larger than for biomass gasification.[9] In addition, there are considerable CO_2 emissions associated with the use of coal as a precursor to liquid hydrocarbon fuels.[10,11] Biomass, conversely, represents a renewable resource that can also reduce GHG emissions by capturing CO_2 during photosynthesis.[12–14] A report by the DOE and the USDA stated the potential for over 1.3 billion

---

This contribution was identified by Professor Dimitrios Papavassiliou (The University of Oklahoma) as the Best Presentation in the session "Modeling and Computation in Energy and the Environment" of the 2013 AIChE Annual Meeting in San Francisco, CA.

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

Correspondence concerning this article should be addressed to C. A. Floudas at floudas@titan.princeton.edu.

dry tons of biomass available for biofuel production in the future.[15] Recently discovered sources of shale gas in the United States have made this feedstock a more attractive precursor to liquid fuels.[8] In addition, the high hydrogen to carbon molar ratio of natural gas can lead to a higher overall conversion to liquid fuels and chemicals.

The process synthesis of biomass and natural gas to liquid fuels and aromatics presents a challenging problem, since neither the optimal process topology nor the optimal distribution of aromatic products can be known a priori for different refinery scales or aromatics production levels. Therefore, a global optimization branch-and-bound strategy is used that guarantees that the value of the objective function is within a few percentage points of the best possible value.[16] The authors emphasize the importance of this deterministic global optimization framework since the BGTL+C_6_C_8 process superstructure includes several alternatives that can produce a wide distribution of fuels and aromatics products.

A global optimization-based framework for the production of liquid fuels and C_6_C_8 petrochemical intermediates is presented in this article. A mixed integer nonlinear optimization (MINLP) model[9,16–25] is used that can analyze the environmental and economic trade-offs of the BGTL+C_6_C_8 process. The MINLP model includes simultaneous heat and power integration that uses heat engines to convert waste heat into electricity.[18,19,26] The MINLP model also includes a superstructure-based approach that minimizes the intake of freshwater into the refinery.[18,19,27–30] An environmental constraint that imposes at most 50% life cycle GHG (LGHG) emissions of typical fossil fuel-based processes is included in the model. The life cycle CO_2 emissions of the BGTL+C_6_C_8 refinery will be calculated and presented. All key process units of the BGTL+C_6_C_8 refinery will be described in the following section.

This article seeks to directly compare the technoeconomic and environmental benefits of a refinery that coproduces liquid fuels and aromatics from biomass and natural gas using a process synthesis approach. A superstructure of alternatives is introduced and the best possible plant design is determined using a global optimization branch-and-bound algorithm. Each unit in the superstructure is rigorously modeled to ensure proper operation. Twenty distinct case studies are investigated that thoroughly analyze the effects of plant capacity and aromatics production levels. The major topological decisions and trade-offs between technological alternatives are examined. The effects of coproducing aromatics alongside liquid fuels is directly quantified using two profitability metrics: (1) the overall profit and (2) the net present value (NPV) of the BGTL+C_6_C_8 refinery.

The process synthesis framework for the BGTL+C_6_C_8 process will include (1) biomass gasification with/without recycle light gas, (2) natural gas conversion via autothermal reforming, steam reforming, partial oxidation, or oxidative coupling, (3) synthesis gas conversion via Fischer–Tropsch (FT) synthesis or methanol synthesis, (4) methanol conversion via methanol-to-gasoline (MTG) or methanol-to-olefins (MTO), (5) hydrocarbon upgrading via ZSM-5 zeolite catalysis, olefin oligomerization, or carbon number fractionation and subsequent treatment, (6) aromatization over a Ga/H-ZSM-5-based catalyst, and (7) separation and production of additional C_6_C_8 petrochemicals via an aromatics complex. Gasoline, diesel, kerosene, and the C_6_C_8 aromatic intermediates will be the major products from the refinery. Liquefied petroleum gas (LPG) and electricity may be sold as byproducts.

Table 1. Feedstock Proximate and Ultimate Analysis for Hardwood

	Proximate Analysis (db, wt %)				Heating Values (kJ/kg)	
Feed Type	Moisture (ar)	Ash	VM*	FC†	HHV‡	LHV§
Hardwood	45	2.14	N/A	N/A	19,130	17,842
	Ultimate Analysis (db, wt %)					
Feed type	C	H	N	Cl	S	O
Hardwood	50.19	5.9	0.32	0	0.03	41.42

Ref. [35]
*VM = volatile matters.
†FC = fixed carbon.
‡HHV = higher heating value.
§LHV = lower heating value.

BGTL+C_6_C_8 Process Superstructure: Conceptual Design and Mathematical Modeling

Previous works by Baliban et al., Elia et al., Onel et al., and Niziolek et al., have described the conceptual design and modeling of a refinery that inputs any combination of coal, biomass, natural gas, and/or municipal solid waste.[9,16–25,31–34] The following sections will describe (1) biomass gasification and handling, (2) natural gas conversion, (3) synthesis gas conversion, (4) methanol conversion, (5) hydrocarbon upgrading, (6) aromatization over a Ga/H-ZSM-5-based catalyst, and (7) an aromatics complex. For brevity, this section will only briefly mention the major sections of the BGTL+C_6_C_8 refinery that have been described previously. The changes and additions to the previous superstructure that inputs biomass and natural gas will be delineated. Additionally, this section will introduce in detail the modeling of an aromatics complex that can produce and separate high-purity benzene, toluene, *ortho*-, *meta*-, and *para*-xylene. For completeness, the full description of the process synthesis superstructure is described in the Supplementary Information. The complete mathematical model of the process synthesis superstructure is included in the Supplementary Information.

Biomass handling and gasification

Hardwood biomass will be input into the BGTL+C_6_C_8 refinery with a representative composition that is shown in Table 1. Initially, the moisture content of the hardwood is reduced to 20 wt % by passing it through a biomass drier. The hardwood is then transferred into the biomass gasifier using a lockhopper and compressed CO_2. The biomass gasifier operates at 30 bar and at a temperature of either 900, 1000, or 1100°C. The synthesis gas effluent is passed through two ash cyclones designed to recycle the solid ash and char back into the gasifiers. The syngas is passed through a tar cracker and then directed to the syngas cleaning section.

Natural gas conversion

The BGTL+C_6_C_8 refinery is designed to input natural gas at pipeline conditions (31 bar and 25°C), with a representative composition that is obtained from the NETL Quality Guidelines for Energy Systems Studies Report and is shown in Table 2.[36,37] The natural gas is first passed through a zinc oxide polishing bed (sulfur guard) to prevent catalyst contamination by removing any mercaptan-based odorizers from the feedstock.[37] The natural gas may then be split to

Table 2. Molar Compositions (*x*) of All Species in the Input Natural Gas

Species	*x*	Species	*x*	Species	*x*
CH_4	0.931	C_2H_6	0.032	N_2	0.016
CO_2	0.010	C_3H_8	0.007	nC_4H_{10}	0.004

six major technologies, which include (a) autothermal reforming, (b) steam reforming, (c) direct conversion to olefins,[22,38–46] (d), direct conversion to methanol,[47–49] (e) fuel combustion, and (f) electricity production via a gas turbine.

Synthesis gas cleaning

The syngas effluent from the gasifiers or the reformers may either use the dedicated sour water-gas-shift (WGS) reactor or directly pass through the syngas scrubber. The WGS reactors operate at a pressure of 26 bar, at temperatures between 300 and 600°C, and may facilitate either the forward or reverse WGS reaction. The effluent from the dedicated WGS reactor is mixed with any bypass syngas and directed to a dual-capture methanol absorption system (Rectisol unit) that removes the acid gases. A Claus system is used to recover the sulfur within the refinery. Any CO_2 captured from the acid gas recovery units is either (1) compressed to 31 bar and recycled within the refinery, (2) compressed to 150 bar for sequestration, or (3) vented to the atmosphere. The clean syngas is directed to the hydrocarbon production section.

Hydrocarbon production and upgrading

FT Hydrocarbon Production. Six FT units are considered in this study for the conversion of synthesis gas to liquid hydrocarbons. Two cobalt-based FT reactors will operate at a pressure of 20 bar and at a temperature of either 240°C (LTFT) or 320°C (HTFT). The cobalt-based FT reactors do not facilitate the WGS reaction. Catalyst deactivation in Co-based FT reactors has been studied since it can alter product selectivity and has been attributed to poisoning, carbon disposition and fouling, oxidation and mixed-oxide formation, and changes in cobalt crystallite size.[4,50] To prevent catalyst oxidation in Co-based reactors, the CO per-pass conversion is set to 60% in this study. The other four FT reactors are iron-based, operate at 20 bar, and promote WGS activity. Two of these units facilitate the reverse WGS reaction by requiring the incoming syngas to have a Ribblett ratio[4,51] of 1 and operate at either 240°C (LTFTRGS) or 320°C (HTFTRGS). The other two iron-based units (MTFTWGS-M, MTFTWGS-N) are based on the FT slurry phase reactors developed by Mobil Research & Development[21,52,53] and facilitate the forward WGS reaction. The wax generated within the FT reactors is directed to the wax hydrocracker. The vapor-phase effluent, which contains C_1—C_{30+} hydrocarbons, is sent for upgrading.

FT Hydrocarbon Upgrading. The vapor-phase effluent leaving the FT reactors is upgraded in one of the two following ways, shown in Figures 1 and 2. It can pass through a ZSM-5 catalytic reactor to be converted into gasoline range hydrocarbons and some distillate.[52,53] The oxygenates present within the effluent can be converted into additional hydrocarbons. The ZSM-5 catalytic reactor operates at 408°C and 16 bar and its effluent is fractionated to separate the gasoline, distillate, and water. The water is directed to the wastewater treatment section, the distillate is hydrotreated, and the gasoline is sent to the LPG–gasoline separation section.

Alternatively, the FT effluent can pass through a series of treatment units designed to separate the hydrocarbons from the water and oxygenates. The water and oxygenates are directed to the wastewater treatment section, while the water-lean hydrocarbons are sent for standard upgrading. A hydrocarbon recovery system separates the water-lean hydrocarbons into C_3—C_5 gases, naphtha, kerosene, distillate, wax, offgas, and wastewater, as shown in Figure 2.[17,54] The upgrading units for these streams are described in a Bechtel design and include a wax hydrocracker, a distillate hydrotreater, a naphtha reformer, a C_4 isomerizer, a C_5/C_6

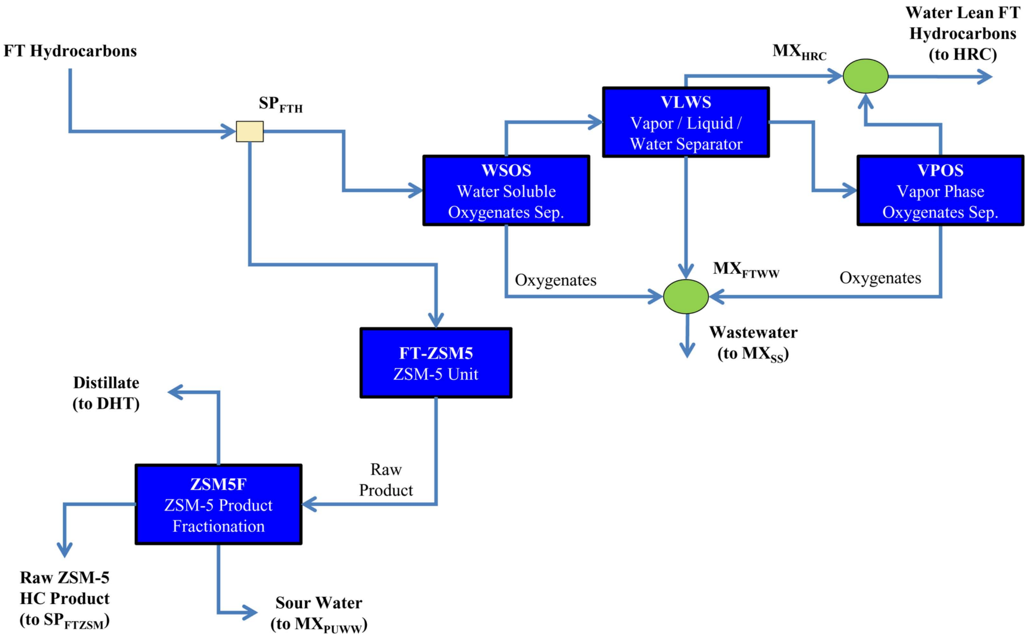


Figure 1. Fischer–Tropsch hydrocarbon upgrading flow diagram.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

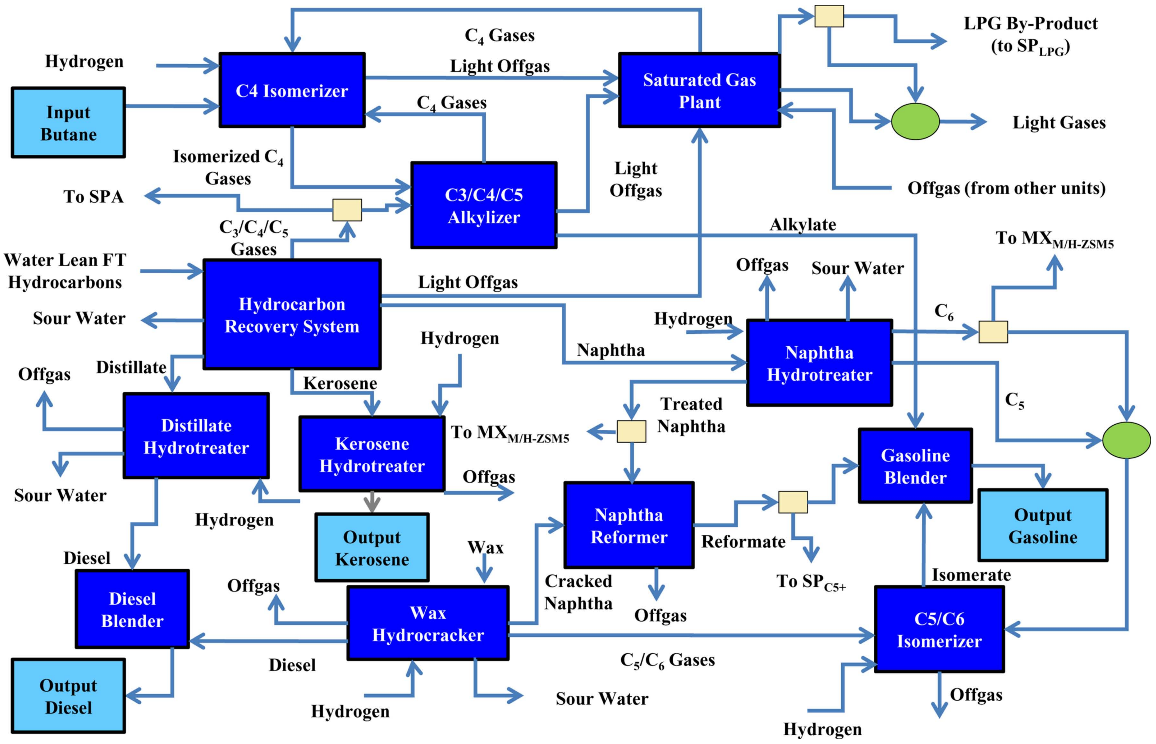


Figure 2. Fischer–Tropsch hydrocarbon upgrading flow diagram.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

isomerizer, a $C_3/C_4/C_5$ alkylation unit, and a saturated gas plant.[54,55] Additionally, some of the naphtha produced within this section is allowed to be sent to a metal-promoted H-ZSM-5 reactor (Cyclar process) to be converted into additional aromatics. The description of this portion of the refinery is described later in the Additional LPG and naphtha processing section.

Both upgrading routes described above produce more desirable naphtha and distillate products at the expense of increasing the capital cost of the BGTL+C_6_C_8 refinery.

Methanol Synthesis. Alternatively, the syngas may be directed to a methanol synthesis reactor that operates at 300°C and 50 bar. The raw methanol product is then cooled and flashed to remove 95% of the methanol. The majority of

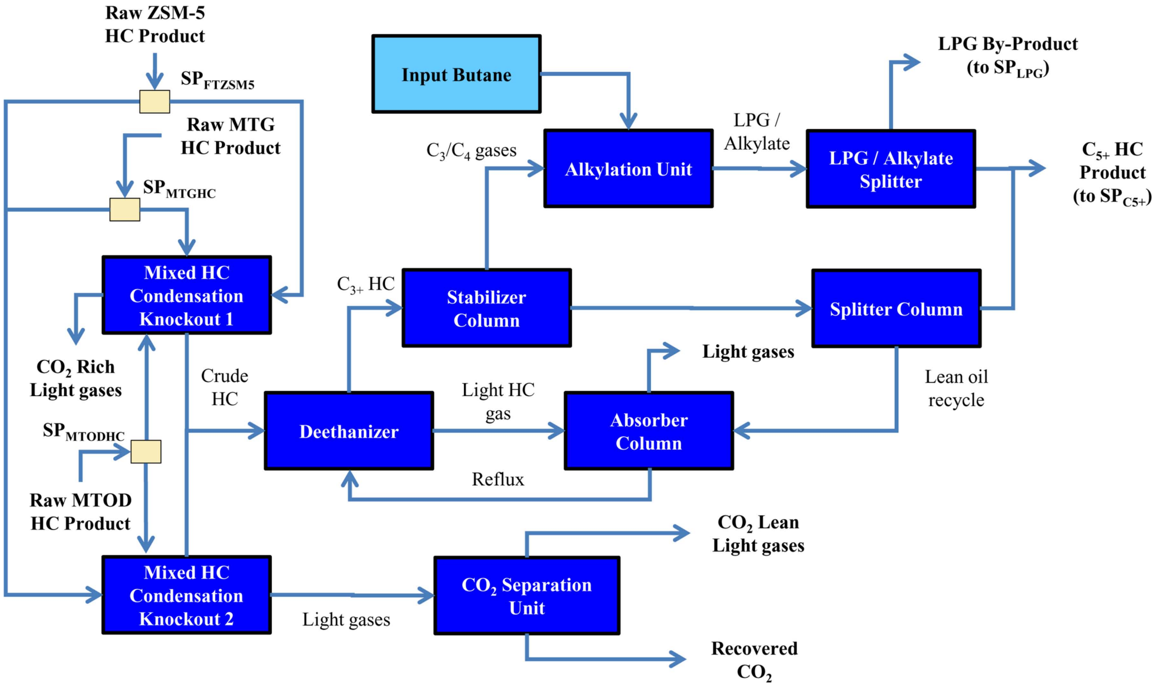


Figure 3. LPG–gasoline separation flowsheet.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

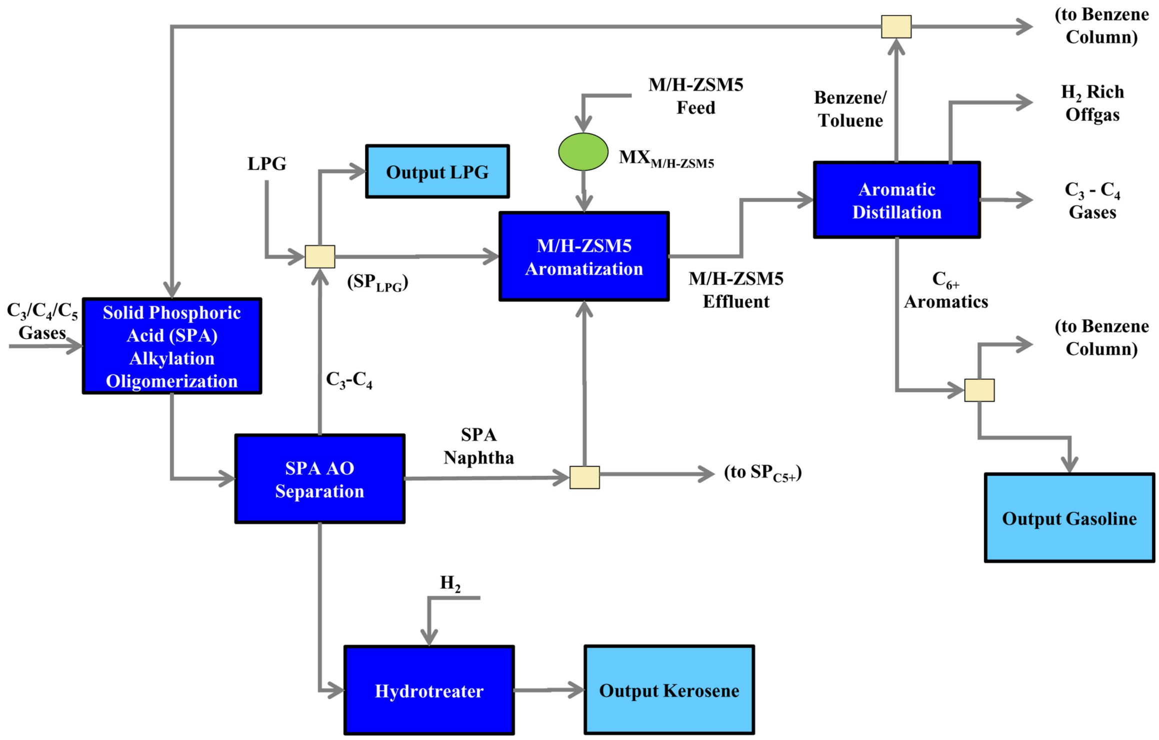


Figure 4. Additional LPG and naphtha processing.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the vapor effluent (95%) is recycled back to the methanol synthesis reactor, while the balance is used as fuel gas in the refinery. The liquid effluent is heated to 300°C to form a vapor and expanded in a turbine. The turbine effluent is directed to a degasser distillation column, where the entrained gases are removed and the methanol is recovered. The methanol is split to one of two methanol conversion units.

Methanol Conversion. The methanol exiting the degasser is split to either the MTG reactor or the MTO reactor.[56–60] The MTG reactor uses a ZSM-5 catalyst, operates at 400°C and 12.8 bar, and converts the methanol into gasoline range hydrocarbons. It is assumed that complete conversion of the methanol takes places. The hydrocarbon products are separated and upgraded in the LPG–gasoline separation section. The MTO reactor operates at 375°C and 1 bar and uses a SAPO-34 catalyst to convert the methanol into olefins.[58,61] The olefins are directed to the Mobil olefins-to-gasoline/distillate (MOGD) reactor, which operates at 400°C and 1 bar.[60] The MOGD effluent is fractionated to separate the gasoline and light gases from the diesel and kerosene. The liquid fuel products exiting the MOGD reactor are modelled as pseudocomponents since a detailed composition of the effluent is not described in literature. The raw hydrocarbon product is directed to the LPG–gasoline separation section, while the distillate is directed to the hydrotreaters.

LPG–Gasoline Separation. The raw hydrocarbon product produced in the MTG, MOGD, or ZSM-5 catalytic reactors is sent to the LPG–Gasoline separation section, shown in Figure 3. The light gases are removed via vapor-liquid equilibrium in one of two knockout units. The crude hydrocarbon mixture is then sent to a de-ethanizer distillation column that will separate any residual C_1 and C_2 hydrocarbons. The light gases are directed to an absorber that can strip away any C_3 species. The absorber uses lean oil from a downstream unit as the absorbing liquid.[57] The light gases exiting the absorber are recycled back to the refinery. The lean oil and absorbed hydrocarbons are refluxed back to the de-ethanizer. [57] The bottoms from the de-ethanizer is directed to a stabilizer column that can remove the C_3 and C_4 hydrocarbons from the gasoline fraction. The C_3/C_4 gases are alkylated to produce iso-octane and LPG. The alkylation unit assumes that butene is completely converted to iso-butane and the alkylate is modeled as iso-butane. [57] The effluent from the alkylation unit is separated into gasoline and LPG byproduct. The bottoms from the stabilizer column is sent to a splitter column that will recover the lean oil necessary in the absorber. The effluent from the splitter column is combined with the gasoline separated from the alkylation unit and either output as gasoline product or directed to the aromatics complex. The LPG byproduct from the alkylation unit is split and either output as LPG or directed to the metal-promoted H-ZSM-5 reactor for aromatization.

Additional LPG and naphtha processing

The C_3—C_5 gases from the FT standard upgrading section can be split to a solid phosphoric acid (SPA)-catalyzed aromatic alkylation unit, which reacts some of the benzene or toluene in the refinery with the C_3—C_5 olefins to produce heavier aromatics.[24] It is assumed that 100% of the C_3—C_5 olefins will react to form either heavier aromatics or C_{6+} olefins.[24]

The Cyclar process uses a Ga/H-ZSM-5 catalyst to convert LPG in the refinery into aromatics using dehydrogenation and subsequent aromatization.[3,62] The process was first developed by BP and UOP.[3] In addition to producing petrochemical-grade aromatics, the Cyclar process also produces a valuable coproduct, hydrogen. A portion of the light naphtha present within the refinery is also allowed to be split to the Cyclar process to be converted into aromatics and

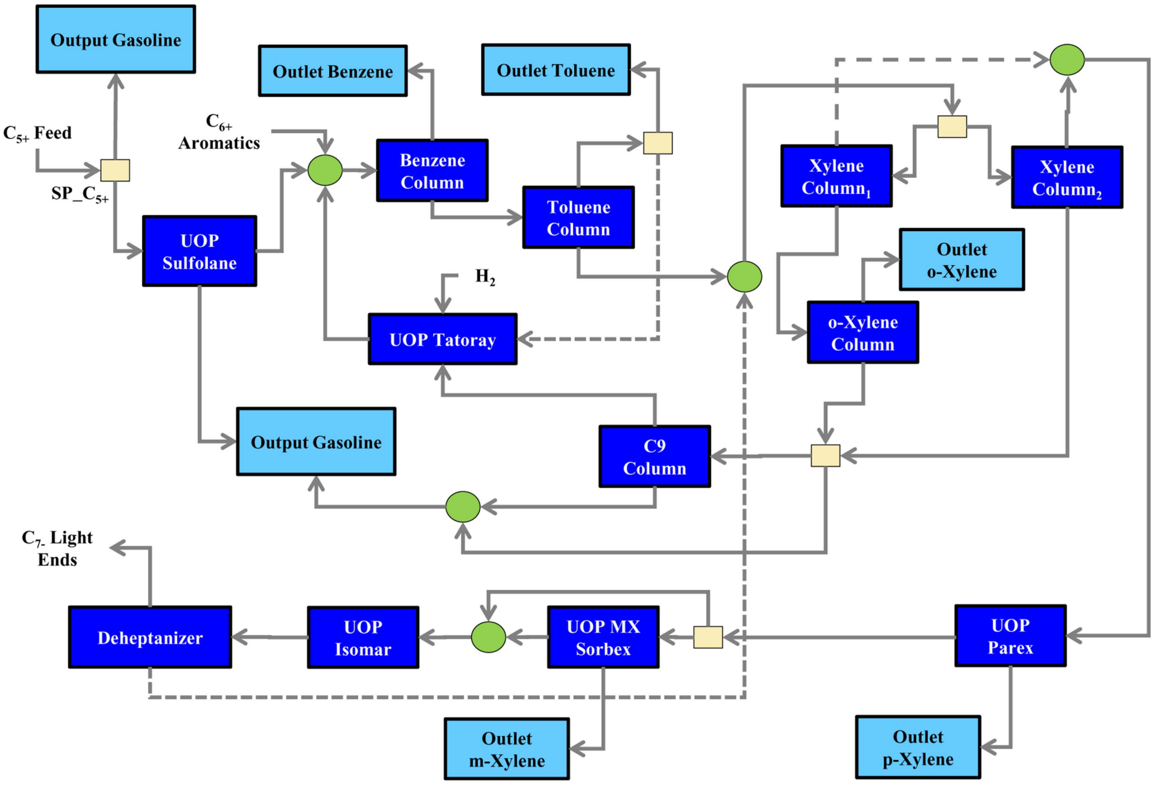


Figure 5. Aromatics upgrading and separation flowsheet.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogen. The global optimization framework will determine whether it is more advantageous to convert the LPG and/or naphtha into aromatics and hydrogen with the addition of another reforming unit. The existence of this process within the refinery depends on the selling price of LPG and aromatics and the investment cost associated with the reformer. The effluent from the Cyclar process is fractionated so that the hydrogen and fuel gas are recycled back into the refinery and the aromatics are directed to the aromatics complex. The flow diagram for this section of the refinery is shown in Figure 4.

Aromatics complex

Figure 5 illustrates the aromatics upgrading and separation flowsheet. The description of each of the units follows.

Sulfolane Unit. The Sulfolane process was developed by UOP in the 1960s and is a commercially available process that recovers aromatics from reformate, pyrolysis gasoline, or coke-oven light oil.[3,63] The UOP Sulfolane reactor operates at a temperature of 110°C and 2.07 bar and will input a stream of C_{5+} hydrocarbons. The solvent used is tetrahydrothiophene 1,1-dioxide, also known as Sulfolane. The UOP Sulfolane is a combination of liquid-liquid extraction and extractive distillation that recovers 99.9% of the benzene, 99.8% of the toluene, and 99% of the C_8 aromatics from the incoming stream. The paraffins that are separated from the hydrocarbon feed are sent to the gasoline blender, while the aromatic effluent is clay treated to remove any impurities before it is sent for further fractionation.[2] The aromatic effluent is mixed with any other aromatic streams from the BGTL+C_6_C_8 refinery and directed to the benzene distillation column.

Benzene Distillation Column. The benzene distillation column inputs a stream of C_{6+} aromatics and separates high purity benzene. The distillate of the benzene distillation column recovers 99.9% of the incoming benzene and has a benzene mass purity of at least 99.8%. The benzene-rich distillate is cooled to 40°C and output as benzene product. The benzene depleted bottom is directed to the toluene distillation column.

Toluene Distillation Column. The toluene distillation column inputs the bottoms from the benzene column and separates out high purity toluene. The toluene distillate contains any leftover benzene, 99.9% of the incoming toluene, and a small portion of C_8 aromatics. A toluene mass purity constraint of at least 99.8% is included in the model to ensure commercial grade purity of the product in the distillate. The distillate is split and either cooled to 40°C and output as toluene product or directed to the UOP Tatoray reactor. The bottom from the toluene column is a C_{8+}-rich aromatic stream that is mixed with any other C_{8+}-rich aromatic streams in the BGTL+C_6_C_8 refinery. The effluent from the mixer is then directed to one of two xylene distillation columns.

Xylene Column 1. The first option for processing the C_{8+}-rich aromatic stream is inputting it to a xylene distillation column that recovers *para*-xylene, *meta*-xylene, and ethylbenzene (with greater than 99.9% recovery) in the distillate stream. The distillate is then mixed with any other C_8-rich aromatic streams and directed to the UOP Parex. The *ortho*-xylene and other heavier aromatics are present in the bottom stream and are directed to the *ortho*-distillation column. The separation of the *ortho*-xylene from the rest of the C_8 aromatics is possible because the boiling point of *o*-xylene (144.4°C) is slightly higher than that of *p*-xylene (138.3°C), *m*-xylene (139.1°C), and ethylbenzene (136.2°C).

This route allows for the production of *ortho*-xylene from the BGTL+C_6_C_8 refinery.

Ortho-Xylene Distillation Column. The bottom from xylene column 1 is directed to the *ortho*-xylene distillation column. The *ortho*-xylene distillation column recovers 99.9% of the incoming *ortho*-xylene with a *o*-xylene mass purity of greater than 99.5%. The distillate is cooled down to 40°C and output as *ortho*-xylene product. The bottom from the *ortho*-xylene distillation column contains mostly C_{9+} aromatics and is split to either the C_9 distillation column or output to the gasoline pool.

Xylene Column 2. Alternatively, if the production of *o*-xylene is not desired in the refinery, the second option for processing the C_{8+}-rich aromatic stream is passing it through a xylene distillation column that operates in a different mode. The distillate from this column recovers over 99.4% of the *p*-xylene, *o*-xylene, *m*-xylene, and ethylbenzene from the incoming feed. The distillate is then mixed with any other C_8-rich aromatic streams and directed to the UOP-Parex. The bottom contains mostly a mixture of C_{9+} aromatics and is split to either the C_9 distillation column or output to the gasoline pool. Only one of the two xylene distillation columns described is allowed to exist within the refinery.

UOP Parex. The UOP Parex is a simulated moving bed technology that was developed in 1971 and selectively recovers *para*-xylene from a mixture of mixed xylenes.[64,65] Since the C_8 aromatic isomers have similar volatilities, separation by conventional distillation is not practical. Prior to the introduction of the Parex system, the separation of *para*-xylene was done by fractional crystallization. However, the *para*-xylene recovery was only limited to 65% in crystallization. The Parex process uses a countercurrent flow of the liquid feed over a solid zeolitic adsorbent.[3] A typical Parex unit consists of two adsorption chambers with 12 beds each.[2] The UOP Parex unit operates at a temperature of 180°C and 1.2 bar and recovers 99% of the incoming *para*-xylene with a mass-purity of at least 99.5%. The *para*-xylene product is output at 40°C. The *para*-xylene depleted effluent is split to either the UOP MX Sorbex process or to the UOP Isomar process.

UOP MX Sorbex. The UOP MX Sorbex process uses continuous adsorptive separation to recover high-purity *meta*-xylene from a mixed-xylene feed. This unit can handle a variety of C_8 feeds, including reformate, hydrogenated pyrolysis gasoline, and the mixed-xylene portion from the UOP Tatoray process.[66] The UOP MX Sorbex recovers 95% of the incoming *meta*-xylene with a mass purity of at least 99.5%. The *meta*-xylene rich stream is cooled to 40°C and output as product. The *meta*-xylene depleted stream is directed to the UOP Isomar unit.

UOP Isomar. Since the raffinate from the Parex process typically contains little or no *para*-xylene, it can be directed to the UOP Isomar process which re-establishes an equilibrium mixture of xylene isomers. Ethylbenzene in the feed can be converted into additional mixed xylenes or to benzene[3] depending on the catalyst used. If the catalyst used is the I-400 EB isomerization catalyst, then the ethylbenzene is converted to mixed xylenes with 30 wt % per pass conversion.[2,3] An I-300 EB dealkylation catalyst converts ethylbenzene to benzene with greater than 70 wt % per pass conversion.[2,3] The catalyst used in this study is the I-400 EB catalyst. The effluent is then sent to a deheptanizer column that purges the C_7 light ends. The C_8-rich aromatic mixture is then sent to be mixed with the bottoms of the toluene column and recycled back to either one of the two xylene distillation columns.

C9 Distillation Column. The bottoms from the *ortho*-xylene distillation column and xylene column 2 are directed to a splitter, where they can either be directed to the C9 distillation column or output as gasoline. The C9 column recovers 99% of the C_9 aromatics and a small portion of the C_{10} aromatics. The distillate is then sent to the UOP Tatoray process to produce additional mixed xylenes and benzene. The bottoms product, which is a C_{10+}-rich aromatic stream, is sent and output as gasoline.

UOP Tatoray. An additional way to create mixed xylenes and benzene from toluene and C_9 aromatics is through the use of the Tatoray process. Toluene disproportionation and the transalkylation of toluene together with C_9 aromatics are the two major reactions that take place within the unit.[3] The reaction takes place within a fixed bed reactor.[3] A typical feed composition and the corresponding effluent can be found in Table 1 of U.S. Patent 7,109,389.[67] The UOP Tatoray process inputs toluene and C_9 aromatics in a 50–50 wt % ratio and operates at a temperature of 430°C and 35 bar.[67] The effluent from the Tatoray process is mixed with the aromatic effluent from the Sulfolane process and is sent to be fractionated. The UOP Tatoray process is modeled mathematically in the process synthesis framework using an atom balance.

Light gas handling

The light gases (C_1—C_2 hydrocarbons, unreacted syngas, and inert species) generated in the BGTL+C_6_C_8 refinery will either be processed in an internal gas loop configuration or an external gas loop configuration. The internal gas loop configuration recycles the light gases back to the hydrocarbon production units to increase the overall conversion. The external gas loop configuration directs the light gases into either a fuel combustor or a gas turbine. The natural gas conversion units also have the ability to input recycle gases. See the Light Gas Handling section in the Supplementary Information for a more complete description.

Hydrogen/oxygen production

A pressure-swing adsorber or an electrolyzer will provide the BGTL+C_6_C_8 refinery high purity hydrogen. Oxygen will be supplied by an air separation unit or an electrolyzer. See the Hydrogen/Oxygen Production section in the Supplementary Information for a more complete description.

Wastewater treatment

The BGTL+C_6_C_8 refinery includes a comprehensive wastewater treatment section[20] that includes a biological digestor and sour stripper to treat process wastewater. This section also provides treated process water and steam to units within the refinery. See the Wastewater Treatment section in the Supplementary Information for a more complete description.

Unit costs

Equation 1 summarizes the information needed to calculate the total direct costs, TDC, of each unit in the BGTL+C_6_C_8 refinery

Table 3. BGTL+C_6_C_8 Refinery Upgrading Unit Reference Capacities, Costs (2014 $), and Scaling Factors

Description	C_o (MM$)	S_o	S_{Max}	Units	Scale Basis	*sf*	Ref
Biomass gasification							
Biomass handling	$4.57	17.90	30.60	kg/s	As received biomass	0.77	*
Biomass gasification	$54.34	17.90	33.30	kg/s	Dry biomass	0.77	†
Natural gas conversion							
Auto-thermal reformer	$21.62	12.20	35.00	kg/s	Feed	0.67	‡
Steam methane reformer	$30.22	12.20	35.00	kg/s	Feed	0.67	‡
Partial oxidation reactor	$639.56	118.80	75.00	kg/s	Natural gas feed	0.67	§§
OC reactor	$282.95	661.90	75.00	kg/s	Natural gas feed	0.67	§§
Synthesis gas handling/clean-up							
Water–gas-shift unit	$3.69	150.00	250.00	kg/s	Feed	0.67	¶
Rectisol unit	$31.59	2.51	8.78	kmol/s	Feed	0.63	*
Hydrocarbon production							
Fischer–Tropsch unit	$12.06	23.79	60.00	kg/s	Feed	0.72	**,††
Hydrocarbon recovery column	$0.64	1.82	25.20	kg/s	Feed	0.70	‡‡
Methanol synthesis	$8.09	35.65	–	kg/s	Feed	0.65	¶
Methanol degasser	$3.76	11.17	–	kg/s	Feed	0.70	¶
Methanol-to-gasoline unit	$5.71	10.60	–	kg/s	Feed	0.65	§§,¶
Methanol-to-olefins unit	$3.42	10.60	-	kg/s	Feed	0.65	§§,¶
Hydrocarbon upgrading							
Distillate hydrotreater	$2.22	0.36	81.90	kg/s	Feed	0.60	‡‡
Kerosene hydrotreater	$2.22	0.36	81.90	kg/s	Feed	0.60	‡‡
Naphtha hydrotreater	$0.67	0.26	81.90	kg/s	Feed	0.65	‡‡
Wax hydrocracker	$8.29	1.13	72.45	kg/s	Feed	0.55	‡‡
Naphtha reformer	$4.62	0.43	94.50	kg/s	Feed	0.60	‡‡
C_5—C_6 isomerizer	$0.85	0.15	31.50	kg/s	Feed	0.62	‡‡
C_4 isomerizer	$9.34	6.21	–	kg/s	Feed	0.60	‡‡
C_3-C_5 alkylation unit	$51.45	12.64	–	kg/s	Feed	0.60	‡‡
Saturated gas plant	$7.71	4.23	–	kg/s	Feed	0.60	‡‡
FT ZSM-5 reactor	$4.85	10.60	–	kg/s	Feed	0.65	**,††
Olefins-to-gasoline/diesel unit	$3.42	10.60	–	kg/s	Feed	0.65	§§
CO_2 separation unit	$5.30	8.54	–	kg/s	Feed	0.62	§§
Deethanizer	$0.57	5.13	–	kg/s	Feed	0.68	§§,¶
Absorber column	$0.90	0.96	–	kg/s	Feed	0.68	§§,¶
Stabilizer column	$1.02	4.57	–	kg/s	Feed	0.68	§§,¶
Splitter column	$1.00	3.96	–	kg/s	Feed	0.68	§§,¶
HF alkylation unit	$8.84	0.61	–	kg/s	Feed	0.65	§§,¶
LPG/alkylate splitter	$1.04	0.61	–	kg/s	Feed	0.68	§§,¶
Cyclar process	$113.28	16.42	–	kg/s	Feed	0.67	¶¶
SPA alkylation oligomizeration	$8.84	0.61	–	kg/s	Feed	0.67	§§,***
Aromatics production complex							
UOP sulfolane	$21.27	15.14	100.00	kg/s	Feed	0.67	†††
UOP isomar	$46.17	1555.50	200.00	kg/s	Feed	0.67	†††
UOP tatoray	$22.38	24.82	200.00	kg/s	Feed	0.67	†††
UOP parex	$154.38	106.20	200.00	kg/s	Feed	0.67	†††
UOP MX sorbex	$97.06	5.58	200.00	kg/s	Feed	0.67	†††
Benzene distillation	$0.56	10.83	200.00	kg/s	Feed	0.52	‡‡‡
Toluene distillation	$1.16	10.04	200.00	kg/s	Feed	0.72	‡‡‡
Xylene$_1$ column	$5.03	12.11	200.00	kg/s	Feed	0.49	‡‡‡
Xylene$_2$ Column	$2.20	11.72	200.00	kg/s	Feed	0.77	‡‡‡
Ortho-xylene distillation	$0.99	12.14	200.00	kg/s	Feed	0.66	‡‡‡
C_9 distillation	$0.94	15.31	200.00	kg/s	Feed	0.53	‡‡‡
Hydrogen/oxygen production							
Pressure-swing absorption	$7.84	0.29	–	kmol/s	Purge gas	0.65	†
Air separation unit	$244.83	145.00	41.70	kg/s	O_2	0.50	‡
Air compressor	$5.93	10.00	30.00	MW	Electricity	0.67	†
Oxygen compressor	$7.94	101.00	20.00	MW	Electricity	0.67	†
Electrolyzer	$0.492	1.00	–	MW	Electricity	0.90	†
Heat and power integration							
Gas turbine	$80.28	266.00	334.00	MW	Electricity	0.75	†
Steam turbine	$65.23	136.00	500.00	MW	Electricity	0.67	†
Wastewater treatment							
Sour Stripper	$3.93	11.52	–	kg/s	Feed	0.53	§§§
Biological digestor	$4.67	115.74	–	kg/s	Feed	0.71	¶¶¶
Reverse osmosis	$0.32	4.63	–	kg/s	Feed	0.85	¶¶¶
Cooling tower	$3.99	4530.30	–	kg/s	Feed	0.78	§§§

[*] Kreutz et al.[69]

[†] Larson et al.[68]

[‡] National Energy Technology Laboratory.[73]

[§] Fox et al.[74]

[¶] National Renewable Energy Laboratory.[57]

[**] Mobil Research and Development.[52]

[††] Mobil Research and Development.[53]

[‡‡] Bechtel Corporation.[54]

[§§] Mobil Research and Development.[56]

[¶¶] Gregor et al.[62]

[***] National Renewable Energy Laboratory.[75]

[†††] Meyers.[3]

[‡‡‡] Aspen Plus PEA.

[§§§] National Energy Technology Laboratory.[70]

[¶¶¶] Balmer.[71]

Table 4. Utility Requirements for the Refinery

Unit	Abbreviation	Base Units (BU)	Electricity (MW per BU)	Fuel (MW per BU)	Cooling Water (MW per BU)	Steam (MW per BU)			
						343.33°C	225.27°C	185.55°C	148.22°C
Inlet biomass	IN_BIO	kg/s as received biomass	0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Biomass dryer	BDR	kg/s dry biomass	0.1080	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Biomass gasification	BGS	kg/s dry biomass	0.3326	1.2655	0.0000	0.0000	0.0000	0.0000	0.0000
Reverse water gas shift	RGS	kg/s feed	0.2613	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
COS—HCN hydrolyzer	CHH	kg/s feed	0.0042	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Acid gas removal	AGR	kmol/s $CO_2 + H_2S$	1.9001	0.0000	0.0000	0.0000	0.0000	0.0000	15.2820
Acid gas thermal analyzer	X_AGR	Thermal heat duty	3.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Fisher–Tropsch Units	FT	kg/s feed	0.0115	0.0727	0.0000	0.0135	0.0000	0.0000	0.0000
ZSM-5 FT upgrading	ZSM5	kg/s feed	0.0115	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Methanol to olefins	MTO	kg/s feed	0.0046	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Hydrocarbon recovery	HRC	kg/s feed	0.0070	0.1693	0.0041	0.0000	0.0000	0.0000	0.1263
Wax hydrocracker	WHC	kg/s feed	0.0553	0.7252	0.0521	0.4553	1.4997	0.0000	−1.3852
Distillate hydrotreater	DHT	kg/s feed	0.0926	0.2986	0.1385	0.0000	0.0000	0.0000	−0.0719
Kerosene hydrotreater	KHT	kg/s feed	0.0926	0.2986	0.1385	0.0000	0.0000	0.0000	−0.0719
Naphta hydrotreater	NHT	kg/s feed	0.0588	1.3310	1.9357	0.0000	0.0000	0.0000	0.0000
Naphta reformer	NRF	kg/s feed	0.1864	2.0211	0.4051	−0.3462	0.0000	0.0000	0.0000
C5 C6 isomerizer	C56I	kg/s feed	0.0134	0.1410	0.0636	0.2171	0.0000	0.0000	−0.0404
C4 isomerizer	C4I	kg/s feed	0.1092	0.0748	0.0932	0.2784	0.0000	0.0417	3.1495
C345 alkylation unit	C345A	kg/s feed	0.5167	0.0000	0.8130	0.3297	0.0000	0.0000	0.9520
Saturated gas plant	SGP	kg/s feed	0.0215	0.7235	2.3769	0.5155	0.0000	0.0000	−0.1278
Air separation unit	ASU	kg/s oxygen produced	0.0189	0.0000	0.0000	0.0000	0.0670	0.0000	0.0769
First sulfur convertor	SC1	kg/s feed	0.1176	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Methanol degasser	MEOH_DEG	MW of enthalpy change	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
LPG alkylate separation	UPZSM5	kg/s feed	0.0046	0.1511	0.4917	0.0000	0.1934	0.0000	0.0000
Offsite	OUT_GAS	kBD of gasoline	0.0600	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Electrolyzer	EYZ	kg/s hydrogen produced	188.9600	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Air compressor	AC	MW of enthalpy change	26.3980	0.0000	25.3980	0.0000	0.0000	0.0000	0.0000
Oxygen compressor	OC	MW of enthalpy change	1.5000	0.0000	0.5000	0.0000	0.0000	0.0000	0.0000
Tail gas compressor	TGC	MW of enthalpy change	0.5650	0.0000	0.4350	0.0000	0.0000	0.0000	0.0000
Sour stripper	SS	MW of enthalpy change	0.0000	0.0000	0.4512	0.0000	0.0000	0.0000	0.5488
CO_2 recycle compressor	CO_2RC	MW of enthalpy change	0.7241	0.0000	0.2759	0.0000	0.0000	0.0000	0.0000
CO_2 sequestration compressor	CO_2SC	MW of enthalpy change	1.5400	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
UOP sulfolane	SULF	kg/s feed	0.0258	0.0000	0.6786	0.0000	0.0000	0.0000	0.9914
UOP isomar	ISOMAR	kg/s feed	0.0006	0.0155	0.0057	0.0000	0.0000	0.0000	0.0059
UOP tatoray	TATRY	kg/s feed	0.3142	0.0749	0.3850	0.0000	0.0000	0.0000	0.2418
UOP parex	PAREX	kg/s feed	0.4990	1.3683	0.0614	0.0000	−0.1254	0.0000	0.0000
UOP MX sorbex	SORBEX	kg/s feed	0.4990	1.3683	0.0614	0.0000	−0.1254	0.0000	0.0000
Benzene distillation	BENZ_DIS	kg/s feed	0.0000	0.0000	0.2433	0.4221	0.0000	0.0000	0.0000
Toluene distillation	TOL_DIS	kg/s feed	0.0000	0.0000	0.4894	0.0000	0.7385	0.0000	0.0000
Xylene distillation	XYL_DIS$_1$	kg/s feed	0.0000	0.0000	3.5169	0.0000	0.0000	3.5169	0.0000
Xylene distillation for *ortho*-prod	XYL_DIS$_2$	kg/s feed	0.0000	0.0000	2.4393	0.0000	2.5750	0.0000	0.0000
Ortho-xylene distillation	ORTHO_DIS	kg/s feed	0.0000	0.0000	1.0819	0.0000	0.0000	1.3090	0.0000
C9A distillation	C_9_DIS	kg/s feed	0.0000	0.0000	0.3872	0.0000	0.0000	0.0000	0.3872

Table 5. Description of the Case Studies Investigated

10,000 Barrels Per Day*		50,000 Barrels Per Day*	
Notation	Amount of Aromatics Produced (MT/day)†	Notation	Amount of Aromatics Produced (MT/day)†
U-10-0	0	U-50-0	0
U-10–50	50	U-50–250	250
U-10–100	100	U-50–500	500
U-10–150	150	U-50–750	750
U-10–200	200	U-50–1000	1000
U-10-VAR	$50 \leq$ Aromatics ≤ 300	U-50-VAR	$250 \leq$ Aromatics ≤ 1500
U-10-VAR2	$50 \leq$ Aromatics ≤ 500	U-50-VAR2	$250 \leq$ Aromatics ≤ 2500
D-10-VAR	$50 \leq$ Aromatics ≤ 300	D-50-VAR	$250 \leq$ Aromatics ≤ 1500
R-10-VAR	$50 \leq$ Aromatics ≤ 300	R-50-VAR	$250 \leq$ Aromatics ≤ 1500
FT-10-VAR	$50 \leq$ Aromatics ≤ 300	FT-50-VAR	$250 \leq$ Aromatics ≤ 1500

*Gasoline equivalent fuels (based on the lower heating value).
†Xylene equivalent chemicals (based on the lower heating value).

$$\mathrm{TDC}=(1+\mathrm{BOP})\times C_o\times\left(\frac{S_r}{S_o}\right)^{\mathrm{sf}} \tag{1}$$

where BOP is the balance of plant (site preparation, civil works, etc.) percentage, C_o is the base component cost, S_o is the base component size (capacity), S_r is the actual component size (capacity), and sf is the scaling cost factor. The cost parameters used in Eq. 1 are obtained from several literature sources and are illustrated in Table 3. The balance of plant is estimated to be 20% of the total installed unit cost and all costs are converted into 2014 dollars using the Chemical Engineering Plant Cost Index.[76]

The indirect costs of the refinery include engineering, contingency, startup, royalties, fees, and spare parts[69] and are assumed to be 32% of the TDC. The TDC are then added with the indirect costs to obtain the total plant costs (TPCs), or the fixed capital investment (FCI). The capital charges (CC) are calculated by taking the product of the levelized capital charge rate (LCCR), the interest during construction factor (IDCF), [69] and the total overnight capital, as shown in Eq. 2

$$\mathrm{CC}=\mathrm{LCCR}\times\mathrm{IDCF}\times\mathrm{TPC} \tag{2}$$

The values of LCCR and IDCF are taken from Kreutz et al.,[69,72] who calculate them to be 14.38%/year and 7.16%/year, respectively. The overall multiplier, 15.41%/year, converts the TPC into total CC. The plant is assumed to operate at a capacity (CAP) of 330 days/year and the operating/maintenance (OM) costs are assumed to be 4.5% of the TPC. These parameters are then used to convert the TPC of a unit into its levelized unit cost, (Cost^U), as shown in Eq. 3

$$\mathrm{Cost}_u^U=\left(\frac{\mathrm{LCCR}\times\mathrm{IDCF}}{\mathrm{CAP}}+\frac{\mathrm{OM}}{365}\right)\cdot\left(\frac{\mathrm{TPC}_u}{\mathrm{Prod}}\right) \tag{3}$$

where Prod levelizes the cost based on the total energy of products produced.

Utility requirements

Utility requirements for several units within the BGTL+C_6_C_8 refinery are shown in Table 4. The units shown in Table 4 are the ones that require black-box energy balances. The heat duties of the remaining units within the refinery (e.g., heat exchangers, compressors, equilibrium units) are calculated using the conservation of energy and total heat balance equations shown in the Supplementary Information (i.e., Eqs. B15 and B16). The global optimization framework determines the total utility cost since the total cost of the hot and cold utilities are simultaneously minimized.

Objective function

The objective function for the MINLP model is illustrated in Eq. 4

$$\mathrm{MIN}\sum_{f\in\mathrm{Feed}}\mathrm{Cost}_f+\mathrm{Cost}^{\mathrm{El}}+\mathrm{Cost}^{\mathrm{Seq}}+\sum_{u\in U_{\mathrm{Inv}}}\mathrm{Cost}_u^U-\sum_{p\in\mathrm{Products}}\mathrm{Cost}_p \tag{4}$$

The summation represents the total negative profit of liquid fuels and aromatics production. The feedstock costs, Cost_F, include contributions from biomass, natural gas, butanes, and freshwater. $\mathrm{Cost}^{\mathrm{El}}$ represents the electricity cost and is negative if the refinery outputs electricity as a byproduct. The CO_2 sequestration cost is denoted as $\mathrm{Cost}^{\mathrm{Seq}}$ and the levelized investment cost is represented by Cost^U. The sales from the products, Cost_P, include contributions from the gasoline, diesel, kerosene, LPG, benzene, toluene, *para*-, *meta*-, and *ortho*-xylene. Each term in the objective function is normalized with respect to the total energy of products (liquid fuels and aromatics) produced.

The process synthesis superstructure represents a large-scale nonconvex MINLP model that is solved to global optimality using a branch-and-bound algorithm.[16] The MINLP

Table 6. Cost Parameters (2014 \$) for the BGTL+C_6_C_8 Refinery

Item	Cost	Item	Cost
Forest residues	\$70/dry metric ton	Natural gas	\$5/TSCF*
Butanes	\$1.84/gal	Freshwater	\$0.50/metric ton
Electricity	\$0.07/kWh	CO_2 TS&M*	\$5/metric ton
Gasoline	\$2.86/gal	Diesel	\$3.04/gal
Kerosene	\$2.96/gal	Propane	\$0.99/gal
Para-xylene	\$1.602/kg	*Meta*-xylene	\$1.405/kg
Ortho-xylene	\$1.367/kg	Benzene	\$1.431/kg
Toluene	\$1.294/kg		

*TS&M—transportation, storage, and monitoring, TSCF—thousand standard cubic feet

Table 7. Topological Information for the Optimal Solutions for the 20 Case Studies is Shown

Biomass and natural gas—10 kBD

Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Biomass Conv.	S/V	S/V	S/V	S/V	S/V	S/V	S/V	S/V	S/V	S/V
Biomass Temp.	900.00	900.00	900.00	900.00	900.00	900.00	900.00	900.00	900.00	900.00
NG Conv.	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR
NG Temp.	900.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
WGS/RGS Temp.	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00
Min. wax FT	–	–	–	–	–	–	–	–	–	Co-HTFT
Nom. wax FT	–	–	–	–	–	–	–	–	–	–
FT upgrading	–	–	–	–	–	–	–	–	–	Fract.
MTG usage	Y	Y	Y	Y	Y	Y	Y	Y	Y	–
MTOD usage	–	–	–	–	–	–	–	Y	Y	–
Ortho_dis	–	Y	Y	–	–	–	–	–	–	Y
MX sorbex	–	–	–	–	–	–	–	–	–	–
UOP tatoray	–	Y	Y	Y	Y	Y	Y	Y	Y	Y
UOP cyclar	–	–	–	–	–	–	Y	Y	Y	Y
CO_2SEQ usage	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
GT usage	–	–	–	–	–	–	–	–	–	–

Biomass and natural gas—50 kBD

Case study	U-50-0	U-50–250	U-50–500	U-50–750	U-50–1000	U-50-VAR	U-50-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Biomass Conv.	S/V	S/V	S/V	S/V	S/V	S/V	S/V	S/V	S/V	S/V
Biomass Temp.	900.00	900.00	900.00	900.00	900.00	900.00	900.00	900.00	900.00	900.00
NG Conv.	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR
NG Temp.	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
WGS/RGS Temp.	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00
Min. wax FT	–	–	–	–	–	–	–	–	–	Co-HTFT
Nom. wax FT	–	–	–	–	–	–	–	–	–	–
FT upgrading	–	–	–	–	–	–	–	–	–	Fract.
MTG usage	Y	Y	Y	Y	Y	Y	Y	Y	Y	–
MTOD usage	–	–	–	–	–	–	–	Y	Y	–
Ortho_dis	–	–	–	–	–	–	–	–	–	–
MX sorbex	–	–	–	–	–	–	–	–	–	–
UOP tatoray	–	Y	Y	Y	Y	Y	Y	Y	Y	Y
UOP cyclar	–	–	–	–	–	–	Y	Y	Y	Y
CO_2SEQ usage	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
GT usage	–	–	–	–	–	–	–	–	–	–

Gasification of the biomass (Biomass Conv.) can proceed through either a solid (S) or solid/vapor (S/V) fueled system. Natural gas conversion (NG Conv.) can proceed through either steam reforming (SMR), autothermal reforming (ATR), partial oxidation (PO), or oxidative coupling (OC). Temperatures (Temp.; °C) of the biomass gasifier and natural gas conversion units, along with the operating temperature of the forward or reverse water-gas-shift reactor, are shown. Presence of any FT units in the refinery will be denoted as either cobalt-based (Co) or iron-based (Fe). The FT hydrocarbon effluent will be upgraded using fractionation (Fract.) or ZSM-5 catalytic conversion (ZSM-5). The conversion of methanol using the MTG process or MTO/MOGD technologies will be denoted using yes (Y) or no (-). Production of *o*-xylene using an *ortho*-xylene distillation column or production of *m*-xylene using the MX Sorbex reactor will be denoted using yes (Y) or no (–). Production of additional benzene and mixed xylenes using the UOP Tatoray process and conversion of LPG/light naphtha using the Cyclar process is illustrated in the table. The utilization of a gas turbine (GT) or a CO_2 sequestration system (CO_2SEQ) is noted using yes (Y) or no (–).

model contains 13,339 continuous variables, 40 binary variables, 16,045 constraints, and 855 nonconvex terms. The nonconvex terms consist of 775 bilinear terms, one trilinear term, six quadlinear terms, and 73 power functions. The complete mathematical model can be found in the Supplementary Information. A mixed-integer linear relaxation of the model is solved via CPLEX at every node in the tree, which then branches to form two children nodes.[77] Two hundred and fifty distinct starting points are generated for the root node and 10 for all others using the solution pool feature of CPLEX. The current binary variables are fixed at each starting point and the resulting nonlinear optimization (NLP) model is solved using CONOPT.[78] The upper bound of the model is only replaced if the solution of the NLP is lower than the existing upper bound. Any nodes that have a lower bound within ϵ tolerance from the best upper bound are eliminated from the branch-and-bound tree. The reader is directed to textbooks by Floudas[79,80] or reviews of global optimization methods[81–83] for a more detailed explanation of branch-and-bound algorithms. Moreover, Baliban et al.,[16] provides a more in-depth explanation of solving large scale MINLP process synthesis models.

Computational studies

The BGTL+C_6_C_8 process synthesis model described previously was used to examine 20 distinct case studies. The optimal solution was determined via a global optimization framework that terminated if all nodes in the branch-and-bound tree were examined or if 100 CPU hours had passed. [16] Three sets of liquid fuels products were considered that (a) represented ratios commensurate with the 2014 United States demand (i.e., 67 vol % gasoline, 22 vol % diesel, 11 vol % kerosene),[1] (b) produced at least 40 vol % diesel, or (c) freely output any composition of liquid fuels. Each set of case studies will examine two refinery capacities: 10 thousand and 50 thousand barrels per day (kBD) of gasoline equivalent (based on lower heating value [LHV]) fuels. Additionally, each case study will be constrained to produce a certain amount of aromatics. The aromatics produced will be dependent on the refinery scale of the BGTL+C_6_C_8 plant. In the unrestricted 10 kBD refineries, the amount of aromatics produced daily will be investigated parametrically (50, 100, 150, or 200 metric tons). Two additional case studies will allow the amount of aromatics to vary between 50 and 300 metric tons and 50 and 500 metric tons daily. In the unrestricted 50 kBD refineries, the amount of aromatics produced daily will be 250, 500, 750, or 1000 metric tons. Two additional case studies will allow the amount of aromatics produced to vary between 250 and 1500 metric tons and 250 and 2500 metric tons daily. The case studies will be denoted as $N-C-A$, where N represents the fuel composition of gasoline/diesel/kerosene in the unrestricted (U), diesel (D), or U.S. ratios (R) cases, C represents the refinery capacity, and A represents the amount of aromatics produced daily. For example, U-10–50 represents a refinery that outputs 10 kBD of gasoline equivalent fuels in any unrestricted composition and coproduces 50 metric tons of aromatics. Furthermore, two case studies (FT-10-VAR and FT-50-VAR) restrict the topology of the optimal solution so that the synthesis gas must be converted through one of the six FT reactors (i.e., the methanol synthesis reactor is excluded) in the process synthesis superstructure. These two case studies have no restriction on the composition of the final liquid products. The explanation of all case studies is provided in Table 5.

Each of the case studies includes an environmental constraint that imposes at least a 50% reduction in LGHG emissions from fossil fuel-based processes. The GHG emissions of a typical petroleum-based refinery (91.6 kg CO_{2eq}/GJ_{LHV}),[84] a HVC production plant (1.7 kg CO_{2eq}/kg of HVC),[85] and a natural gas combined cycle plant (101.3 kg CO_{2eq}/GJ) that produces electricity[70] are used to calculate the GHG emissions threshold for the BGTL+C_6_C_8 refinery. If electricity is input to the refinery, the GHG emissions from electricity are added to the life cycle emissions of the BGTL+C_6_C_8 refinery; whereas the GHG emissions from electricity are subtracted from the life cycle emissions of the BGTL+C_6_C_8 refinery if electricity is output from the refinery.

The cost parameters used in the process synthesis model are illustrated in Table 6. The costs associated with the delivery of the feedstock are included in the feedstock costs; while the delivery costs of the products are not included in the product costs. The transportation, storage, and monitoring costs of CO_2 are displayed in Table 6, whereas the costs associated with the capture and compression of CO_2 are included in the investment costs of the BGTL+C_6_C_8 plant.[21]

Once the optimal process topology is determined, the minimum number of heat exchanger matches will be calculated based on (1) the fluid flow rates and operating conditions of the heat engines, (2) the amount of electricity produced by the heat engines, (3) the amount of cooling water required by the heat engines, and (4) the location of all pinch points in the subnetworks.[19,20,79,86] The minimum annualized cost of the heat exchanger network can then be determined and added to the overall BGTL+C_6_C_8 refinery investment cost.[21]

Optimal process topologies

The optimal process topologies selected within the BGTL+C_6_C_8 refinery are shown in Table 7. Table 7 illustrates (1) the operation of the biomass gasifier, (2) the temperature of the biomass gasifier, (3) the selection of the natural gas conversion unit, (4) the operating temperature of the natural gas conversion unit, (5) the selection of the synthesis gas conversion units, (6) the selection of the FT upgrading technology, (7) the methanol conversion units, (8) the selection of the *ortho*-xylene distillation column, (9) the selection of the UOP Tatoray or UOP Cyclar processes, (10) the selection of a CO_2 sequestration system, and (11) the existence of a gas turbine.

As explained in the Supplementary Information, the biomass gasifier can input either solid biomass or a combination of solid biomass and recycle gases. Table 7 demonstrates that each of the case studies selected the solid and vapor-fueled gasifier. Additionally, the process synthesis superstructure includes 3 discrete operating temperatures for the biomass gasifier: 900, 1000, or 1100°C. Gasifiers operating at lower temperatures have less favorable conditions for CO_2 consumption because the equilibrium constant of the forward WGS reaction is higher. Furthermore, these gasifiers will require less oxygen for combustion and produce less waste heat for steam generation. Gasifiers operating at higher temperatures have more favorable conditions for CO_2 consumption and will produce more waste heat for steam generation. As Table 7 illustrates, the operating temperature of the

Table 8. Overall Cost Results ($/GJ) for the 20 Case Studies

Biomass and natural gas—10 kBD

Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Biomass	2.82	2.85	2.87	2.88	2.90	2.93	2.69	2.63	2.66	3.10
NG	4.26	4.29	4.32	4.34	4.37	4.42	4.06	3.97	4.01	4.51
Butane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.51
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Investment	6.37	6.52	6.57	6.68	6.71	6.75	6.72	6.85	6.86	8.05
CO_2 TS&M	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.11
O&M	1.66	1.70	1.71	1.74	1.75	1.75	1.75	1.78	1.78	2.09
Electricity	−0.29	−0.24	−0.18	0.00	0.09	0.25	0.61	0.19	0.25	−0.78
LPG	−1.41	−1.42	−1.42	−1.43	−1.43	−1.44	−0.19	0.00	−0.15	0.00
Benzene	0.00	−0.23	−0.44	−0.64	−0.83	−1.16	−2.06	−1.28	−1.39	−0.50
Toluene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.04	0.00	−1.23
Para-xylene	0.00	−0.59	−1.13	−3.22	−4.15	−5.84	−8.31	−5.05	−5.60	−1.21
Ortho-xylene	0.00	−0.48	−0.93	0.00	0.00	0.00	0.00	0.00	0.00	−1.15
Meta-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gasoline	−21.84	−21.05	−20.32	−19.63	−18.99	−17.83	−15.88	−10.42	−11.58	−6.50
Diesel	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−7.38	−3.95	−6.70
Kerosene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−2.01	−5.43
Total ($/GJ)	−8.38	−8.60	−8.91	−9.23	−9.53	−10.13	−10.55	−8.69	−9.04	−5.12
Lower bound ($/GJ)	−9.12	−9.03	−9.33	−9.54	−10.07	−10.60	−10.69	−8.81	−9.45	−5.52
Gap (%)	8.11	4.82	4.46	3.31	5.29	4.48	1.32	1.29	4.31	7.24

Biomass and natural gas—50 kBD

Case study	U-50-0	U-50-250	U-50-500	U-50-750	U-50-1000	U-50-VAR	U-50-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Biomass	3.11	3.12	3.09	3.10	3.16	3.18	2.95	2.89	2.91	3.08
NG	4.68	4.71	4.66	4.68	4.76	4.79	4.44	4.35	4.39	4.38
Butane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.81
Water	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Investment	4.70	4.85	4.90	4.96	5.01	5.07	5.03	4.87	4.92	5.91
CO_2 TS&M	0.07	0.07	0.07	0.07	0.07	0.07	0.08	0.08	0.08	0.11
O&M	1.22	1.26	1.27	1.29	1.30	1.32	1.31	1.27	1.28	1.54
Electricity	−1.18	−1.05	−0.79	−0.68	−0.72	−0.54	−0.17	−0.59	−0.52	−0.28
LPG	−1.41	−1.42	−1.42	−1.43	−1.43	−1.44	−0.19	0.00	−0.15	0.00
Benzene	0.00	−0.23	−0.44	−0.64	−0.83	−1.16	−2.06	−1.28	−1.39	−0.63
Toluene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.04	0.00	−1.48
Para-xylene	0.00	−1.15	−2.22	−3.22	−4.15	−5.84	−8.31	−5.05	−5.60	−3.32
Ortho-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Meta-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gasoline	−21.84	−21.05	−20.32	−19.63	−18.99	−17.83	−15.88	−10.42	−11.58	−8.42
Diesel	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−7.38	−3.95	−0.59
Kerosene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−2.01	−9.07
Total ($/GJ)	−10.63	−10.89	−11.20	−11.51	−11.81	−12.38	−12.80	−11.31	−11.60	−7.96
Lower bound ($/GJ)	−11.11	−11.78	−12.21	−12.63	−12.70	−13.03	−13.05	−11.60	−11.66	−8.49
Gap (%)	4.32	7.63	8.31	8.92	7.04	5.04	1.90	2.45	0.48	6.29

The contributions to the total costs (in $/GJ) of the BGTL+$C_6_C_8$ refineries come from biomass, natural gas, butane, water, CO_2 transportation/storage/monitoring, investment, input electricity, and operating and maintenance. The contributions to the total revenues (in $/GJ) come from LPG, output electricity, benzene, toluene, *para*-xylene, *ortho*-xylene, *meta*-xylene, gasoline, diesel, and kerosene. The total figure represents the difference between the costs and the revenues. The more negative this value is the more profitable a refinery becomes. The overall profit can be determined by taking the negative of the "Total ($/GJ)" value. The lower bound values are reported along with the optimality gap between the optimal solution and the lower bound.

biomass gasifier was selected to be 900°C in each of the case studies.

Natural gas conversion can proceed through either steam–methane reforming, autothermal reforming, partial oxidation to methanol, or oxidative coupling to produce olefins. Three discrete operating temperatures were allowed for both the steam–methane reformer (800, 850, or 900°C) and the autothermal reformer (900, 950, or 1000°C). Although the cost of an autothermal reformer is less than that of a steam reformer (Table 3), the auxiliary cost of the air separation unit makes the ATR more capital intensive at lower scales. However, because the scaling factor for the ASU (0.5) is lower than that of both reformers (0.67), there is a point at which the capital and operating costs associated with an ATR become more economical than those associated with the operation of an SMR. Hence, it is anticipated that at lower scales SMR is the favored technology and at higher scales ATR becomes the preferred technology. Baliban et al.,[22] investigated this topological shift in a previous study on the conversion of only natural gas to liquid fuels. However, because the presence of the biomass gasifier requires the existence of an air separation unit in the BGTL+$C_6\_C_8$ refinery, the incremental capital cost of an ATR is less than it would be in a GTL refinery. Therefore, the natural gas conversion technology selected in each of the case studies was the autothermal reformer. For the case study that did not produce any chemicals, U-10-0, the operating temperature of the ATR was 900°C; whereas the operating temperature for the rest of the case studies was selected to be 1000°C.

The sour WGS reactor could operate at four distinct temperatures of 300, 400, 500, or 600°C. Each of the case studies selected a WGS reactor that operated at 300°C.

The selection of the hydrocarbon production and upgrading routes was dictated by the composition of liquid fuels

Table 9. Breakdown of the Investment Costs for the 20 Case Studies

Biomass and natural gas—10 kBD

Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Syngas generation	194	200	206	213	219	232	243	213	218	218
Syngas cleanup	149	153	157	161	165	172	180	162	165	167
Hydrocarbon production	71	73	75	77	79	84	89	77	79	100
Hydrocarbon upgrading	121	124	127	131	136	144	154	170	170	262
Chemicals production	0	28	44	70	85	112	191	127	135	64
Hydrogen/oxygen production	126	129	132	134	137	142	148	135	137	137
Heat and power integration	63	63	64	62	62	62	58	60	60	96
Wastewater integration	28	28	28	27	27	27	25	26	26	33
Total (MM $)	751	798	832	876	910	975	1090	970	990	1078

Biomass and natural gas—50 kBD

Case study	U-50-0	U-50-250	U-50-500	U-50-750	U-50-1000	U-50-VAR	U-50-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Syngas generation	819	851	878	909	943	1004	1060	914	937	943
Syngas cleanup	534	554	572	592	614	653	692	598	613	617
Hydrocarbon production	281	292	302	313	324	345	367	315	323	430
Hydrocarbon upgrading	501	520	539	558	576	614	657	575	601	1059
Chemicals production	0	99	158	208	252	331	564	376	400	271
Hydrogen/oxygen production	334	346	362	374	384	409	441	376	386	395
Heat and power integration	215	215	210	210	216	217	213	210	210	292
Wastewater integration	88	89	87	87	88	89	86	86	86	90
Total (MM$)	2772	2965	3108	3250	3397	3662	4080	3450	3555	4098

The costs of the syngas generation, syngas cleaning, hydrocarbon production, hydrocarbon upgrading, chemicals production, hydrogen/oxygen production, heat and power integration, and wastewater treatment sections of the BGTL+C_6-C_8 refinery are shown. All values are shown in MM$.

produced by the BGTL+C_6_C_8 refinery. In the unrestricted case studies, the synthesis gas was directed to the methanol synthesis reactor. Subsequently, the methanol was sent to the MTG reactor to produce gasoline and LPG. In the 10 kBD case studies, there is an important topological shift in the type of chemicals produced. At low chemicals production (50 and 100 metric tons/day), the C_{8+}-rich stream was directed to the xylene Column 1. From there, the bottom is directed to the *o*-xylene distillation column to produce *ortho*-xylene. However, as the chemicals production increased, the C_{8+}-rich stream was directed to the xylene Column 2, where the bottoms from this column was then directed to the C_9 distillation column, while the distillate was sent to the UOP Parex for *para*-xylene separation. None of the 50 kBD case studies that produced chemicals selected to produce *o*-xylene. Each of the unrestricted case studies that produced chemicals selected the UOP Tatoray process to convert the toluene and C_9 aromatics in the aromatics complex into additional benzene and xylenes. The unrestricted parametric case studies, as well as the U-10-VAR and U-50-VAR case studies, did not select to utilize the Cyclar process. Due to the high capital costs associated with the Cyclar process, it is much more profitable to extract the aromatics from the gasoline already present within the process. However, since aromatics are much more valuable than liquid fuels, the U-10-VAR2 and U-50-VAR2 case studies display an important topological shift. After the maximum amount of aromatics from the MTG gasoline are extracted, then the LPG cut is directed to the Cyclar process to produce additional aromatics. That is, the profit from selling the more valuable aromatics via the Cyclar process is larger than the one obtained from selling LPG. Therefore, aromatics production from LPG via the Cyclar process is still profitable, but only as the second option behind extraction from the gasoline.

The diesel case studies split the methanol produced in the methanol synthesis reactor to both the MTG and MTO and olefins-to-gasoline/distillate processes. The MOGD unit produced the diesel necessary to meet the requirements (40% diesel by volume) for this set of case studies. As explained in the Supplementary Information, since the liquid fuel products exiting the MOGD reactor are modelled as pseudocomponents, the only means of producing aromatics is by extracting them from the gasoline present in the MTG effluent or by passing the LPG by-product from the MTG reactor over a metal-promoted H-ZSM-5 catalyst using the Cyclar process. In fact, both of these routes are used as the MTG gasoline is directed to the aromatics complex for extraction of the aromatics and the LPG is converted into an aromatic-rich blend.

Likewise, the U.S. ratios case studies also selected both the MTG and MOGD processes to produce liquid fuels in ratios commensurate with 2014 U.S. demand. The MTG process produced the necessary amount of gasoline, while the MOGD reactor produced the required distillate. Both the max diesel and U.S. ratios case studies selected to include the UOP Tatoray process as well as the Cyclar process. Neither selected to produce *ortho*-xylene as a byproduct.

The FT-10-VAR and FT-50-VAR case studies both selected to produce hydrocarbons via the cobalt-based high temperature FT reactor. The FT hydrocarbons were separated via standard fractionation. In the FT-10-VAR case study, *ortho*-xylene is produced; whereas the FT-50-VAR case study does not produce any *ortho*-xylene. Both case studies selected the existence of the UOP Tatoray process, as well as the Cyclar process. The Cyclar process was used to reform the LPG and light naphtha into additional aromatics.

All of the case studies selected to bypass the UOP MX Sorbex process for *meta*-xylene production. Despite being the second most valuable xylene, the high capital costs associated with the MX Sorbex reactor make *meta*-xylene production less economical than directing the *para*-xylene depleted raffinate from the UOP Parex reactor to the UOP Isomar unit to reestablish an equilibrium mixture of xylenes.

Table 10. Net Present Value Parameters for the BGTL+C_6_C_8 Refinery

Parameter	Value	Parameter	Value
Operating days	330 days	O&M costs	4.5% of FCI
Working capital	15% of FCI	Local taxes and insurance	3% of FCI
Discount rate	10%	Supervision and clerical labor	15% of operating labor
Lifetime	30 years	SARE	10% of gross sales
Depreciation	10 year MACRS	Investment period	3 years
Tax rate	40%	Supplies	15% of O&M

Table 11. Operating Labor for a 10kBD BGTL+C_6_C_8 Refinery

Major Refinery Section	Operators/Shift	Major Refinery Section	Operators/Shift
Syngas generation	6	Syngas cleaning	3
Hydrocarbon production	6	Hydrocarbon upgrading	6
Chemicals production	9	Hydrogen/oxygen production	3
Heat and power integration	3	Wastewater network	3

Furthermore, all of the case studies selected the existence of a CO_2 sequestration system to meet the environmental constraint present in the model. None of the case studies used a gas turbine.

Overall profit of liquid fuels and aromatics

The breakdown (in \$/GJ) of the overall profit for each of the case studies is shown in Table 8. The total profit takes (1) the feedstock costs, (2) the CO_2 sequestration costs, (3) the investment costs, (4) the operating and maintenance (O&M) costs, (5) the electricity costs or sales, (6) the sales from LPG, (7) the sales from aromatics, and (8) the sales from liquid products into account. Each of the figures is normalized with respect to the total energy (in GJ) of aromatics and liquid fuels (gasoline, diesel, and kerosene) produced. Additionally, the lower bound (in \$/GJ) is shown for each of the case studies and the corresponding optimality gap is calculated. The optimality gap between the optimal solutions and the corresponding lower bounds ranges between 0.5 and 9% for each of the case studies investigated. The total figure (total: \$/GJ) shown in Table 8 is presented as the difference between the costs associated with the production of aromatics and liquid fuels and the total revenue obtained from selling these products. A more negative value corresponds to a more profitable BGTL+C_6_C_8 refinery.

The total cost of all the feedstocks (biomass, natural gas, butane, and freshwater) represents the largest expenditure associated with most (except for the D-10-VAR and R-10-VAR case studies) of the BGTL+C_6_C_8 refineries. The capital investment represents the second largest expense in the case studies shown. In the unrestricted, nominal case study (U-10-0) with no chemicals coproduction, the overall profit is \$8.39/GJ. As the chemicals production parametrically increases, the refineries become more profitable despite increased investment and feedstock costs. In the U-10–50 case, the overall profit increases to \$8.60/GJ as the refinery produces benzene, *ortho*-xylene, and *para*-xylene in addition to gasoline and LPG. As noted in the previous section, there is a topological shift between the U-10–100 and U-10–150 case studies, after which the refinery no longer selects the existence of the *ortho*-xylene distillation column and mainly produces the most valuable xylene isomer: *para*-xylene. In the unrestricted, variable chemicals case (U-10-VAR2), the refinery produces 500 metric tons of aromatics and has an overall profit of \$10.55/GJ. The most profitable products in this case study include gasoline (\$15.88/GJ) and *para*-xylene (\$8.31/GJ). In the U-10 case studies with lower chemicals production, the refineries produce electricity (evident in the U-10-0, U-10–50, and U-10–100 case studies). However, as the chemicals production increases, the refineries require electricity (evident in the U-10–200, U-10-VAR, and U-10-VAR2 case studies). This is in direct contrast with the U-50 case studies, which show no shift from the production of electricity to the requirement of electricity, and consistently sell electricity to the grid as a by-product.

In the unrestricted, 50 kBD (U-50) case studies, the normalized contribution of the total unit investment cost is much smaller than in the U-10 case studies. This is because the refineries can take advantage of economies of scale. The authors note that economies of scale are most evident when comparing refineries that produce 10 kBD of liquid fuels or less. This is because these plants will only require a single train for most sections of the plant; therefore, when scaling up, the refinery can take full advantage of the low scaling factor (0.5–0.7). As the refinery capacity increases, multiple trains of the same unit will need to be introduced to meet the production requirement, and the scaling factor will begin to approach 0.9.[69] In the nominal case study (U-50-0), the total profit is \$10.63/GJ. In each of the U-50 parametric case studies investigated, the refinery outputs gasoline, LPG, benzene, and *para*-xylene. As the BGTL+C_6_C_8 refinery produces more chemicals, the profit increases. In the U-50–250 case study, the profit increases to \$10.89/GJ, with the aromatics and gasoline contributing \$1.38/GJ and \$21.05/GJ to the overall profit, respectively. In the variable chemicals

Table 12. 10 Year MACRS Recovery [88]

Year	Depreciation Rate (%)	Year	Depreciation Rate (%)
1	10.00	7	6.55
2	18.00	8	6.55
3	14.40	9	6.56
4	11.52	10	6.55
5	9.22	11	3.28
6	7.37		

Table 13. Capacity and Maintenance Factors

Year	Capacity Factor (%)	Year	Maintenance Factor (%)
1	50	1	75
2	90	2	95
3	100	3	100

case study (U-50-VAR2), the refinery chooses to produce the chemicals at the upper threshold of the constraint (2500 metric tons per day). This case study has the largest overall profit at \$12.80/GJ, while outputting gasoline (\$15.88/GJ), LPG (\$0.19/GJ), electricity (\$0.17/GJ), benzene (\$2.06/GJ), and *para*-xylene (\$8.31/GJ). Consistent with the U-10 case studies, as the amount of chemicals produced increases, the feedstock and investment costs increase.

In the maximization of diesel case studies (D-10-VAR and D-50-VAR), the BGTL+C_6_C_8 refineries produce 40 vol % of diesel and 60 vol. % of gasoline using the MTG and MTO/olefins-to-gasoline-and-distillate reactors. The amount of aromatics produced in each case study is 270 and 1350 MT/day, respectively. The authors note that the refinery cannot produce aromatics at the upper threshold (300 and 1500 MT/day), even though aromatics production is more profitable (evident from the parametric unrestricted case studies), because the MOGD products (gasoline, diesel, and kerosene) are modelled as pseudocomponents. The refinery extracts the aromatics from the MTG effluent and additionally produces more aromatics by sending the LPG to the Cyclar process.

Similarly, the U.S. ratios case studies (R-10-VAR and R-50-VAR) send a portion of the LPG to the Cyclar process in order to produce aromatics. These case studies produce the upper limit of aromatics (300 and 1500 MT/day, respectively). The FT case studies extract the aromatics from the naphtha produced within the refinery and send the light naphtha and LPG to the Cyclar process to be converted into petrochemical-grade aromatics. The amount of aromatics produced in the FT-10-VAR case study is 181 MT/day and 1184 MT/day in the FT-50-VAR case study. All three liquid fuels are produced.

The results shown in Table 8 illustrate that the composition of liquid products produced has a significant effect on the overall profit of the refineries. The sequence of most profitable to least profitable refineries (comparing only the variable chemicals case studies) is: (1) unrestricted liquid fuels composition (\$10.13/GJ), (2) U.S. ratios (\$9.04/GJ), (3) maximization of the diesel product (\$8.69/GJ), and (4) unrestricted FT-based fuels (\$5.12/GJ).

Investment costs

The TPCs, or the FCIs, along with the breakdown for each of the major sections of the BGTL+C_6_C_8 refinery, are shown in Table 9. The major sections include syngas generation, syngas cleaning, hydrocarbon production, hydrocarbon upgrading, chemicals production, hydrogen/oxygen production, heat and power integration, and wastewater treatment. Syngas generation represents the largest contributor to the TPC in all case studies except for FT-10-VAR and FT-50-VAR, as shown in Table 9. It represents between 22–26 and 26–30% of the TPC in the 10 and 50 kBD case studies, respectively. Syngas cleanup and hydrocarbon upgrading

Table 14. Total Manufacturing Costs for U-10-VAR2 Case Study

Biomass and Natural Gas—10 kBD									
Year	Raw Materials	CO_2 TS&M	Labor	O&M	Supplies	Depreciation	Electricity Cost	Insurance	Total Man
−2	0	0	0	0	0	0	0	0	0
−1	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
1	−84,319,348	−1,184,131	−5,536,440	−32,752,830	−4,912,924	−109,005,890	−7,661,875	−32,701,767	−278,075,205
2	−151,774,826	−1,499,899	−8,943,480	−41,486,918	−6,223,038	−196,210,601	−13,791,375	−32,701,767	−452,631,904
3	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−156,968,481	−15,323,750	−32,701,767	−435,227,781
4	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−125,574,785	−15,323,750	−32,701,767	−403,834,085
5	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−100,503,430	−15,323,750	−32,701,767	−378,762,730
6	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−80,337,341	−15,323,750	−32,701,767	−358,596,640
7	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−71,398,858	−15,323,750	−32,701,767	−349,658,157
8	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−71,398,858	−15,323,750	−32,701,767	−349,658,157
9	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−71,507,864	−15,323,750	−32,701,767	−349,767,163
10	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−71,398,858	−15,323,750	−32,701,767	−349,658,157
11	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	−35,753,932	−15,323,750	−32,701,767	−314,013,232
12	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
13	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
14	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
15	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
16	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
17	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
18	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
19	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
20	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
21	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
22	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
23	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
24	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
25	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
26	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
27	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
28	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
29	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300
30	−168,638,696	−1,578,841	−9,795,240	−43,670,440	−6,550,566	0	−15,323,750	−32,701,767	−278,259,300

Table 15. NPV Analysis for U-10-VAR2 Case Study

Biomass and Natural Gas—10 kBD

Year	Investment	Working Capital	Total Man	Gross Sales	SARE	Net Profit Before Tax	Net Profit After Tax	Depreciation Credit	Cash Flow	Discounted Cash Flow	Total Discounted Cash Flow
−2	−272,514,724	0	0	0	0	0	0	0	−272,514,724	−329,742,816	−329,742,816
−1	−545,029,449	0	0	0	0	0	0	0	−545,029,449	−599,532,393	−929,275,210
0	−272,514,724	−163,508,835	0	0	0	0	0	0	−436,023,559	−436,023,559	−1,365,298,769
1	0	0	−278,075,205	330,323,747	−33,032,375	19,216,167	11,529,700	109,005,890	120,535,590	109,577,809	−1,255,720,959
2	0	0	−452,631,904	594,582,744	−59,458,274	82,492,565	49,495,539	196,210,601	245,706,141	203,062,926	−1,052,658,033
3	0	0	−435,227,781	660,647,493	−66,064,749	159,354,963	95,612,978	156,968,481	252,581,459	189,768,189	−862,889,845
4	0	0	−403,834,085	660,647,493	−66,064,749	190,748,659	114,449,196	125,574,785	240,023,980	163,939,608	−698,950,236
5	0	0	−378,762,730	660,647,493	−66,064,749	215,820,014	129,492,008	100,503,430	229,995,439	142,809,072	−556,141,164
6	0	0	−358,596,640	660,647,493	−66,064,749	235,986,103	141,591,662	80,337,341	221,929,003	125,273,136	−430,868,028
7	0	0	−349,658,157	660,647,493	−66,064,749	244,924,586	146,954,752	71,398,858	218,353,610	112,049,927	−318,818,101
8	0	0	−349,658,157	660,647,493	−66,064,749	244,924,586	146,954,752	71,398,858	218,353,610	101,863,570	−216,954,530
9	0	0	−349,767,163	660,647,493	−66,064,749	244,815,581	146,889,348	71,507,864	218,397,212	92,621,737	−124,332,793
10	0	0	−349,658,157	660,647,493	−66,064,749	244,924,586	146,954,752	71,398,858	218,353,610	84,184,769	−40,148,024
11	0	0	−314,013,232	660,647,493	−66,064,749	280,569,512	168,341,707	35,753,932	204,095,639	71,534,276	31,386,253
12	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	60,474,239	91,860,491
13	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	54,976,581	146,837,072
14	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	49,978,710	196,815,781
15	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	45,435,191	242,250,972
16	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	41,304,719	283,555,690
17	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	37,549,744	321,105,435
18	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	34,136,131	355,241,566
19	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	31,032,846	386,274,412
20	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	28,211,679	414,486,091
21	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	25,646,981	440,133,072
22	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	23,315,437	463,448,508
23	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	21,195,852	484,644,360
24	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	19,268,956	503,913,316
25	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	17,517,233	521,430,549
26	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	15,924,757	537,355,306
27	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	14,477,052	551,832,358
28	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	13,160,956	564,993,314
29	0	0	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	189,794,066	11,964,506	576,957,820
30	0	163,508,835	−278,259,300	660,647,493	−66,064,749	316,323,444	189,794,066	0	353,302,901	20,247,278	597,205,098

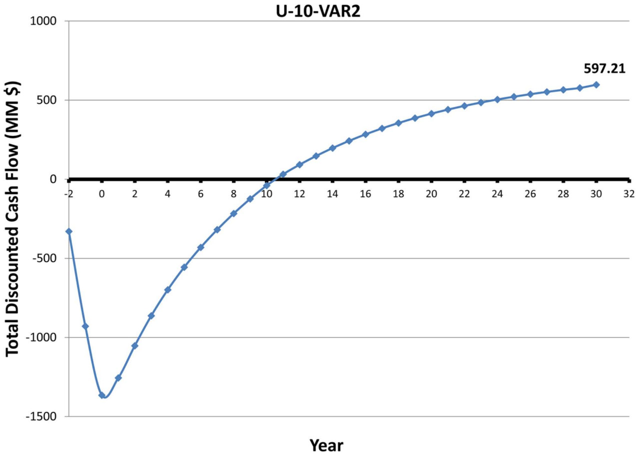


Figure 6. Discounted cash flow over the span of the lifetime for the U-10-VAR2 case study.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

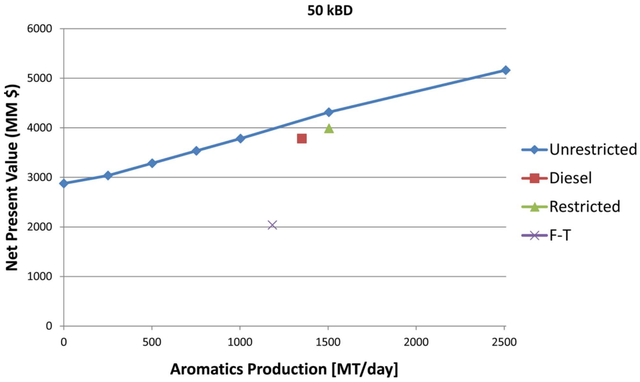


Figure 8. Net present values for the 50 kBD case studies.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

represent the next two largest contributors to the TPC. As the amount of chemicals produced increases in the parametric, unrestricted case studies, the chemicals production section begins to contribute a larger portion to the TPC. Additionally, the costs associated with the upstream sections (syngas generation, syngas cleanup, etc.), will also increase because of the larger flow rate required to meet the aromatics demand. The wastewater treatment section is the smallest contributor to the TPC and represents around 2–4% of the TPC in the 10 and 50 kBD case studies. The TPC can be expressed as an "overnight" cost by factoring in the preproduction costs, inventory capital, financing costs, and other owner's costs.[69,70]

As Table 9 illustrates, the TPC ranges from \$970 to \$1090 MM for the 10 kBD plants and \$3450 to \$4098 MM for the 50 kBD plants with variable chemicals production. For a BGTL+C_6_C_8 refinery that produces 2500 metric tons of aromatics per day (U-50-VAR2), the total cost for the aromatics complex is \$564 MM and the total investment cost for the refinery is \$4080 MM.

Net present value

The NPV is used to compare projects with different payment schedules but similar lifetimes and has been described in previous textbooks.[87] This section will describe in detail the assumptions made to calculate the NPV for each of the BGTL+C_6_C_8 refineries. The main parameters used in the NPV analysis are outlined in Table 10.

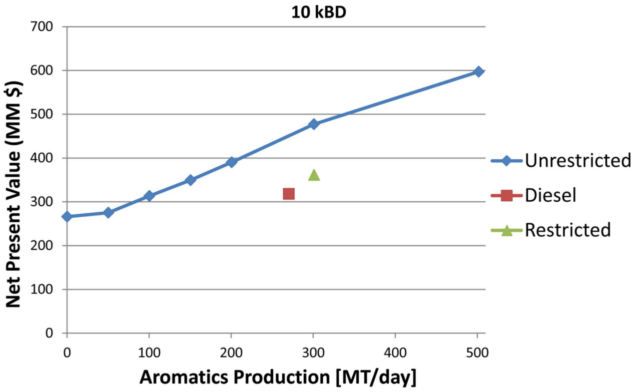


Figure 7. Net present values for the 10 kBD case studies.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The plant is assumed to operate for 330 days/year and the operating and maintenance costs are assumed to be 4.5% of the FCI. Working capital is defined as the funds required to operate the plant due to delays in payment and is necessary to meet the initial payroll and expenses.[87] The working capital is assumed to be 15% of the FCI and is recovered at the end of the plant lifetime. Depending on where the plant is located, the local property taxes can range anywhere between 1 and 4% of the FCI.[88] Additionally, the property insurance depends on which process is being carried out and usually amounts to 1% of the FCI per year.[88] Local taxes and insurance are assumed to be 3% of the FCI per year. The time value of money is an important consideration to take into account when calculating the present worth of an investment.[88] The discount rate, or nominal risk free interest rate, quantifies the opportunity cost of not investing the money in a risk free market, and instead, investing it in this project. The discount rate is used to obtain the present worth of a future amount of money.[88] In this analysis, the discount rate is assumed to be 10%. The operating supplies for a plant are considered to be consumable materials (such as charts, lubricants, test chemicals, etc.) and are assumed to be 15% of the operating and maintenance costs.[88]

Every major section of the BGTL+C_6_C_8 plant is assigned a certain number of operators, which is outlined in Table 11 for a 10 kBD plant. Thus, the BGTL+C_6_C_8 refinery (that produces 10 kBD of liquid fuels) requires 39 operators (30 operators for a plant in the nominal case study). It is assumed that the plant operates at three shifts (8 h/shift), and thus requires 117 total operators. It is assumed the operators work 40 h/week, 2080 h/year, and have a salary rate of \$35/h. Since the relationship between labor requirements and production capacity is not a linear one,[88] a scaling factor of 0.3 is used to calculate the operating labor for a 50 kBD plant. Since a certain amount of operating supervision and clerical assistance is always required, the cost for this portion of the analysis is assumed to be 15% of the cost for the operating labor.[88] The cost for supervision and clerical assistance is assumed to remain fixed at 100% capacity rate, even when the plant operates at reduced capacities (i.e., during the start-up periods of the plant).[88]

Table 16. Payback Period in Years for Each Case Study

10 kBD										
Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Payback period (years)	14	14	13	13	12	12	11	14	14	-
50 kBD										
Case study	U-50-0	U-50-250	U-50-500	U-50-750	U-50-1000	U-50-VAR	U-50-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Payback period (years)	8	8	8	8	8	7	7	8	8	12

The lifetime of the plant was assumed to be 30 years with a salvage value of zero. The standard modified accelerated cost recovery system, MACRS (which uses a classical double-declining-balance method and switches to straight-line at a point, and makes use of the half-year convention) was applied.[88] The depreciation period for the plant was 10 years, and the depreciation rate for the 10-year recovery period is shown in Table 12. The capital investment of the plant is spent over a 3-year construction period, where 25, 50, and 25% of the investment is made in the first, second, and third years, respectively.

The sales, administration, and research expenses (SARE) are general expenses involved with the operations of the refinery. In this analysis, the SARE are assumed to be 10% of the gross sales.[87] A federal tax rate of 40% is used. To calculate earnings, Eqs. 5–7 are used

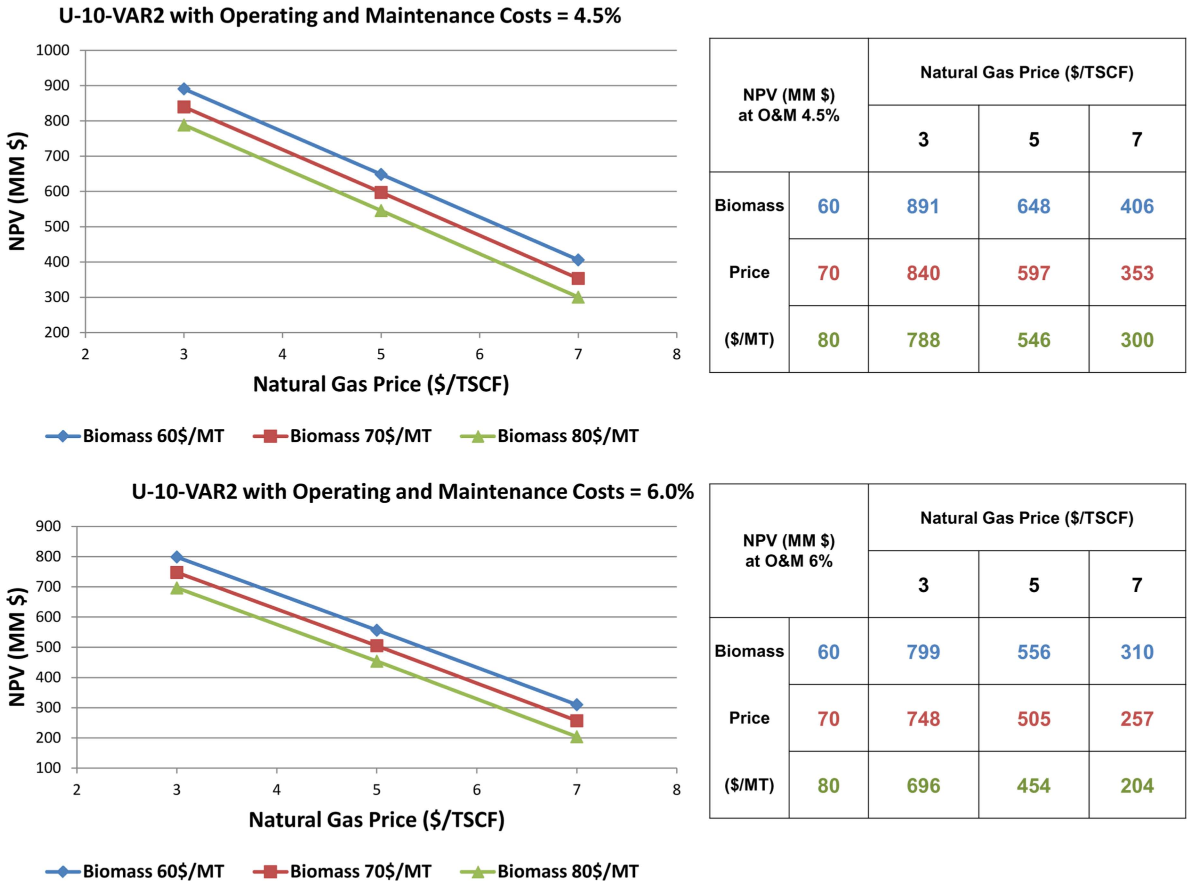
$$\text{Gross Profit} = \text{Gross Sales} - \text{Manufacturing Cost} \qquad (5)$$

$$\text{Net Profit Before Taxes} = \text{Gross Profit} - \text{SARE Expenses} \qquad (6)$$

$$\text{Net Annual Earnings} = \text{Net Profit Before Taxes} \cdot (1 - \text{Tax Rate}) \qquad (7)$$

The total manufacturing costs include (1) the raw materials cost, (2) sequestered CO_2 transportation, storage, and maintenance costs, (3) labor costs, (4) operating and maintenance costs, (5) the cost of supplies, (6) depreciation, (7) local taxes and insurance, and (8) any costs associated with the purchase of electricity. The gross sales include the profit obtained from selling the liquid fuels, chemicals, and electricity. Items (1), (2), (4), and the total gross sales are calculated using Table 8 and are converted to \$/year with 330 days/year of operation. The cash flow for each year can be calculated using Eq. 8:

$$\text{Cash Flow}_i = \text{Investment}_i + \text{Working Capital}_i + \text{Net Annual Earnings}_i + \text{Depreciation Credit}_i \qquad (8)$$



NPV (MM $) at O&M 4.5%		Natural Gas Price ($/TSCF)		
		3	5	7
Biomass	60	891	648	406
Price	70	840	597	353
($/MT)	80	788	546	300

NPV (MM $) at O&M 6%		Natural Gas Price ($/TSCF)		
		3	5	7
Biomass	60	799	556	310
Price	70	748	505	257
($/MT)	80	696	454	204

Figure 9. Parametric analysis for the U-10-VAR2 case study.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 17. Overall Material Balances for the 20 Case Studies

Biomass and natural gas—10 kBD										
Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Biomass (dt/h)	92.54	96.74	100.95	105.03	109.20	117.54	121.29	103.72	106.81	115.51
NG (mscf/h)	1.95	2.04	2.13	2.22	2.31	2.48	2.56	2.19	2.25	2.35
Butane (kBD)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41
Water (kBD)	1.31	1.04	0.77	0.00	0.00	0.00	0.00	0.00	0.00	7.11
Gasoline (kBD)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	5.73	6.49	3.38
Diesel (kBD)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.82	2.08	3.27
Kerosene (kBD)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.09	2.73
LPG (kBD)	1.86	1.94	2.02	2.10	2.18	2.34	0.35	0.00	0.24	0.00
Benzene (MT/day)	0.00	9.08	18.17	27.40	36.53	54.79	109.12	59.28	65.31	21.86
Toluene (MT/day)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.27	0.00	59.56
P-xylene (MT/day)	0.00	20.88	41.76	123.04	164.05	246.07	392.60	208.65	235.72	47.18
O-xylene (MT/day)	0.00	20.18	40.37	0.00	0.00	0.00	0.00	0.00	0.00	52.57
M-xylene (MT/day)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seq. CO_2 (ton/h)	21.63	23.02	24.40	26.49	28.12	31.36	39.86	34.98	34.99	57.28
Vented CO_2 (ton/h)	86.94	91.05	95.15	98.17	101.91	109.40	104.85	89.61	93.47	117.91
Biomass and natural gas—50 kBD										
Case study	U-50-0	U-50-250	U-50-500	U-50-750	U-50-1000	U-50-VAR	U-50-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Biomass (dt/h)	509.18	530.73	544.08	565.35	595.38	638.47	664.03	568.45	584.39	594.06
NG (mscf/h)	10.75	11.20	11.48	11.93	12.56	13.47	14.01	12.00	12.33	11.82
Butane (kBD)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.39
Water (kBD)	24.54	22.36	17.00	14.73	16.54	11.55	1.26	12.66	11.77	46.39
Gasoline (kBD)	50.00	50.00	50.00	50.00	50.00	50.00	50.00	28.67	32.47	22.69
Diesel (kBD)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	19.11	10.41	1.50
Kerosene (kBD)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.44	23.59
LPG (kBD)	9.32	9.72	10.11	10.51	10.90	11.69	1.73	0.00	1.19	0.00
Benzene (MT/day)	0.00	45.66	91.33	136.99	182.65	273.97	545.60	296.41	326.54	141.60
Toluene (MT/day)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.35	0.00	371.59
P-xylene (MT/day)	0.00	205.06	410.12	615.18	820.23	1230.34	1962.98	1043.27	1178.59	670.60
O-xylene (MT/day)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
M-xylene (MT/day)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Seq. CO_2 (ton/h)	156.93	165.79	166.01	174.56	192.44	210.02	259.94	227.38	227.99	299.08
Vented CO_2 (ton/h)	528.48	548.62	552.30	571.90	609.00	649.45	640.07	548.41	568.65	596.94

The inputs to the BGTL+C_6_C_8 refinery are biomass, natural gas, butane, and water, while the outputs include gasoline, diesel, kerosene, LPG, benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene, sequestered CO_2, and vented CO_2.

where the year is represented by *i* and ranges from −2 to 30 to account for the construction period (3 years). The discount rate is used to obtain the worth of the cash flow in year zero using Eq. 9

$$\text{Discounted Cash Flow}_i = \text{Cash Flow}_i \cdot (1+\text{Discount Rate})^{(0-i)} \tag{9}$$

The NPV is then calculated by summing the discounted cash flows over the span the plant lifetime, as shown in Eq. 10

$$\text{NPV} = \sum_{i=-2}^{30} \text{Discounted Cash Flow}_i \tag{10}$$

Since the refinery will not be operating at full capacity in the first few years of operation, the following assumptions on production capacity are illustrated in Table 13. In the first 2 years of operation, the plant will only operate at 50 and 90% of its full capacity. Additionally, for plants operating below their plant capacity, the maintenance costs are scaled down as well.[88] The capacity factor is used to scale the raw materials cost, the operating labor cost, the electricity cost, and gross sales. The maintenance factor is used to scale the CO_2 TS&M cost, O&M cost, and supplies cost.

The breakdown for the manufacturing costs for the U-10-VAR2 case study are shown in Table 14. During the construction period, the plant does not incur any manufacturing costs. During the first year of operation, the manufacturing costs total $278 MM. As the capacity factor approaches 1, the raw materials and maintenance costs increase. Additionally, because of the MACRS recovery scheme, the depreciation costs increase in the second year of operation. Between years 2–10, the total manufacturing costs range between $349 and $453 MM. After the depreciation period ends, the manufacturing costs remain constant at $278 MM.

The NPV analysis for case study U-10-VAR2 is shown in Table 15. The cash flow during the construction period is negative due to the FCI and the working capital, and the total discounted cash flow is as low as −$1365 MM during the last year of construction, as shown in Table 15. During the first year of operation, the refinery yields a profit of $12 MM, but because of the depreciation credit, the cash flow increases to $121 MM. As the refinery begins to operate at full capacity and because of the 10-year MACRS depreciation scheme, the cash flows increase to as high as $252 MM in the third year. After the depreciation period ends, the cash flow remains constant at $190 MM for years 12–29. However, the discounted cash flow is $60 MM in year 12 and $12 MM in year 29. The total discounted cash flow becomes positive in year 11. The working capital is recovered at the end of the plant lifetime and the cash flow is $353 MM in the last year of operation. At the end of the plant lifetime, the NPV is $597 MM, showing that the BGTL+C_6_C_8 refinery is highly profitable. The total

Table 18. Overall Energy Balances for the 20 Case Studies

Biomass and natural gas—10 kBD

Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Biomass	459	479	500	521	541	583	601	524	529	572
Natural gas	533	558	582	606	630	678	699	598	616	642
Butane	0	0	0	0	0	0	0	0	0	25
Gasoline	637	637	637	637	637	637	637	365	414	215
Diesel	0	0	0	0	0	0	0	272	148	233
Kerosene	0	0	0	0	0	0	0	0	75	189
LPG	113	118	123	128	132	142	21	0	15	0
Benzene	0	4	9	13	17	26	51	28	31	10
Toluene	0	0	0	0	0	0	0	1	0	28
P-xylene	0	10	20	59	78	118	188	100	113	23
O-xylene	0	10	19	0	0	0	0	0	0	25
M-xylene	0	0	0	0	0	0	0	0	0	0
Electricity	−10	−8	−6	0	3	10	28	8	10	−29
Efficiency (%)	76.62	75.90	75.24	74.28	73.69	72.65	67.56	68.41	68.83	60.72

Biomass and natural gas—50 kBD

Case study	U-50-0	U-50-250	U-50-500	U-50-750	U-50-1000	U-50-VAR	U-50-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Biomass	2524	2630	2697	2802	2951	3164	3291	2817	2896	2944
Natural gas	2934	3058	3136	3258	3431	3679	3826	3275	3367	3228
Butane	0	0	0	0	0	0	0	0	0	206
Gasoline	3186	3186	3186	3186	3186	3186	3186	1827	2069	1446
Diesel	0	0	0	0	0	0	0	1359	741	107
Kerosene	0	0	0	0	0	0	0	0	377	1633
LPG	567	591	614	638	662	710	105	0	73	0
Benzene	0	21	43	64	86	129	257	139	154	67
Toluene	0	0	0	0	0	0	0	5	0	176
P-xylene	0	98	196	294	392	588	938	499	563	321
O-xylene	0	0	0	0	0	0	0	0	0	0
M-xylene	0	0	0	0	0	0	0	0	0	0
Electricity	−193	−179	−139	−124	−136	−108	−39	−116	−105	−54
Efficiency (%)	72.29	71.62	71.65	71.07	69.92	68.99	63.58	64.76	65.14	59.20

The energy inputs come from biomass, natural gas, butane or electricity; while the energy outputs are the liquid fuels, the aromatics, LPG, or electricity. Electricity is denoted as a positive value if it is input into the system and as a negative value if it is output from the system. The overall efficiency of the refineries is calculated by dividing the energy outputs by the energy inputs.

discounted cash flow is plotted over the lifetime of the plant in Figure 6. The curve shows a steep decrease during the construction period and then recovers the initial investment around year 11. Toward the end of the plant lifetime, the curve becomes less steep because the discount factor decreases the value of the earnings.

Figure 7 shows the NPV for the case studies producing 10 kBD of liquid fuels. Note that the FT case study is not shown on this graph. The large capital investment, coupled with manufacturing costs, exceed the revenues from the products, thus resulting in a refinery that does not return the initial investment. The unrestricted case studies have the largest NPVs for any level of chemicals production. Additionally, the graph shows that the production of aromatics increases the profitability of the biomass and natural gas refineries.

Figure 8 shows the NPV for the case studies producing 50 kBD of liquid fuels. Note that the NPVs are about 8–10 times larger than those of the 10 kBD plants, clearly showing the effect of economies of scale. Once again, the unrestricted case studies have the largest NPV for any level of chemicals production. The NPVs are between \$266–\$597 MM for the 10 kBD plants (shown in Figure 7) and \$2039–\$5163 MM for the 50 kBD plants (shown in Figure 8).

Finally, Table 16 illustrates the amount of time it takes to pay back the initial investment of the refineries. The most profitable 10 kBD refinery takes about 11 years, while the most profitable 50 kBD refinery takes about 7 years.

Parametric analysis

The values for the NPV displayed in Figures 7 and 8 are based on a natural gas price of \$5.00/TSCF and a hardwood biomass price of \$70/dry metric ton. Because of the uncertainty surrounding these costs and because they represent the largest portion of the overall cost associated with the BGTL+C_6_C_8 refineries (as shown in Table 8), there exists a need to investigate the impact that higher or lower feedstock costs have on the profitability of these refineries. Therefore, the NPV is calculated for the U-10-VAR2 case study, assuming that the biomass and natural gas are priced ±\$10.00/dry metric ton and ±\$2.00/TSCF from their nominal values, respectively. Note that the price of electricity should change accordingly with the price of natural gas, since the resale value of electricity may be affected by the purchase price of natural gas. Natural gas cost is assumed to be 80% of the total cost of electricity.[70] Therefore, the electricity prices change linearly between 0.0476 and 0.0924 \$/kWh depending on the natural gas price.

Figure 9 illustrates the results from the parametric analysis. Two sets of graphs are shown, one with operating and maintenance costs of 4.5% of the FCI (top plot), and the other one with operating and maintenance costs of 6.0% of the FCI. The tables to the right of the graphs are the values of the NPV for the different scenarios investigated. Since natural gas contributes a larger portion to the other overall cost of the refineries (Table 8), it has a much more pronounced effect on the NPV. For operating and maintenance

Table 19. Carbon Accounting (in kg/s) is Shown for the 20 Case Studies

Biomass and natural gas—10 kBD

Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Biomass	12.90	13.49	14.07	14.64	15.23	16.39	16.91	14.46	14.89	16.10
Natural gas	8.54	8.92	9.31	9.69	10.07	10.84	11.19	9.57	9.85	10.27
Butane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38
Gasoline	11.88	11.85	11.83	11.80	11.78	11.73	11.67	6.70	7.59	3.94
Diesel	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.11	2.79	4.33
Kerosene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.35	3.38
LPG	1.40	1.46	1.51	1.57	1.63	1.75	0.26	0.00	0.18	0.00
Benzene	0.00	0.10	0.19	0.29	0.39	0.59	1.17	0.63	0.70	0.23
Toluene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.63
P-xylene	0.00	0.22	0.44	1.29	1.72	2.58	4.11	2.19	2.47	0.49
O-xylene	0.00	0.21	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.55
M-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vented CO_2	6.59	6.90	7.21	7.44	7.73	8.29	7.95	6.79	7.09	8.94
Seq. CO_2	1.64	1.75	1.85	2.01	2.13	2.38	3.02	2.65	2.65	4.34
Conversion (%)	61.91	61.72	61.55	61.46	61.34	61.11	61.26	60.99	60.94	50.68

Biomass and natural gas—50 kBD

Case study	U-50-0	U-50-250	U-50-500	U-50-750	U-50-1000	U-50-VAR	U-10-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Biomass	70.99	73.99	75.86	78.82	83.01	89.02	92.58	79.25	81.48	82.82
Natural gas	46.95	48.93	50.17	52.13	54.89	58.87	61.22	52.40	53.88	51.65
Butane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.10
Gasoline	59.38	59.25	59.13	59.00	58.88	58.63	58.37	33.49	37.93	26.38
Diesel	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.56	13.96	1.99
Kerosene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.77	29.27
LPG	6.98	7.28	7.57	7.87	8.16	8.75	1.30	0.00	0.89	0.00
Benzene	0.00	0.49	0.98	1.46	1.95	2.93	5.83	3.17	3.49	1.51
Toluene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	3.92
P-xylene	0.00	2.15	4.30	6.44	8.59	12.89	20.56	10.93	12.35	7.02
O-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
M-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vented CO_2	40.06	41.59	41.87	43.36	46.17	49.23	48.52	41.57	43.11	45.25
Seq. CO_2	11.90	12.57	12.58	13.23	14.59	15.92	19.71	17.24	17.28	22.67
Conversion (%)	56.26	56.26	57.11	57.10	56.26	56.26	55.95	55.65	55.70	50.96

Biomass, natural gas, and butane are the carbon inputs, while the carbon outputs are the liquid products, the aromatics, the LPG byproduct, vented CO_2, or sequestered (Seq.) CO_2. Carbon conversion for each case study is calculated by dividing the total carbon exiting as either liquid product, aromatics, or LPG by the total carbon input into the refinery.

costs of 4.5%, the NPV ranges between $300 MM and $891 MM. For operating and maintenance costs of 6.0%, the NPV ranges between $204 and $799 MM.

Material and energy balances

Material and energy balances for the BGTL+C_6_C_8 refineries are shown in Tables 17 and 18, respectively. Biomass is shown in dry tons per hour (dt/h), while natural gas is shown in million standard cubic feet per hour (mscf/h). Butane, water, gasoline, diesel, kerosene, and LPG are shown in thousand barrels per day (kBD). The aromatics are displayed in metric tons per day (MT/day). The amount of vented and sequestered CO_2 is also shown in tons per hour (ton/h). The unrestricted case studies solely produce gasoline as the only liquid fuel product and LPG as byproduct through the MTG process. As the amount of chemicals parametrically increases in the unrestricted case studies, the amount of LPG produced also increases because of the larger flow rate through the MTG reactor. In the nominal case studies (U-10-0 and U-50-0), the amount of LPG produced is approximately 19 vol % that of gasoline produced. In the variable case studies (U-10-VAR and U-50-VAR), the amount of LPG produced is approximately 23 vol % that of gasoline produced. However, in the U-10-VAR2 and U-50-VAR2 case studies, the LPG generated from the MTG process is used by the Cyclar process and converted into additional aromatics. Therefore, the amount of LPG output from the refinery is much less. Additionally, as the amount of chemicals increases in the unrestricted case studies, the amount of feedstock necessary to meet this demand also increases. The main aromatic produced in the refinery is consistently *para*-xylene in each of the case studies. In the U-10-VAR2 case study, the amount of benzene and *para*-xylene produced is 109.12 and 392.60 metric tons per day, respectively.

The maximization of diesel case studies (D-10-VAR and D-50-VAR) produce gasoline and diesel in a 60–40% ratio by volume and output benzene, toluene, and *para*-xylene from the refinery. No byproduct LPG is produced since all of it is sent to the Cyclar process to produce additional aromatics in the refinery. These case studies use both MTG and MTO/MOGD technologies to produce these products. The U.S. ratios case studies (R-10-VAR and R-50-VAR) produce the three liquid fuel products in ratios commensurate with U.S. demand while outputting benzene, *para*-xylene, and LPG. Not all the LPG produced from the MTG process is directed to the Cyclar process. These case studies also use both the MTG and MTO/MOGD technologies as well as the Cyclar Process. In the D-10-VAR case study, the amount of benzene, toluene, and *para*-xylene produced is 59.28, 2.27, and 208.65 metric tons per day, respectively; while in the R-10-VAR case study, the amount of benzene and *para*-xylene produced is 65.31 and 235.72 metric tons per day, respectively.

Table 20. The Greenhouse Gas (GHG) Balances for the 20 Case Studies

Biomass and natural gas—10 kBD

Case study	U-10-0	U-10-50	U-10-100	U-10-150	U-10-200	U-10-VAR	U-10-VAR2	D-10-VAR	R-10-VAR	FT-10-VAR
Biomass	−41.92	−43.82	−45.73	−47.58	−49.47	−53.24	−54.94	−46.98	−48.38	−52.32
Natural gas	4.63	4.84	5.05	5.25	5.46	5.87	6.06	5.18	5.34	5.56
Butane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
Gasoline	42.78	42.78	42.78	42.78	42.78	42.78	42.78	24.53	27.78	14.46
Diesel	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.61	10.14	15.95
Kerosene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.97	12.47
LPG	5.21	5.43	5.65	5.87	6.09	6.53	0.97	0.00	0.67	0.00
Benzene	0.00	0.36	0.71	1.07	1.43	2.14	4.27	2.32	2.56	0.86
Toluene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	2.30
P-xylene	0.00	0.80	1.60	4.72	6.30	9.44	15.07	8.01	9.05	1.81
O-xylene	0.00	0.77	1.55	0.00	0.00	0.00	0.00	0.00	0.00	2.02
M-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vented CO_2	24.15	25.29	26.43	27.73	28.31	30.39	29.12	24.89	25.96	32.75
Seq CO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.03
LGHG	34.86	36.46	38.05	39.40	40.91	43.94	43.45	36.66	38.10	35.93
GHGAF	68.74	69.18	69.62	70.06	70.50	71.38	60.29	58.37	59.69	58.93
GHGAE	0.98	0.81	0.65	−0.02	−0.35	−1.01	−2.80	−0.77	−1.02	2.95
GHGAC	0.00	2.92	5.84	8.75	11.67	17.51	29.21	15.73	17.53	10.55
GHGI	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50

Biomass and natural gas—50 kBD

Case study	U-50-0	U-50-250	U-50-500	U-50-750	U-50-1000	U-50-VAR	U-10-VAR2	D-50-VAR	R-50-VAR	FT-50-VAR
Biomass	−230.64	−240.40	−246.45	−256.09	−269.69	−289.21	−300.79	−257.49	−264.71	−269.09
Natural gas	25.44	26.51	27.18	28.25	29.74	31.90	33.17	28.40	29.19	27.99
Butane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38
Gasoline	213.90	213.90	213.90	213.90	213.90	213.90	213.90	122.64	138.90	97.07
Diesel	0.00	0.00	0.00	0.00	0.00	0.00	0.00	93.05	50.69	7.32
Kerosene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	24.86	107.83
LPG	26.05	27.15	28.26	29.36	30.46	32.67	4.84	0.00	3.34	0.00
Benzene	0.00	1.79	3.57	5.36	7.15	10.72	21.35	11.60	12.78	5.54
Toluene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.44	0.00	14.38
P-xylene	0.00	7.87	15.74	23.61	31.48	47.22	75.35	40.04	45.24	25.74
O-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
M-xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vented CO_2	146.80	152.40	153.42	158.86	169.17	0.00	177.80	152.34	157.96	165.82
Seq CO_2	0.07	0.08	0.08	0.08	0.09	0.10	0.12	0.11	0.11	0.14
LGHG	181.63	189.30	195.70	203.34	212.31	227.70	225.74	191.12	198.36	183.11
GHGAF	343.72	345.92	348.11	350.31	352.51	356.90	301.46	291.83	298.47	291.83
GHGAE	19.53	18.09	14.11	12.59	13.75	10.97	3.97	11.75	10.61	5.44
GHGAC	0.00	14.59	29.18	43.77	58.36	87.54	146.05	78.66	87.63	68.95
GHGI	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50

The total GHG emissions (in CO_2 equivalents - kg CO_2 eq/s), as well as the GHG emissions avoided from liquids production (GHGAF), emissions due to electricity usage (GHGAE), GHG emissions avoided from chemicals production (GHGAC), and overall GHG emissions (LGHG), are also illustrated.

In the FT-10-VAR case study, the refinery outputs benzene, toluene, *para*-xylene, and *ortho*-xylene. The amounts produced are 21.86, 59.56, 47.18, and 52.57 metric tons per day, respectively. In the FT-50-VAR case study, the refinery outputs benzene, toluene, and *para*-xylene. The amounts produced are 141.60, 371.59, and 670.60 metric tons per day, respectively. Each of the case studies examined sequesters a portion of the CO_2 produced in the refinery to meet the environmental constraint (50% reduction in LGHG emissions from petroleum-based processes) imposed in the model.

The overall energy balances (shown in Table 18) are illustrated for each of the case studies. The feedstocks and electricity represent the energy inputs, while the energy outputs are the liquid products, LPG, electricity, and aromatics. The values in Table 18 are expressed in MW and are based on the LHV of the component. Electricity is shown as a negative value if it is output as a byproduct and as a positive value if it is input into the BGTL+C_6_C_8 plant. The overall energy efficiency of each refinery is calculated by summing the energy contributions from the outputs and dividing it by the energy contributions of the inputs. The relative energy contributions from biomass and natural gas are roughly equal in each of the case studies. In the U-10 case studies, the overall efficiency ranges between 67 and 77%, while the U-50 case studies have an overall efficiency between 64 and 73%. The D-10-VAR and R-10-VAR each have an overall efficiency between 68 and 69%, while the D-50-VAR and R-50-VAR case studies have an efficiency around 65%.

Carbon and GHG balances

The overall carbon balance for each of the BGTL+C_6—C_8 refineries is shown in Table 19. The carbon inputs into the refinery include biomass, natural gas, and butane. The liquid products, the LPG byproduct, the aromatics, vented CO_2, and sequestered CO_2 account for the carbon outputs from the refinery. The amount of carbon input by air into the refineries is considered negligible and is, therefore, neglected in the balances. The carbon conversion for each of the case studies is calculated by summing the carbon output as products (liquid fuels, LPG, and aromatics) and dividing it by the carbon input by the feedstocks (biomass, natural gas, and butane). In the 10 kBD case studies, the carbon conversion ranges between 50 and 62%. The carbon conversion in the 50 kBD case studies is between 50 and 58%.

The total GHG emissions (in kg CO_2 equivalent/s) for the major inputs and outputs of the BGTL+C_6_C_8 refineries are shown in Table 20. To ensure at least a 50% reduction in LGHG emissions, an environmental constraint is imposed in the MINLP model. The LGHG emissions are calculated by summing the respective emissions rates from each stage of production and include (a) the acquisition and transportation of the biomass, natural gas, and butane feeds, (b) the atmospheric CO_2 that is absorbed by biomass during photosynthesis, (c) the transportation and use of the liquid products, LPG, and aromatics, (d) venting of CO_2, and (e) the transportation and sequestration of CO_2. To calculate the amount of CO_2 absorbed from the atmosphere in part (b), the carbon content of biomass is used. A recent study has challenged the climate benefits from natural gas use because CH_4 system leakage rates have been consistently underestimated.[89] However, for the purposes of this study, the GHG emissions from (a) to (e) are used to calculate the well-to-wheel emissions of the refineries using the GREET model and by assuming transportation distances of 50 miles for feedstocks, 100 miles for products, and 50 miles for CO_2.[90]

The GHG emissions avoided from liquid fuels (GHGAF), electricity (GHGAE), and chemicals (GHGAC) are calculated to compare the relative LGHG emissions levels to typical fossil fuel-based processes. The GHGAF is calculated by multiplying the total energy of fuels produced by a typical petroleum-based emissions level (i.e., 91.6 kg CO_{2eq}/GJ_{LHV}). The GHGAE is calculated by multiplying the energy produced by electricity by a typical natural gas-based emissions level (i.e., 101.3 kg CO_{2eq}/GJ). The GHGAC is calculated by multiplying the total mass of aromatics produced by a typical HVC production plant emissions level (i.e., 1.7 kg CO_{2eq}/kg of HVC).[85] If the GHGAE is negative, then electricity is input into the refinery. The GHG emissions index (GHGI) is calculated by dividing the LGHG by the summation of GHGAF, GHGAE, and GHGAC. A GHGI value less than 1 indicates that the process has lower overall LGHG emissions than current processes. As Table 20 indicates, the GHGI is equal to 0.50 for all the case studies, which means that the BGTL+C_6_C_8 refiners can achieve a 50% reduction in GHG emissions compared with fossil fuel-based processes. The case studies in this manuscript were intended to demonstrate that the utilization of biomass together with natural gas can significantly mitigate the overall LGHG emissions of a refinery.

Conclusions

This article investigates the thermochemical coproduction of liquid transportation fuels and C_6—C_8 aromatics from biomass and natural gas within a global optimization framework. The process synthesis superstructure described in this article includes multiple synthesis gas conversion routes along with multiple aromatics production technologies designed to produce and separate benzene, toluene, *ortho*-, *meta*-, and *para*-xylene. These five aromatic compounds represent high value chemicals that are shown to considerably increase the profitability of the refineries using metrics such as net present value and total overall profit. Twenty case studies are illustrated to show the effect of liquid fuels composition, aromatics production levels, and refinery scale on the optimal plant topology and overall profitability of the refinery. The environmental and economic benefits of coproducing liquid fuels and aromatics were directly compared. The importance of using global optimization coupled with a process synthesis approach to investigate these types of problems was illustrated, since the optimal plant topology nor the optimal distribution of products could be known a priori. Parametric analysis is carried out on one case study to investigate the effect that the variability of feedstock cost, as well as operating and maintenance cost, have on the NPV. The case studies investigated in this article also show that the utilization of biomass together with natural gas can significantly lower GHG emissions from petroleum-based processes.

The NPV for a plant that only produces unrestricted liquid fuels (10 kBD) from biomass and natural gas is $266 MM. As the amount of chemicals parametrically increases, the NPV also increases and becomes as high as $597 MM for a plant producing 500 metric tons of aromatics per day. The same trends are evident for 50 kBD plants. The NPV for a plant that only produces unrestricted liquid fuels (50 kBD) from biomass and natural gas is $2876 MM. As the amount of chemicals parametrically increases, the NPV also increases and becomes as high as $5163 MM for a plant producing 2500 metric tons of aromatics per day. The results presented in this article clearly demonstrate that the economic competitiveness of biomass and natural gas refineries increases with the coproduction of liquid transportation fuels and aromatics while simultaneously reducing lifecycle greenhouse gas emissions.

Acknowledgments

The authors acknowledge partial financial support from the National Science Foundation (NSF EFRI-0937706 and NSF CBET-1158849).

Literature Cited

1. Energy Information Administration. Monthly Energy Review—May 2014. Document Number: DOE/EIA-0035(2014/05). Available at: http://www.eia.gov/totalenergy/data/monthly, 2014. Last accessed July 1, 2014.
2. Beccari M, Romano U. *Encyclopaedia of Hydrocarbons: Refining and Petrochemicals, Vol. 2*. Rome, Italy: ENI, 2006.
3. Meyers RA. *Handbook of Petroleum Refining Processes*, *Vol. 3*. New York: McGraw-Hill, 2004.
4. Klerk A. *Fischer-Tropsch Refining*. Weinheim, Germany: Wiley-VCH Verlag & Co. KGaA, 2011.
5. Kulprathipanja S. *Zeolites in Industrial Separation and Catalysis*. Weinheim, Germany: Wiley Online Library, 2010.
6. Tsai TC, Liu SB, Wang I. Disproportionation and transalkylation of alkylbenzenes over zeolite catalysts. *Appl Catal A*. 1999;181:355–398.
7. Alario F, Guisnet M. Para-xylene manufacturing: catalytic reactions and processes. *Catal Sci Ser*. 2002;3:189–208.
8. Energy Information Administration. Annual Energy Outlook 2013 with Projections to 2035. Document Number: DOE/EIA-0383(2012). Available at: http://www.eta.doe.gov/oiaf/aeo/, 2011. Last accessed Sept 1, 2014.
9. Baliban RC, Elia JA, Floudas CA. Biomass and natural gas to liquid transportation fuels: process synthesis, global optimization, and topology analysis. *Ind Eng Chem Res*. 2013;52:3381–3406.
10. Sudiro M, Bertucco A. Production of synthetic gasoline and diesel fuel by alternative processes using natural gas and coal: process simulation and optimization. *Energy*. 2009;34:2206–2214.
11. Agrawal R, Singh NR, Ribeiro FH, Delgass WN. Sustainable fuel for the transportation sector. *Proc Natl Acad Sci USA*. 2007;104: 4828–4833.
12. Water Science and Technology Board. Water implications of biofuels production in the United States, 2008.
13. Lynd LR, Larson E, Greene N, Laser M, Sheehan J, Dale BE, McLaughlin S, Wang M. The role of biomass in America's energy future: framing the analysis. *Biofuels Bioprod Biorefin*. 2009;3:113–123.

14. National Academy of Sciences and National Academy of Engineering and National Research Council. Liquid Transportation Fuels from Coal and Biomass: Technological Status, Costs, and Environmental Issues. Prepublication. Washington, D. C., EPA 2009.
15. Department of Energy. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply. Document Number: DOE/GO-102005-2135. Available at: http://www1.eere.energy.gov/biomass/publications.html, 2005. Last accessed Jan 10, 2014.
16. Baliban RC, Elia JA, Misener R, Floudas CA. Global optimization of a MINLP process synthesis model for thermochemical based conversion of hybrid coal, biomass, and natural gas to liquid fuels. *Comput Chem Eng*. 2012;42:64–86.
17. Baliban RC, Elia JA, Floudas CA. Toward novel biomass, coal, and natural gas processes for satisfying current transportation fuel demands, 1: process alternatives, gasification modeling, process simulation, and economic analysis. *Ind Eng Chem Res*. 2010;49:7343–7370.
18. Elia JA, Baliban RC, Floudas CA. Toward novel biomass, coal, and natural gas processes for satisfying current transportation fuel demands, 2: simultaneous heat and power integration. *Ind Eng Chem Res*. 2010;49:7371–7388.
19. Baliban RC, Elia JA, Floudas CA. Optimization framework for the simultaneous process synthesis, heat and power integration of a thermochemical hybrid biomass, coal, and natural gas facility. *Comput Chem Eng*. 2011;35:1647–1690.
20. Baliban RC, Elia JA, Floudas CA. Simultaneous process synthesis, heat, power, and water integration of thermochemical hybrid biomass, coal, and natural gas facilities. *Comput Chem Eng*. 2012;37: 297–327.
21. Baliban RC, Elia JA, Weekman VW, Floudas CA. Process synthesis of hybrid coal, biomass, and natural gas to liquids via Fischer–Tropsch synthesis, ZSM-5 catalytic conversion, methanol synthesis, methanol-to-gasoline, and methanol-to-olefins/distillate technologies. *Comput Chem Eng*. 2012;47:29–56.
22. Baliban RC, Elia JA, Floudas CA. Novel natural gas to liquids (GTL) technologies: process synthesis and global optimization strategies. *AIChE J*. 2013;59:505–531.
23. Baliban RC, Elia JA, Floudas CA. Biomass to liquid transportation fuels (btl) systems: process synthesis and global optimization framework. *Energy Environ Sci*. 2013;6:267–287.
24. Baliban RC, Elia JA, Floudas CA, Gurau B, Weingarten MB, Klotz SD. Hardwood biomass to gasoline, diesel, and jet fuel: 1. Process synthesis and global optimization of a thermochemical refinery. *Energy Fuels*. 2013;27:4302–4324.
25. Baliban RC, Elia JA, Floudas CA, Xiao X, Zhang Z, Li J, Cao H, Ma J, Qiao Y, Hu X. Thermochemical conversion of duckweed biomass to gasoline, diesel, and jet fuel: process synthesis and global optimization. *Ind Eng Chem Res*. 2013:11436–11450.
26. Duran MA, Grossmann IE. Simultaneous optimization and heat integration of chemical processes. *AIChE J*. 1986;32:123–138.
27. Karuppiah R, Grossmann IE. Global optimization for the synthesis of integrated water systems in chemical processes. *Comput Chem Eng*. 2006;30:650–673.
28. Ahmetovic E, Grossmann IE. Optimization of energy and water consumption in corn-based ethanol plants. *Ind Eng Chem Res*. 2010;49: 7972–7982.
29. Grossmann IE, Martín M. Energy and water optimization in biofuel plants. *Chin J Chem Eng*. 2010;18:914–922.
30. Ahmetovic E, Grossmann IE. Global superstructure optimization for the design of integrated process water networks. *AIChE J*. 2010;57: 434–457.
31. Onel O, Niziolek AM, Hasan M, Floudas CA. Municipal solid waste to liquid transportation fuels—part I: mathematical modeling of a municipal solid waste gasifier. *Comput Chem Eng*. 2014;71:636–647.
32. Niziolek AM, Onel O, Hasan FM, Floudas CA. Municipal solid waste to liquid transportation fuels—part II: process synthesis and global optimization strategies. *Comput Chem Eng*. In press. doi:10.1016/j.compchemeng.2014.10.007.
33. Niziolek AM, Onel O, Elia JA, Baliban RC, Xiao X, Floudas CA. Coal and biomass to liquid transportation fuels: Process synthesis and global optimization strategies. *Ind Eng Chem Res*. 2014;53: 17002–17025.
34. Onel O, Niziolek AM, Elia JA, Baliban RC, Floudas CA. Biomass and natural gas to liquid transportation fuels and olefins (BGTL+C2_C4): process synthesis and global optimization. *Ind Eng Chem Res*. 2015;54:359–385. doi:10.1021/ie503979b.
35. Drift A, Doorn J. Analysis of biomass data in ECN database Phyllis. Available at: http://www.ecn.nl/phyllis/, 2002. Last accessed October 1, 2013.
36. National Energy Technology Laboratory. Quality Guidelines for Energy System Studies, 2004.
37. National Energy Technology Laboratory. Assessment of Hydrogen Production with CO_2 Capture Volume 1: Baseline State-of-the-Art Plants. DOE/NETL-2010/1434 2010.
38. Keller GE, Bhasin MM. Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *J Catal*. 1992;73:9–19.
39. Jones AC, Leonard JJ, Sofranko JA. The oxidative conversion of methane to higher hydrocarbons over alkali-promoted Mn/SiO_2. *J Catal*. 1987;103:311–319.
40. Lee JS, Oyama ST. Oxidative coupling of methane to higher hydrocarbons. *Catal Rev Sci Eng*. 1988;30:249–280.
41. Jones AC, Leonard JJ, Sofranko JA. The oxidative conversion of methane to higher hydrocarbons over alkali-promoted Mn/SiO_2. U.S. Patents 4,443,644, 4,443,645, 4,443,646, 4,443,647, 4,443,648, 4,443,649, 4,444,984, 1984; 4,448,322, 4,499,323, 4,523,049, 4,523,050, 4,544,784, 4,560,821, 1985; 4,567,307, 1986.
42. Hall KR. A new gas to liquids (GTL) or gas to ethylene (GTE) technology. *Catal Today*. 2005;106:243–246.
43. Fox JM, Chen TP, Degen BD. An evaluation of direct methane conversion processes. *Chem Eng Prog*. 1990:42–50.
44. Lunsford JH. The catalytic oxidative coupling of methane. *Agnew Chem Int Ed Engl*. 1995;34:970–980.
45. Hall KR, Holtzapple MT, Capareda SC. Integrated biofuel production system. U.S. Patent 8,153,850, 2012.
46. Hall KR, Bullin JA, Eubank PT, Akgerman A, Anthony RG. Method for converting natural gas to olefins. U.S. Patents 6,130,260, 2000; 6,323,247, 2001; 6,433,235, 2002; 6,602,920, 2003; 7,045,670, 7,119,240, 2006; 7,183,451, 7,208,647, 7,250,449, 2007; 7,408,091, 2008.
47. Zhang Q, He D, Li J, Xu B, Liang Y, Zhu Q. Comparatively high yield methanol production from gas phase partial oxidation of methane. *Appl Catal A*. 2002;224:201–207.
48. Zhang Q, He D, Zhu Q. Recent progress in direct partial oxidation of methane to methanol. *J Nat Gas Chem*. 2003;12:81–89.
49. Rasmussen CL, Glarborg P. Direct partial oxidation of natural gas to liquid chemicals: chemical kinetic modeling and global optimization. *Ind Eng Chem Res*. 2008;47:6579–6588.
50. Tsakoumis NE, Rønning M, Borg Ø, Rytter E, Holmen A. Deactivation of cobalt based Fischer–Tropsch catalysts: a review. *Catal Today*. 2010;154:162–182.
51. Steynberg A, Dry M. *Fischer-Tropsch Technology*. Amsterdam, The Netherlands: Elsevier, 2004.
52. Mobil Research and Development Corporation. Slurry Fischer-Tropsch/Mobil Two Stage Process of Converting Syngas to High Octane Gasoline. USDOE contract DE-AC22-80PC30022, 1983.
53. Mobil Research and Development Corporation. Two-Stage Process For Conversion of Synthesis Gas to High Quality Transporation Fuels. USDOE contract DE-AC22-83PC60019, 1985.
54. Bechtel. Aspen Process Flowsheet Simulation Model of a Battelle Biomass-Based Gasification, Fischer-Tropsch Liquefaction and Combined-Cycle Power Plant. Contract Number: DE-AC22-93PC91029. Available at: http://www.fischer-tropsch.org/, 1998. Last accessed Dec 3, 2013.
55. Bechtel. Baseline design/economics for advanced Fischer-Tropsch technology. Contract No. DE-AC22-91PC90027, 1992.
56. Mobil Research and Development Corporation. Research guidance studies to assess gasoline from coal by methanol-to-gasoline and sasol-type Fischer-Tropsch technologies. USDOE contract EF-77-C-O1-2447, 1978.
57. National Renewable Energy Laboratory. Gasoline from wood via integrated gasification, synthesis, and methanol-to-gasoline technologies. USDOE contract DE-AC36-08GO28308, 2011.
58. Tabak SA, Yurchak S. Conversion of methanol over ZSM-5 to fuels and chemicals. *Catal Today*. 1990;6:307–327.
59. Tabak SA, Krambeck FJ. Shaping process makes fuels. *Hydrocarbon Process*. 1985;64:72–74.
60. Tabak S, Krambeck F, Garwood W. Conversion of propylene and butylene over ZSM-5 catalyst. *AIChE J*. 1986;32:1526–1531.
61. Mokrani T, Scurrell M. Gas conversion to liquid fuels and chemicals: the methanol route-catalysis and processes development. *Catal Rev*. 2009;51:1–145.
62. Gregor JH, Gosling CD, Fullerton HE. Upgrading Fischer-Tropsch LPG with the Cyclar process. Contract No. DE-AC22-86PC90014, 1989.
63. EPA O. Evaluation of benzene-related petroleum processing operations. Document Number: EPA 450/3-79-022. Office of Air Quality, Planning and Standards, Research Triangle Park NC, EPA, 1978.

64. Kurup AS, Hidajat K, Ray AK. Optimal operation of an industrial-scale Parex process for the recovery of p-xylene from a mixture of C8 aromatics. *Ind Eng Chem Res.* 2005;44:5703–5714.
65. Broughton D, Gerhold C. Continuous sorption process employing fixed bed of sorbent and moving inlets and outlets. U.S. Patent No. 2,985,589, 1961.
66. UOP. *Aromatics and Derivatives: MX Sorbex Process*, Available at: http://www.uop.com/processing-solutions/petrochemicals/benzene-para-xyleneproduction/ 1999. Last accessed March 1, 2013.
67. Kong D, Yang D, Li H, Guo H, Ruan T. Process for the disproportionation and transalkylation of toluene and heavy aromatics. U.S. Patent No. 7,109,389, 2006.
68. Larson ED, Jin H, Celik FE. Large-scale gasification-based coproduction of fuels and electricity from switchgrass. *Biofuels Bioprod Bioref.* 2009;3:174–194.
69. Kreutz TG, Larson ED, Liu G, Williams RH. Fischer-Tropsch fuels from coal and biomass. Proceedings of the 25th International Pittsburgh Coal Conference, 2008.
70. National Energy Technology Laboratory. Cost and performance baseline for fossil energy plants. Volume 1: Bituminous coal and natural gas to electricity final report. Document Number: DOE/NETL-2007/1281. Available at: http://www.netl.doe.gov/energy-analyses/baseline_studies.html, 2007. Last accessed Dec 6, 2013.
71. Balmer P, Mattsson B. Wastewater treatment plant operation costs. *Water Sci Technol.* 1994;30:7–15.
72. Kreutz T, Williams R, Consonni S, Chiesa P. Co-production of hydrogen, electricity and CO_2 from coal with commercially ready technology. Part B: economic analysis. *Int J Hydrogen Energy.* 2005;30:769–784. Last accessed October 20, 2013.
73. National Energy Technology Laboratory. Analysis of natural gas-to liquid transportation fuels via Fischer-Tropsch. DOE/NETL-2013/1597, 2013.
74. Fox JM, Chen TP, Degen BD. Direct Methane Conversion Process Evaluations. Contract No. DE-AC22-87PC79814, 1988.
75. National Renewable Energy Laboratory. Process design and economics for conversion of lignocellulosic biomass to ethanol: Thermochemical pathway by indirect gasification and mixed alcohol synthesis. USDOE contract DE-AC36-08GO28308, 2011.
76. *Chemical Engineering* magazine. Chemical Engineering Plant Cost Index. Available at: http://www.che.com/pci/, 2012.
77. CPLEX. *ILOG CPLEX C++ API 12.1 Reference Manual*, Armonk, NY: International Business Machines Corporation, 2009.
78. Drud A. CONOPT: A GRG code for large sparse dynamic nonlinear optimization problems. *Math Program.* 1985;31:153–191.
79. Floudas CA. *Nonlinear and Mixed-Integer Optimization*. New York: Oxford University Press, 1995.
80. Floudas CA. *Deterministic Global Optimization: Theory, Methods and Applications*. Dordrecht, The Netherlands: Kluwer Academic Publishers, 2000.
81. Floudas CA, Pardalos PM. State of the art in global optimization: computational methods and applications. *J Global Optim.* 1995;7:113.
82. Floudas CA, Akrotirianakis IG, Caratzoulas S, Meyer CA, Kallrath J. Global optimization in the 21st century: advances and challenges. *Comput Chem Eng.* 2005;29:1185–1202.
83. Floudas CA, Gounaris CE. A review of recent advances in global optimization. *J Global Optim.* 2009;45:3–38.
84. Larson ED, Fiorese G, Liu G, Williams RH, Kreutz TG, Consonni S. Co-production of decarbonized synfuels and electricity from coal+biomass with CO_2 capture and storage: an Illinois case study. *Energy Environ Sci*., 2010;3:28–42, doi:10.1039/B911529C.
85. Benchaita T. Greenhouse gas emissions from new petrochemical plants. Inter-American Development Bank, 2013.
86. Floudas CA, Ciric AR, Grossmann IE. Automatic synthesis of optimum heat exchanger network configurations. *AIChE J.* 1986; 32:276–290.
87. Biegler LT, Grossmann IE, Westerberg AW, Kravanja Z. *Systematic Methods of Chemical Process Design*. Upper Saddle River, NJ: Prentice Hall PTR, 1997.
88. Peters MS, Timmerhaus KD, West RE, Timmerhaus K, West R. *Plant Design and Economics for Chemical Engineers*, *Vol. 4*. New York: McGraw-Hill, 1968.
89. Brandt AR, Heath GA, Kort EA, O'Sullivan F, Petron G, Jordaan SM, Tans P, Wilcox J, Gopstein AM, Arent D, Wofsy S, Brown NJ, Bradley R, Stucky GD, Eardley D, Harriss R. Methane leaks from north American natural gas systems. *Science.* 2014;343:733–735.
90. Argonne National Laboratory. GREET 1.8b, The Greenhouse Gases, Regulated Emisssions, and Energy Use in Transportation (GREET) Model. 2007. September, 2008.

Manuscript received Nov. 4, 2014, and revision received Dec. 21, 2014.