

Comparative techno-economic analysis and process design for indirect liquefaction pathways to distillate-range fuels via biomass-derived oxygenated intermediates upgrading

Eric C. D. Tan, National Renewable Energy Laboratory, Golden, CO, USA

Lesley J. Snowden-Swan, Pacific Northwest National Laboratory, Richland, WA, USA

Michael Talmadge, Abhijit Dutta, National Renewable Energy Laboratory, Golden, CO, USA

Susanne Jones, Karthikeyan K. Ramasamy, Michel Gray, Robert Dagle, Asanga Padmaperuma, Mark Gerber, Pacific Northwest National Laboratory, Richland, WA, USA

Asad H. Sahir, Ling Tao, Yanan Zhang, National Renewable Energy Laboratory, Golden, CO, USA

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Abstract: This paper presents a comparative techno-economic analysis (TEA) of five conversion pathways from biomass to gasoline-, jet-, and diesel-range hydrocarbons via indirect liquefaction with a specific focus on pathways utilizing oxygenated intermediates. The four emerging pathways of interest are compared with one conventional pathway (Fischer-Tropsch) for the production of the hydrocarbon blendstocks. The processing steps of the four emerging pathways include biomass-to-syngas via indirect gasification, syngas clean-up, conversion of syngas to alcohols/oxygenates followed by conversion of alcohols/oxygenates to hydrocarbon blendstocks via dehydration, oligomerization, and hydrogenation. Conversion of biomass-derived syngas to oxygenated intermediates occurs via three different pathways, producing: (i) mixed alcohols over a MoS₂ catalyst, (ii) mixed oxygenates (a mixture of C₂₊ oxygenated compounds, predominantly ethanol, acetic acid, acetaldehyde, ethyl acetate) using an Rh-based catalyst, and (iii) ethanol from syngas fermentation. This is followed by the conversion of oxygenates/alcohols to fuel-range olefins in two approaches: (i) mixed alcohols/ethanol to 1-butanol rich mixture via Guerbet reaction, followed by alcohol dehydration, oligomerization, and

Correspondence to: Eric C.D. Tan, National Renewable Energy Laboratory, Golden, CO 80401, USA. E-mail: eric.tan@nrel.gov

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Correction added on 26 October 2016, after first online publication: the authors Asad H. Sahir, Ling Tao and Yanan Zhang were added to the author list.



hydrogenation, and (ii) mixed oxygenates/ethanol to isobutene rich mixture and followed by oligomerization and hydrogenation. The design features a processing capacity of 2000 tonnes/day (2205 short tons) of dry biomass. The minimum fuel selling prices (MFSPs) for the four developing pathways range from \$3.40 to \$5.04 per gasoline-gallon equivalent (GGE), in 2011 US dollars. Sensitivity studies show that MFSPs can be improved with co-product credits and are comparable to the commercial Fischer-Tropsch benchmark (\$3.58/GGE). Overall, this comparative TEA study documents potential economics for the developmental biofuel pathways via mixed oxygenates. © 2016 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: biomass; biorefinery; biofuel; indirect liquefaction; oxygenates; process design; techno-economic analysis; sustainability

Introduction

There has been considerable interest in producing biomass-derived liquid fuels for the last three decades. Various thorough reviews of the full range of processes for producing liquid transportation fuels from biomass have been published.^{1–5} The US Department of Energy's Bioenergy Technologies Office (BETO) has been enabling the development of technologies for the production of infrastructure-compatible, cost-competitive liquid hydrocarbon fuels from lignocellulosic biomass feedstocks.⁶ BETO has been focused on growing America's energy future by reducing dependence on foreign oil and by lowering net greenhouse gas (GHG) emissions. To meet these challenges, the program portfolio is expanding to include research and development of advanced biofuels that will enable the deployment of a range of technologies to produce infrastructure-compatible hydrocarbon fuels. Building on the foundation of progress in cellulosic ethanol production,^{7–9} BETO is considering ways of converting ethanol and other oxygenated intermediates to hydrocarbon fuels. Conversion pathways through higher alcohols and oxygenates have the ability to target gasoline-, jet-, and diesel-range molecules as needed. Additionally, oxygenated intermediate routes may be particularly well-suited for intermediate chemical co-production to help improve biorefinery economics.

This work describes conceptual process design and techno-economic analysis (TEA) of distillate-range fuel production via indirect liquefaction (IDL) of biomass through various syngas-to-distillates conversion technologies. Comparison with fossil-based hydrocarbons is not in the scope of this work. This paper summarizes the analysis performed by researchers at National Renewable Energy Laboratory (NREL) and Pacific Northwest National Laboratory (PNNL) in support of BETO's IDL Program to identify opportunities and research gaps for conversion pathways aligned with the objectives mentioned above, with the specific conversion routes illustrated in Fig. 1:

- Pathway 1A: syngas to molybdenum disulfide (MoS_2)-catalyzed alcohols followed by fuel production via alcohol condensation (Guerbet reaction), dehydration, oligomerization, and hydrogenation
- Pathway 1B: syngas fermentation to ethanol followed by fuel production via alcohol condensation (Guerbet reaction), dehydration, oligomerization, and hydrogenation
- Pathway 2A: syngas to rhodium (Rh)-catalyzed mixed oxygenates followed by fuel production via carbon coupling/deoxygenation (to isobutene), oligomerization, and hydrogenation
- Pathway 2B: syngas fermentation to ethanol followed by fuel production via carbon coupling/deoxygenation (to isobutene), oligomerization, and hydrogenation
- Commercial benchmark: syngas to liquid fuels via Fischer-Tropsch technology as a commercial benchmark for comparisons

This study leverages past research performed for BETO to produce oxygenated intermediates, mixed C_{2+} alcohols⁸ and mixed C_{2+} oxygenates¹⁰ and incorporates the latest developments from current research on the upgrading of oxygenates to hydrocarbon fuels, as indicated in Fig. 1. Additionally, all renewable ethanol feedstock sources can potentially play a role in enabling economically and environmentally sustainable distillate fuel technology routes. Therefore, the use of intermediate ethanol via syngas fermentation is also considered in the current analysis, leveraging earlier TEA performed at NREL and PNNL.¹¹ Each syngas conversion pathway producing an oxygenated intermediate, regardless of the source or type of intermediate, requires subsequent conversion to hydrocarbons. These alcohols/oxygenates-to-hydrocarbon fuels steps are the least developed and most in need of further research. The cases presented here are target cases that represent what is potentially achievable with further research and process optimization.

In order to assess the economic viability and potential of these conversion processes, we have developed conceptual

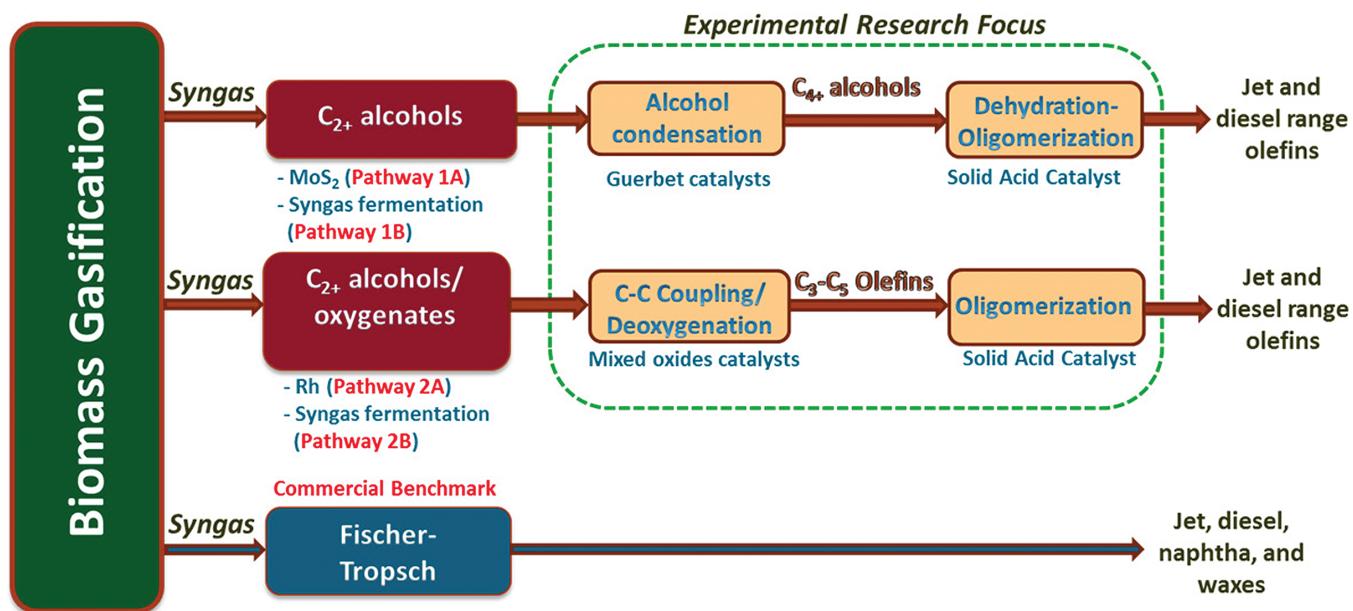


Figure 1. Syngas-to-distillates pathways.

process models with economic projections to estimate the minimum fuel selling price (MFSP). The MFSP can be used by policymakers and researchers to help refine research objectives and associated performance targets that will be necessary to produce cost-competitive fuels from biomass. TEA also facilitates direct biomass conversion research by examining the sensitivity of the MFSP to process alternatives and projected research advances, as well as to track research progress via state of technology assessments. If not otherwise mentioned, all currency is in 2011 US dollars. The 2011 cost year basis is chosen to be consistent with BETO program and is commonly used in recent biofuel TEA literature. The analysis presented here also includes consideration of the life-cycle implications of the baseline process models, by tracking sustainability metrics for the modeled biorefineries, including GHG emissions, fossil energy consumption, and consumptive water use.

Methods and assumptions

Economic assumptions

The TEA reported here uses n^{th} -plant economics. The key assumption associated with n^{th} -plant economics is that a successful industry has been established with many operating plants using similar process technologies. Higher project costs associated with first-of-a-kind plants are not included, such as financing risk, delayed start-ups, equipment

overdesign, and other costs associated with pioneer plants. As a critical tool in biofuels process development, TEA calculates biofuel MFSP using a process model and an economic model.¹² The process model solves mass and energy balances for each unit operation, and the economic model estimates capital and operating costs from the process model based on economic assumptions. In this study we develop TEA models for assessing the evaluated pathways for producing gasoline and diesel fuels from biomass. The MFSP is calculated using a discounted cash flow rate of return (DCFROR) analysis. MFSP is a function of cash inflows and outflows from capital costs, product sales, operating costs, and financial assumptions. The summary of assumptions for n^{th} -plant economic analysis applied in this study can be found in Tan *et al.*¹³

Process description and assumptions

The plant size in the present design is 2000 dry metric tonne/day (DMT/day). NREL and the Oak Ridge National Laboratory jointly performed a rigorous analysis to determine the optimal cellulosic ethanol plant size, taking into account the increased feedstock transportation costs associated with a larger collection radius and the economy of scale advantages derived from increased plant capacity for government purposes.¹⁴ It was determined that 2000 DMT/day was appropriately optimal. Additionally, recent studies on biochemical and thermochemical refinery capacity noted that under advanced feedstock logistic supply

systems that include depots and preprocessing operations there are cost advantages that support larger biorefineries up to 10 000 DMT/day facilities.^{15,16} It was demonstrated that the economies of scale enabled by advanced logistics offsets much of the added logistics costs from additional depot processing and transportation; the ability to mitigate moisture and ash in the system will improve the storage and conversion processes. Additionally, being able to utilize feedstocks from further distances will alleviate the risk of biomass supply to the conversion facility.

Detailed process description and assumptions are provided in the Conceptual process design section.

Sustainability metrics

Key sustainability metrics for the conceptual processes are presented to quantify environmental impacts. Direct biorefinery emissions (i.e., CO₂, NO₂, and SO₂), water consumption, and other process-related metrics were derived from the conversion process models described above. The boundary for all metrics is the biorefinery (or the fuel production stage), which was the focus of this research. Upstream processes (i.e., feedstock production and transportation) and downstream processes (i.e., fuel distribution and vehicle operation) are not incorporated

in the quantification of the metrics. Embodied emissions and resource consumption from the biorefinery related to construction and maintenance, material and energy inputs, and emission/consumption credits associated with co-products were also included.

For the conversion stage life-cycle inventory analysis, SimaPro v.8.0.2 software¹⁷ was used to develop and link units quantifying life-cycle impacts. Greenhouse gas basis values and non-renewable (fossil) energy consumption values for electricity and natural gas were applied consistent with the basis from Argonne National Laboratory's Greenhouse Gases, Regulated Emissions, and Energy use in Transportation (GREET) Model software.¹⁸ Ecoinvent v.2.2 database¹⁹ and the US Life Cycle Inventory (LCI)²⁰ processes will be used to fill the data gaps. The Ecoinvent processes were modified to reflect US conditions and the US LCI processes were adapted to account for embodied emissions and fossil energy usage. The material and energy flows of the conversion step capture the impacts of input raw materials, and outputs, such as emissions, wastes, and co-products as predicted by the process model (Table 1). The quantification of the relative sustainability metrics for the five conversion pathways allows the comparison and assessment of the sustainability of pathways relative to each other.

Table 1. Material and energy flows for the conversion pathways.

Fuel Products (GGE1/hr)	Pathway 1A	Pathway 1B	Pathway 2A	Pathway 2B	Benchmark (FT)
Naphtha	--	--	1,459	918	2,154
Jet Fuel	2,474	2,757	4,013	2,517	2,308
Diesel Fuel	2,735	2,925	613	384	1,563
Total	5,209	5,682	6,085	3,819	6,025
Co-products					
Export Electricity ² (kWh/GGE)	1.2	0.57	-0.75	0.82	1.0
Acetic Acid (g/GGE)	--	132	--	200	--
Butanediol (g/GGE)	--	--	--	--	--
Resource Consumption (g/GGE)					
Feedstock - Wood Chips	17,781	16,329	15,059	24,244	15,368
Magnesium Oxide (MgO)	0.59	0.54	0.52	0.82	0.54
Fresh Olivine	45	43	45	64	41
Tar Reformer Catalyst	2.4	0.54	2.0	0.73	1.4
50 wt% Caustic	3.5	3.2	--	4.5	--
Boiler Chemicals	0.31	0.14	0.13	0.17	0.091
Cooling Tower Chemicals	0.11	0.32	1.1	0.45	9.1
Cooling Tower Make-up	2,449	16,329	3,901	24,948	25,038
Boiler Feed Water Make-up	6,759	8,165	3,357	12,247	4,325
Diesel Fuel	6.4	5.4	5.2	9.1	5.2

Table 1. (Continued)

Hydrogen	45	29	--	--	--
Natural Gas	--	--	136	--	--
Nutrients	--	5.4	--	9.1	--
Guerbet Catalyst ³	0.16	0.17	--	--	--
Dehydration Catalyst ³	0.17	0.17	--	--	--
Oligomerization Catalyst ³	0.59	0.73	1.6	1.5	--
Dimerization Catalyst ³	0.033	0.041	--	--	--
Hydrogenation Catalyst ³	0.12	0.12	0.056	0.054	--
Rhodium Catalyst ³	--	--	0.30	0.30	--
Isobutene Catalyst ³	--	--	0.26	0.26	--
Hydrotreating Catalyst ³	--	--	--	--	0.091
Product Upgrading Catalyst ³	--	--	--	--	0.091
Fischer-Tropsch Catalyst ³	--	--	--	--	0.23
Waste Streams (g/GGE)					
Sand and Ash Purge	227	195	181	290	277
Scrubber Solids	9.3	118	--	159	168
Tar Reformer Catalyst Disposal	2.3	0.50	-2.0	0.68	0.68
Wastewater	590	862	3,946	1,247	1,211
Air Emissions (g/GGE)					
Nitrogen (N ₂)	48,534	43,091	38,056	53,137	36,359
Oxygen (O ₂)	1,633	3,084	680	2,503	1,974
Carbon Dioxide (CO ₂)	21,137	17,236	16,874	24,713	10,810
Water (H ₂ O)	6,350	4,536	11,567	6,630	4,891
Sulfur Dioxide (SO ₂)	2.4	8.6	--	13	1.7
Nitrogen Dioxide (NO ₂)	6.4	3.3	--	12	10

¹The gasoline baseline used in the gallon gasoline equivalent (GGE) calculation is 116,090 BTU/gal (LHV).

²“+” electricity is exported; “-” electricity is purchased.

³Catalyst consumptions are amortized over catalyst lifetime.

Conceptual process design

Simplified block flow diagrams for the conceptual processes are shown in Figs 2–4. The diagrams depict the major processing steps for the conversion of blended biomass to syngas (or synthesis gas) via indirect steam gasification, syngas clean-up, synthesis of alcohols, or oxygenated intermediates, and sequential synthesis of distillate-range hydrocarbons.

The common process areas for all pathways are the upstream processes (from biomass feedstock handling and preparation to syngas cleanup), product recovery, steam and power generation, and utilities. These areas are described below, followed by the description of the unique process areas of each pathway in the subsequent respective sections.

The production of syngas from biomass via indirect steam gasification has been reported,^{7,8,13} and thus will only be briefly described here.

Feed handling and preparation

The ultimate analysis of the modeled woody biomass feedstock has been reported (Table 3 in Tan *et al.*¹³) The assumed moisture content is 10 wt%, with an ash content of <1% and nominally sized to 2 mm for the gasifier. A cross-flow dryer is included in the system to allow preheating of the feed prior to feeding to the reactor, using process waste heat. This also allows for contingencies during wet weather when additional feed drying may be necessary. The feedstock is delivered at \$88 per dry tonne (or \$80 per dry US ton). The biomass cost includes the costs associated with the feedstock logistics, including harvest and collection,

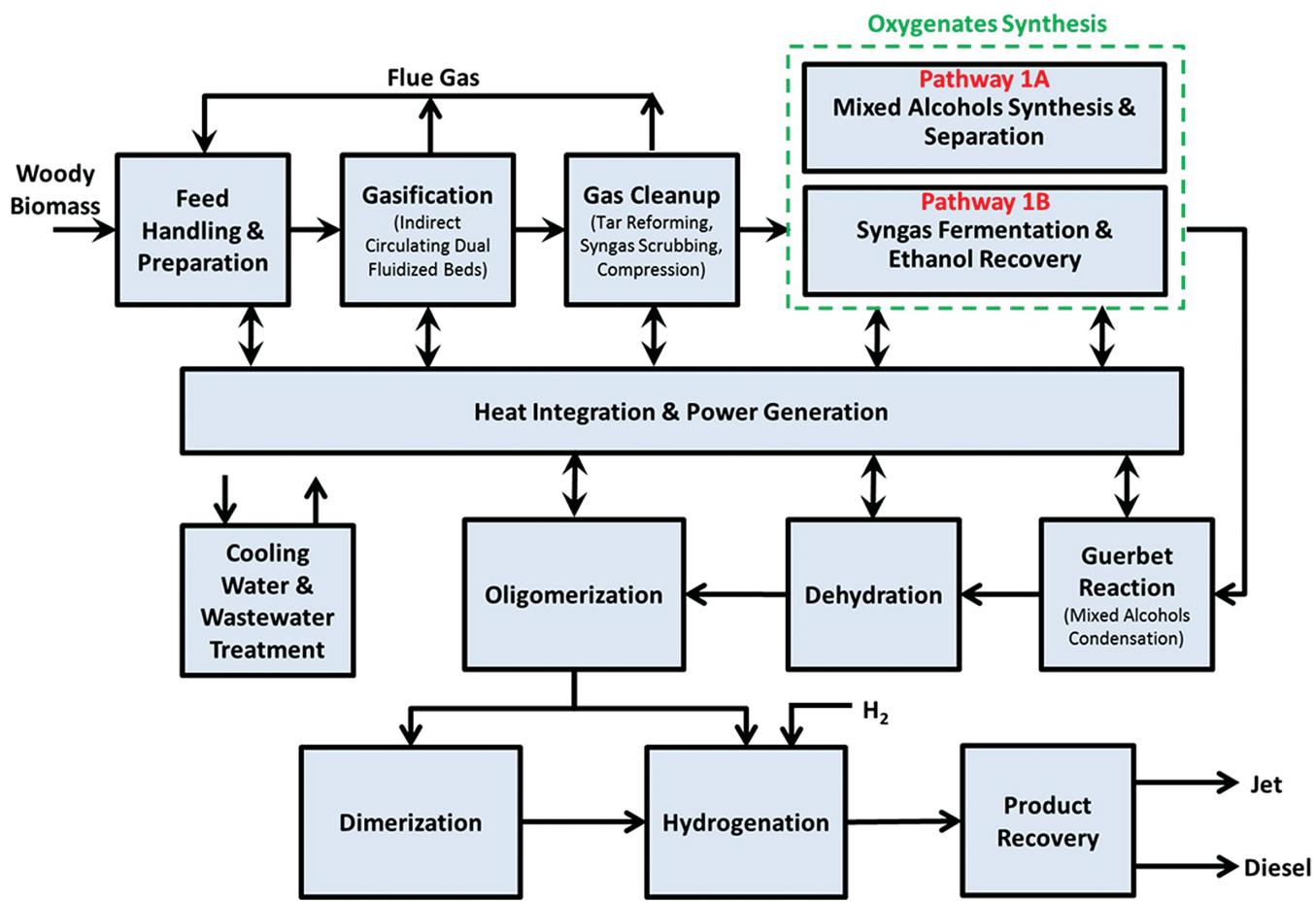


Figure 2. Main process steps for Pathways 1A and 1B.

preprocessing, and transportation. The unit operation costs for the supply of blended woody biomass to a gasification process have been documented by Jacobson *et al.*²¹

Gasification

Raw syngas is produced with a low-pressure indirectly heated entrained flow gasifier operating at 1633°F (889°C) and 33 psi (2.28 bar). Within the gasifier, biomass (10 wt% moisture content) thermally deconstructs to a mixture of syngas components (such as CO, H₂, CO₂, and CH₄), tars, and solid char containing residual unconverted carbon from the biomass. Cyclones at the exit of the gasifier separate the char and olivine (heat carrier) from the syngas. The solids flow to the char combustor where the char is burned in air in a fluidized bed, resulting in olivine temperatures greater than 1800°F (982°C). The hot olivine and residual ash are carried out of the combustor by the combustion gases and separated using a pair of cyclones. The first cyclone captures olivine while the second cyclone captures ash and olivine fines. Hot olivine flows back into

the gasifier, completing the gasification loop. The hot flue gas from the char combustor is utilized for process heat and feedstock preheating. Ash and olivine fines are cooled, moistened to minimize dust, and removed as waste. Fresh olivine make-up is added to account for attrition losses. All pathways apply the same gasification design basis.

Syngas cleanup

Syngas cleanup consists of steam reforming of tar and other hydrocarbons to produce additional CO and H₂, syngas quench, and scrubbing. Tars, methane, and light hydrocarbons are reformed in a circulating, fluidized, solid catalyst system, with reforming and regeneration operations in separate beds. Raw syngas contacts the reforming catalyst in an entrained flow reactor producing reformed gas and a partially deactivated catalyst. The catalyst is reactivated in a regenerator vessel where coke residue from the reforming reactions is removed via oxidation. The catalyst regenerator burns carbon (coke) deposits off the catalyst particles, regenerating the

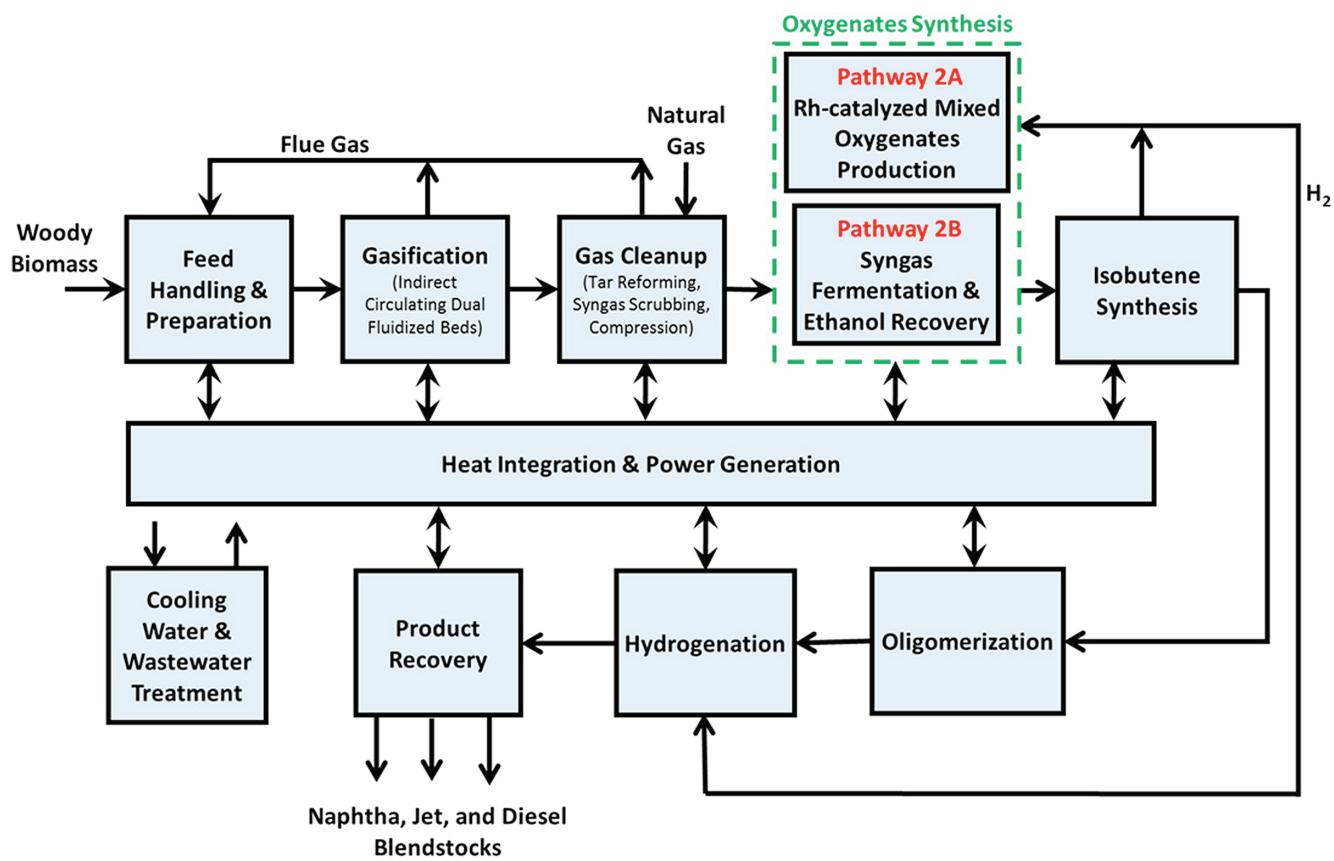


Figure 3. Main process steps for Pathways 2A and 2B.

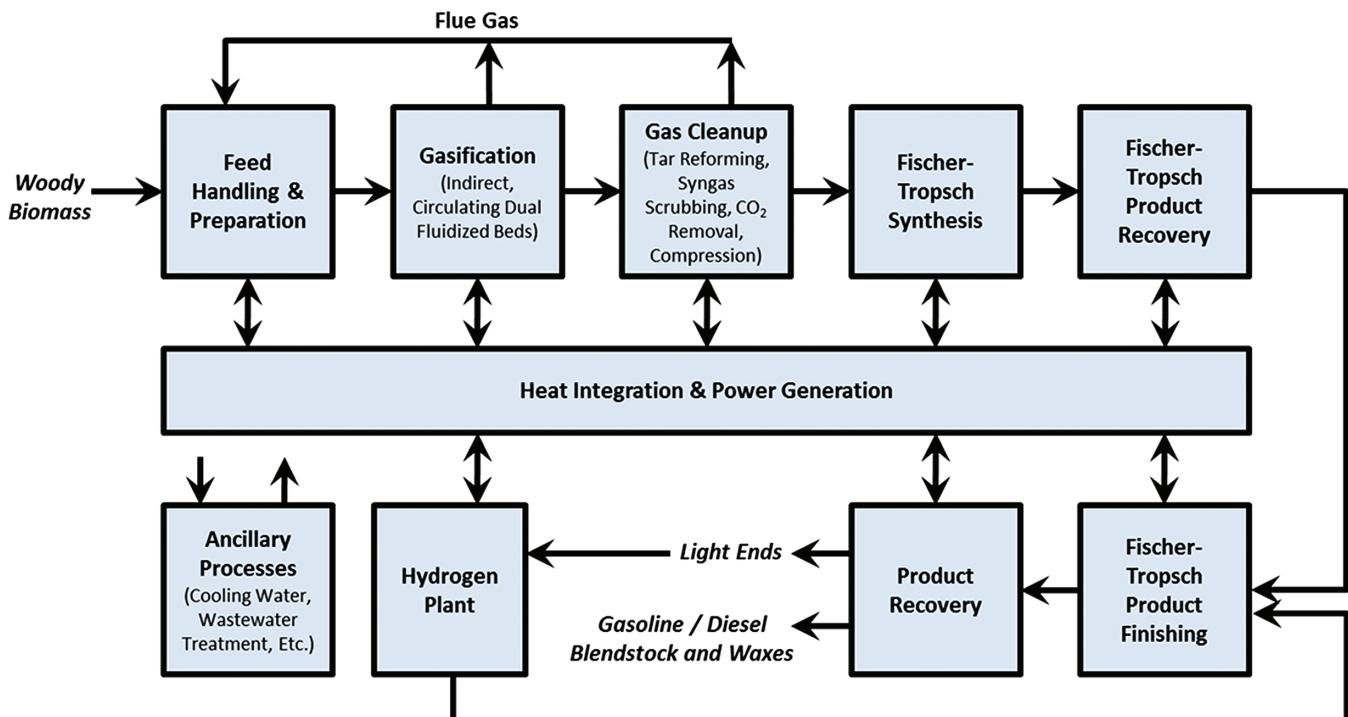


Figure 4. Main process steps for commercial benchmark Fischer-Tropsch process.

catalyst activity and providing heat for the reforming reactions.

Product recovery

The separation of hydrocarbon products is similar to separations used in a petroleum refinery. Distillation is used to separate the final products (naphtha- and distillate-range hydrocarbons).

Steam and power generation

A conventional steam cycle produces heat (as steam) for the gasifier and reformer operations and electricity for internal power requirements with the possibility to export excess electricity as a co-product. The steam cycle is integrated with the biomass conversion to the downstream alcohols/oxygenates-to-hydrocarbons processes. Previous analyses of gasification processes have shown the importance of properly utilizing the heat from the high-temperature streams to improve efficiency of the overall plant design.

Utilities

Outside battery limits systems, such as the cooling tower, flare, and product storage, are included in this area.

Pathway 1A: Syngas to MoS₂-catalyst-derived mixed alcohols to olefins to fuels

The simplified block diagram for Pathway 1A is shown in Fig. 2. The processing steps of this thermochemical conversion pathway include the conversion of biomass to syngas via indirect gasification, gas cleanup via reforming of tars and other hydrocarbons, catalytic conversion of syngas to mixed alcohols that undergo alcohol condensation (or Guerbet reaction) to primarily convert ethanol to longer carbon chain alcohols (C₄₊), alcohol dehydration, oligomerization coupled with dimerization, and hydrogenation. The biomass to mixed alcohols conversion steps (i.e., gasification, syngas cleanup, mixed alcohols synthesis, and alcohol separation) leverage technologies recently advanced⁸ and demonstrated with the production of mixed alcohols from biomass.⁷

Mixed alcohols synthesis and separation

The design of the mixed alcohols synthesis step is based on the earlier works.^{7,8} Briefly, pressurized syngas at 1895 psi (130.7 bar) is fed to two vertical reactors (shell and tube type) operating in parallel with down-flow orientation. Molybdenum disulfide (MoS₂) catalyst is packed in the tubes and catalyzes the conversion of syngas to mixed C₂₊ alcohols at or above 570°F (300°C). The heat of reac-

tion is removed by generating steam on the shell side. Unconverted syngas and gas-phase by-products flow to an acid gas removal system where dimethyl ether of polyethylene glycol (DEPG), a physical solvent, removes most of the H₂S and a portion of the CO₂. The DEPG system cooling is provided by an ammonia-water absorption refrigeration system. Most of the cleaned syngas is recompressed and recycled to the alcohol synthesis reactors. CO₂ and H₂S from the DEPG system are further processed in an amine-based acid gas enrichment unit and a Merichem LO-CAT sulfur recovery unit where H₂S is converted to elemental sulfur and stockpiled for disposal. Sulfur is required to maintain the activity of MoS₂ catalyst; the H₂S co-feed strategy is implemented with details found in Dutta *et al.*⁸

Cooled crude alcohols are de-pressurized and de-gassed in a flash separator. The evolved gases are recycled to the alcohol synthesis reactor and to the gas cleanup section as a feed to the tar reformer. Water is removed from the depressurized liquid stream using a molecular sieve system. The dehydrated alcohol stream (<0.5 wt% H₂O) is then introduced to an alcohol distillation column, which separates methanol from ethanol and higher molecular weight alcohols. Methanol is recycled to the alcohol synthesis reactor to increase ethanol and higher alcohol product yields.

Guerbet reaction

The Guerbet reaction, which involves the coupling of two alcohol molecules, is an important and potentially viable process to increase the value of short chain alcohols (i.e., ethanol). Mixed alcohols are sent to the Guerbet reactor with acid-base bifunctional metal oxide catalyst (MgO-Al₂O₃ with Mg/Al molar ratio of 3 to 1). MgO-Al₂O₃ catalysts, which are derived from hydrotalcite at PNNL, have been shown to generate n-butanol selectively via Guerbet reaction.^{22,23}

PNNL researchers have been investigating the one-step catalytic process of ethanol coupling to 1-butanol. At 653°F (345°C) and 35 psia (2.41 bar), short-chain alcohols (i.e., ethanol and propanol) are allowed to convert to a longer chain alcohol (at least C₄) through an alcohol coupling process. Note that methanol cannot undergo self-coupling via the Guerbet reaction but it can be coupled with alcohols having two or more carbon atoms.²⁴ Unconverted short-chain alcohol (primarily ethanol) is separated in a distillation column and is recycled back to the Guerbet reactor for additional coupling, thus increasing the overall ethanol conversion. A small fraction (5%) of recycle stream is purged and sent to the fuel combustor to prevent a build-up of other species in the loop. The column bottom product (about 90 wt% of 1-butanol) is sent to an alcohol dehydration reactor. The reactor systems used in the downstream alcohol-to-

hydrocarbon conversion steps utilize well-known reactor technologies like fixed catalyst beds. Use of commercially relevant and proven reactor designs in these processes will reduce the risk associated with the investment and reliability of plant operations. Assumed design parameters for the Guerbet reaction are summarized in Table 2.

Table 2. Design basis for Guerbet reactor.

Design Parameters	
Reactor Temperature, °F (°C)	653 (345)
Reactor Pressure, psia (bar)	35 (2.41)
Catalyst	MgO-Al ₂ O ₃
WHSV (hr ⁻¹)	1.0
Single-Pass Conversion	60% (ethanol)
Catalyst Life, yr	4
Oxygenates Selectivities (C), wt%	
Butanol	69.20
Pentanol	8.00
Hexanol	9.30
Heptanol	2.80
2-methyl-1-butanol	4.20
2-ethyl-1-butanol	4.20
Octanol	1.00
Others	1.30

Alcohol dehydration

The 1-butanol rich alcohol stream enters a dehydration reactor operating at 716°F (380°C) and 35 psia (2.41 bar) at which condition alcohols can be dehydrated to olefins over an organosilane modified γ -alumina catalyst. It has been reported that 1-butanol can be effectively dehydrated to 1-butene over the organosilane modified γ -alumina catalyst.²⁵ Most of the residual 1-butanol and other alcohols in the reactor effluent are recovered in a distillation column and recycled back to the dehydration reactor with the aim of maximizing the yield of olefin intermediates. 1-butene is significantly easier to undergo oligomerization than ethylene.^{26,27}

Oligomerization

Following the alcohol dehydration step is the oligomerization of olefins to produce distillate-range olefins with carbon numbers in the C₈-C₂₀ range. 1-butene along with other C₄₊ olefins are compressed and oligomerized at 482°F (250°C) and 435 psia (30 bar) over a packed bed of HZSM-23 zeolite catalyst. The yields and selectivities of the oligomers are based on the patent literature, as shown in Table 3.²² The product distributions of the mixed oligomerized olefins are 26.2% C₈, 43.0% C₁₂, 21.9% C₁₆, 7.0% C₂₀, and 3.6% C₂₄₊. The C₈ olefins (including 2,4-dimethyl-1-decene, 2-methyl-1-undecene, and 1-dodecene) are distil-

Table 3. Design basis for oligomerization reactor.

Design Parameters		
Reactor Temperature, °F (°C)	482 (250)	
Reactor Pressure, psia (bar)	435 (30)	
Catalyst	HZSM-23	
WHSV (hr ⁻¹)	0.21	
Single-Pass Conversion	95% (n-butene)	
Catalyst Life, yr	3	
Product Distribution		
C Selectivity (%)		
C8	26.20	
	2,3-dimethyl-1-hexene	20.10
	2-methyl-1-heptene	72.30
	1-octene	7.60
C12	43.00	
	2,4-dimethyl-1-decene	23.20
	2-methyl-1-undecene	71.10
	1-dodecene	5.70
C16	21.90	
	2,4-dimethyl tetradecene	26.20
	2-methyl-1-pentadecene	68.70
	1-hexadecene	5.10
C20+	8.90	
	1-eicosene	100.00

Note: The species presented in this table are modeled compounds used for modeling the process and bulk properties of C₈-C₂₀₊ oligomers and can be different from the experiments and research.

lated and sent to a dimerization reactor. The C₈ olefins are easily removed by distillation and subsequently dimerized using a heterogeneous catalyst (powdered Nafion) to a mixture of C₁₆ compounds. The dimerization is operated at 241°F (116°C) and 54 psia (3.7 bar) with 100% C₈ conversion and 90% C₁₆H₃₂ dimer yield.²⁸ The consolidated oligomers are then sent to a hydrotreater for the hydrogenation step.

Hydrogenation

The oligomerized olefins are sent to a hydrogenation reactor that operates at conditions similar to a process developed by ABB Lummus Crest and IFP for total hydrogenation of steam-cracked C₄.²⁹ Although the process is designed for C₄₊, it can be applied for treating a wide range of olefins. The reaction occurs at 113°F (45°C) and 500 psia (34.5 bar) with an excess of hydrogen (1.8 mole H₂/mole olefins). For Pathways 1A and 1B, to maximize the yield of oxygenated intermediates, the required hydrogen is imported instead of being derived from the syngas stream. For Pathways 2A and 2B, hydrogen recovered from the isobutene synthesis is supplied to the hydrogenation step. Conversion of olefins to paraffins is assumed to be 100%. The reactor effluent is used to heat process streams and then cooled with an air fin and a water cooler. After cooling, the non-condensable gases are separated from the product and a small amount is purged and used as fuel gas for the tar reformer catalyst regenerator. The remaining gases (including hydrogen) are recycled back to the hydrogenation reactor.

Pathway 1B: Syngas fermentation to ethanol to olefins to fuels

The simplified block diagram for Pathway 1B is shown in Fig. 2. The processing steps of this hybrid thermochemical/biochemical conversion pathway are similar to those of Pathway 1A. The main difference is the oxygenated intermediates synthesis steps in which ethanol is produced via syngas fermentation, followed by ethanol recovery. The value of ethanol can be increased via Guerbet reaction, which involves the coupling of two ethanol molecules to long chain alcohols, i.e., 1-butanol. This process has the potential to integrate efficiently with downstream conversion steps to upgrade ethanol to naphtha (gasoline blendstock) and kerosene-range (jet fuel or diesel blendstock) hydrocarbons through Guerbet reaction and oligomerization.

Fermentation of syngas

The syngas fermentation is modeled based on data from the literature.^{30–33} The clean syngas is cooled to suitable conditions for fermentation (approximately 100°F or 37.8°C)

and compressed to approximately 30 psia (2.1 bar). It is assumed that the additional syngas cleanup (such as sulfur, COS, or H₂S removal) is not required.^{30,33,34} The syngas then enters the fermentation vessels through nozzles or other means of vapor distribution to adequately distribute the syngas for maximized mass transfer into the aqueous phase. The fermenter designs can be continuously stirred tank reactors (CSTRs), bubble columns, trickle bed columns, or a number of other configurations. In addition to reactor design, internal or external circulation of the aqueous phase through the fermenter vessels/contacting media is also utilized to promote mixing and mass transfer. The organism present in the fermenters is an anaerobic bacterium, generally from the *Clostridium* family, that consumes carbon monoxide (CO) and hydrogen (H₂) by the following reactions to yield ethanol as the primary product.



CO serves as the carbon source for ethanol production while H₂ acts as the primary source of energy for the organism. However, if H₂ is the limiting syngas component, the organism will convert CO to H₂ by internal water gas shift reaction shown below.³⁰ Since CO is consumed by the water gas shift reaction, ethanol is decreased by limited H₂ availability/utilization.



An on-site seed train is associated with the fermentation section of the plant to harvest the *Clostridia* organisms for make-up to the fermentation process. The fermentation broth is sent to product recovery with an ethanol concentration (titer) of approximately 50 grams per liter of solution. Although the low-severity conversion process utilizes microbial cells to biologically convert CO to ethanol, which is the primary focus of the process development, the biological conversion of syngas process has the flexibility to yield various co-products (such as acetic acid and 2,3-butanediol) depending on bacterial strain used for conversion.^{31–33}

Fermentation product recovery

The syngas fermentation product separation and recovery section of the biorefinery is consistent with the design configuration presented in the 2011 NREL biochemical ethanol design report.⁹ The fermentation broth is separated into ethanol, co-products, and water by distillation and solid-liquid separation. Ethanol is distilled to a nearly azeotropic

mixture with water and then purified to 99.5% using vapor-phase molecular sieve adsorption. It has been reported that water has a detrimental effect on the Mg/Al mixed oxide catalyst used for the Guerbet chemistry²⁴ and therefore additional water in the reactant mixture potentially decreases the rates of 1-butanol production. Water recovered from the product recovery sections is either (i) recycled to the fermenters to satisfy the vapor–liquid ratio targets for mass transfer or (ii) purged to wastewater treatment.

Pathway 2A: Syngas to Rh-derived oxygenates to isobutene to higher olefins to fuels

This pathway (Fig. 3) leverages work described in Phillips *et al.*³⁵ and Dutta *et al.*⁸ and integrates research progress from Gerber *et al.*¹⁰ on Rh-catalyzed mixed oxygenates production and current research on oxygenates upgrading to fuels.³⁶ The combined steps of Rh-catalyzed oxygenates production and mixed oxides-catalyzed isobutene production are synergistic in that the high carbon conversion efficiency of the oxygenate synthesis step compensates for the carbon lost to CO₂ in the isobutene synthesis step. The reactor systems used in the mixed oxygenate synthesis and upgrading to hydrocarbon processing steps are likely to use well-known reactor technologies such as fixed catalyst beds. Use of commercially relevant and proven reactor designs in these processes will reduce the risk associated with the investment and reliability of plant operations. This pathway may be a good candidate for chemical product or co-product scenarios where a portion of isobutene, a high-value chemical, can be split off and sold to enhance plant economics.

Process design details for the common areas (feed handling, gasification and syngas clean-up, hydrogenation, product recovery, heat integration and power, and utilities) are identical to that of the previously described pathways. Only mixed oxygenate synthesis, isobutene synthesis, and oligomerization are described below.

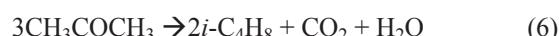
Mixed oxygenate synthesis

The reformed, scrubbed syngas is compressed to 450 psia (31 bar) in a multi-stage compressor. Acid gas removal is achieved through the use of a monoethanolamine (MEA) system, followed by a LO-CAT process and polishing to remove sulfur to parts per billion (ppb) levels. The cleaned syngas is mixed with downstream hydrogen recovered from the isobutene synthesis to adjust the H₂:CO ratio to 1.3 and then enters a two-stage compressor where the pressure is increased to 1220 psia (84.1 bar), the operating

pressure for mixed oxygenates synthesis. Pressurized syngas is fed to the tube side of a vertical tubular reactor (shell and tube type). An Rh-based catalyst is packed within the tubes of the reactor, which is oriented in a down-flow configuration. The catalyst contains Rh and Mn, with Ir as a promoter, and is supported on carbon. Reactions at or above 500°F (260°C) convert the syngas to oxygenates and hydrocarbon products at high carbon selectivity. The oxygenated product mixture contains molecules that are well-matched for the downstream isobutene synthesis chemistry, in particular ethanol, acetaldehyde, ethyl acetate, and acetic acid. The product slate and associated component selectivities used in the model are based on PNNL experimental data,¹⁰ listed in Table 4. Reaction heat is removed via saturated steam (600 psia or 41.4 bar) generation in the shell side of the reactor. Reactor effluent is cooled through heat exchange with process streams, then with an air fin and a water cooler. After the reactor effluent is cooled, oxygenated organics and water are condensed and sent to downstream upgrading equipment to produce hydrocarbon fuels. Recycle of unreacted syngas to the mixed oxygenates reactor is adjusted to maintain a combined CO and H₂ partial pressure of 1000 psi (68.9 bar) in the reactor feed, with the remainder recycled back to the tar reformer. Capital costs for this section are primarily based on Dutta *et al.*,⁸ Tan *et al.*,¹³ and Phillips *et al.*³⁵

Isobutene synthesis

The mixed oxygenates stream is de-pressurized to 200 psig (13.8 bar), pre-heated to 842°F (500°C), and fed to a shell and tube type reactor. The reaction mixture is passed through the Zn_xZr_yO_z catalyst filled tubes, where ethanol and other oxygenates are converted to isobutene, propylene, and other side-products. Multiple reaction steps are involved in the conversion of ethanol to isobutene, as given in Eqns (4)–(6):³⁷



Acetaldehyde, ethyl acetate, and acetic acid in the oxygenate mixture are also produced in this chemistry, resulting in a high conversion rate for this process. Heat is supplied for the endothermic reaction via a heat transfer fluid, such as Dowtherm. Natural gas is combusted to provide heat to the Dowtherm fluid. Natural gas is used instead of off-gas fuel gas from the process to maximize final fuel

Table 4. Design basis for mixed oxygenates reactor (Rh catalyst).

Design Parameters	
Operating Pressure, psia (bar)	1,220 (84.1)
H ₂ +CO Partial Pressure, psi (bar)	1,000 (68.9)
Operating Temperature, °F (°C)	500 (260)
Catalyst	RhMnIr/C
GHSV (hr ⁻¹)	3,247
H ₂ :CO Ratio	1.3
Single-Pass Conversion	35%
Catalyst Life, yr	4
Catalyst Rh Loading, wt%	5.6
C Selectivity to C ₂₊ Oxygenates	85%
Individual Oxygenates Selectivity %	
Methanol	0.90
Ethanol	32.80
N-Propanol	1.50
Isobutanol	0.10
1-Butanol	1.40
1-Pentanol	0.20
Acetaldehyde	18.40
Ethyl Acetate	15.70
Acetic Acid	12.10
N-Butyraldehyde	1.20
Propionaldehyde	0.60
Methyl Acetate	1.00
Methane	9.50
Ethane	1.00
Propane	0.30
I-Butane	0.10
N-Pentane	0.00
Ethylene	0.50
Propylene	1.50
1-Butene	0.80
Trans-2-Butene	0.10
Cis-2-Butene	0.10

yields (off-gas is used for heat in the tar reformer catalyst regenerator and supplemented by recycled syngas from the mixed oxygenates reactor). The design basis for the reactor is given in Table 5 and is based on PNNL data.³⁶ Testing showed that lower pressures favor higher selectivity toward isobutene over propylene. Selectivities chosen for the model (which is considered a target case) are from testing at 15 psia; however, similar performance results are thought to be attainable through further research and development of the process.

Table 5. Design basis for isobutene reactor.

Design Parameter	
Operating pressure, psia (bar)	215 (14.8)
Operating temperature, °F (°C)	840 (449)
Catalyst	Zn ₁ Zr _{2.5} O ₂
GHSV (hr ⁻¹)	2,000
Single-Pass Conversion	100%
Catalyst Life, yr	4
Carbon Selectivity %	
C ₃ =	5.76
i-C ₄ =	47.4
1-C ₄ =	1.70
C ₅ =	7.38
CH ₄	2.75
CO ₂	31.6
CO	1.51
C ₂ =	0.95
C ₂ -C ₅ alkanes	0.24
Acetone	0.27
Other oxygenates	0.48

The effluent from the mixed oxides catalyst reactor is cooled to 130°F (54.4°C) via the inlet feed to the reactor and fed to a vapor/liquid separator, reducing the water content to 1.3 mol%. It is necessary to remove water prior to oligomerization to mitigate catalyst poisoning; a water content of 5 mol% in the oligomerization feed can reduce conversion by 3%.³⁸ A small compressor is used to raise the pressure to 270 psia (18.6 bar). This stream contains about 36 wt% olefins diluted with mostly CO₂ and H₂ (by-products shown in Eqns (4)–(6)), along with CO, methane, water, and other light components. A gas absorption system is used to remove the CO₂, H₂, and light gasses to increase the partial pressure of reactants in the oligomerization reactor feed. A slip stream of olefin product from the oligomerization reactor is used as the solvent and is recovered and recycled in a distillation step. The resulting feed stream for oligomerization consists of about 95 wt% olefins. The light gases from absorption are fed to a PSA system to recover hydrogen, which is used for downstream hydrogenation and to adjust the molar H₂:CO ratio in the mixed oxygenates reactor feed. All equipment in this section is costed using Aspen Capital Cost Estimator, except the refrigeration system, which is scaled on cost estimates provided in Arne,³⁹ and the PSA, which is scaled based on costs given in Tan *et al.*¹³

Oligomerization

While several catalysts have been tested for oligomerization of isobutene, Amberlyst has been shown to offer the highest selectivity toward C₇–C₁₆ fuel-range olefins and cyclic compounds³⁸ and is the catalyst chosen for this design. The produced light olefins from the gas absorption process are compressed to 261 psia (18 bar) and oligomerized over a packed bed of Amberlyst 36 catalyst. The reactor consists of multiple stages with inter-stage air cooling to manage the heat generated from the exothermic oligomerization reactions. It is assumed that an inlet temperature of 230°F (110°C) is sufficient to initiate the reaction, and a temperature rise of 75°F (41.7°C) is allowed over each bed (305°F or 151.7°C is the temperature maximum for Amberlyst 36). Using these assumptions, the reactor design requires five fixed bed stages. The design parameters for the reactor are given in Table 6 and are based on experimental data.³⁶ For the purposes of simplifying the process model, the data was adjusted to group carbon numbers and limit the number of possible reactions occurring between species. The small amount of ketone present is assumed to be inert in the oligomerization reactor.⁴⁰ Hexene and heptene are separated via distillation and recycled back to the oligomerization reactor to increase fuel yields. A simplifying assumption is made that hexene and heptene react only with themselves to form dimers and trimers. In reality, these compounds would also react with feed C₃, C₄, and C₅ olefins, as well as longer chain olefins stemming from these reactants. Hexene conversion of 90%

to dimers and trimers has been shown over Amberlyst 35 at similar conditions to these.⁴¹ Hexene conversions to dimers and trimers are assumed to be 56.5% and 23.7%, respectively. Heptene conversion is assumed to be slightly lower than hexene at 80%,⁴² with the same selectivities to dimer and trimers as hexene. Aspen Capital Cost Estimator is used to cost all equipment in this section.

Pathway 2B: Syngas fermentation to ethanol to isobutene to higher olefins to fuels

As depicted in Fig. 3, the processing steps of this hybrid thermochemical/biochemical conversion pathway include the conversion of biomass to synthesis gas via indirect gasification, gas cleanup via reforming of tars and other hydrocarbons, and fermentation of syngas to produce ethanol intermediate. The ethanol intermediate is then processed to hydrocarbon products by the same pathway as the mixed oxygenates conversion described for Pathway 2A. Although the production of ethanol intermediate from syngas fermentation is the primary focus of the process development, the biological conversion of syngas process has the flexibility to yield various co-products depending on bacterial strain used for conversion. Acetic acid and 2,3-butanediol are two possible co-products.³² The process design for feed handling, gasification and syngas cleanup are identical to that of the previously described pathways. The process design for syngas fermentation to ethanol and intermediate product recovery are identical to that of

Table 6. Design basis for oligomerization reactor using Amberlyst 36 catalyst.

Design Parameters							
Temperature, °F (°C)	230°F (110 °C) at stage inlet, allow 75°F (41.7 °C) rise over each bed						
Pressure, psia (bar)	261 (18)						
Catalyst	Amberlyst 36						
WHSV, hr ⁻¹	0.756						
Single-Pass Conversion, %	100						
Catalyst Life, yr	1.0						
Selectivities	C ₆ =	C ₇ = ¹	C ₈ =	C ₁₀	C ₁₂ (branched)	C ₁₂ (cyclic)	C ₁₄ ²
C ₃ =	0.824	0.176					
C ₄ = ³		0.1794	0.162		0.344	0.154	0.097
C ₅ = ⁴				0.772			0.043

¹Formed through C₃=/C₄= oligomerization and cracking of a portion of produced C₁₄=.

²For the purposes of simplifying the model, a portion of C₄= is assumed to oligomerize/crack to form C₁₄= to emulate the data.

³The balance of C₄ and C₅ are hydrogenated to alkanes from hydrogen thought to be generated from the catalyst.

⁴Formed through C₃+C₄ (0.134) and via C₁₄ cracking (0.045).

Pathway 1B. Oxygenates to hydrocarbons, hydrogenation, product recovery, heat integration and power generation, and utilities are identical to that previously described for Pathway 2A.

Commercial benchmark: Fischer-Tropsch

The TEA scenario for the Fischer-Tropsch (FT) commercial benchmark is based on NREL's work on co-processing of natural gas and biomass to liquid fuels (unpublished work). The case considered in this analysis (Fig. 4) is consistent with the GTL biomass only (no natural gas co-processing). FT synthesis is considered a relatively mature conversion technology from clean syngas and serves as a basis for comparison with the newly developed pathways for this analysis.

Fischer-Tropsch synthesis

The FT process involves the catalytic conversion of syngas into a mixture of reaction products which could be refined to synthetic fuels, lubricants, and petrochemicals.

One of the important advantages that the FT process offers is its capability of producing liquid hydrocarbon fuels directly from syngas, which are nearly free from sulfur and relatively low in aromatic content. An important aspect of this process is the adjustment of the H₂ to CO ratio, which is usually determined by the upstream gasification and reforming technologies and operating conditions. The FT reactions involve catalytic CO polymerization and hydrogenation, where the chain growth and termination of the reaction products can be described by a carbon number distribution, as shown in Fig. 5. The carbon number distribution in an FT process is typically described by the Anderson-Schulz-Flory (ASF) distribution,⁴³ which describes the molar concentration (x_n) of a carbon chain with n carbons in terms of a chain growth probability (α) such that the carbon numbers (n) and molar concentrations (x_n) have a logarithmic relationship.

$$\ln(x_n) = n \ln(\alpha) + \ln((1-\alpha)/\alpha) \quad (7)$$

where $\alpha = x_{n+1} / x_n$.

The base FT model applied for this analysis considers a cobalt catalyst-based slurry column reactor operating in the low-temperature FT range at 446°F (230°C). The FT operating conditions are chosen to maximize the production of hydrocarbon fuels using the ASF distribution shown in Fig. 5. It was determined that an evaluation based on an α value of 0.84 will maximize the yield of the

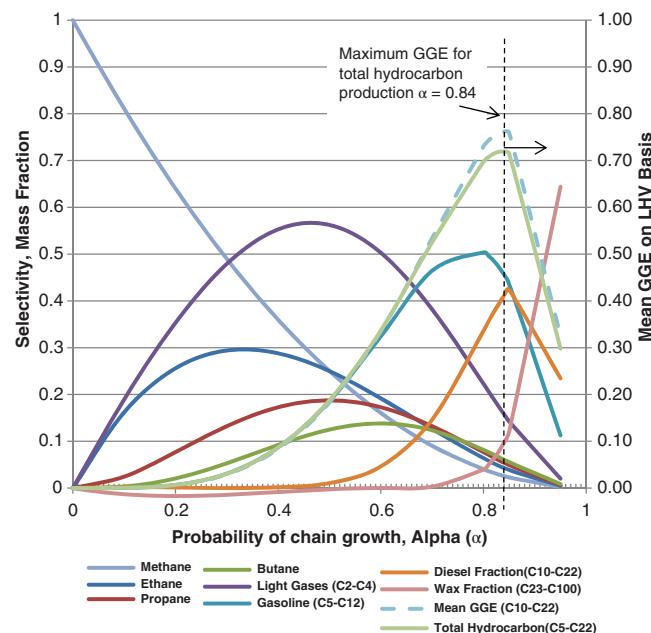


Figure 5. Anderson-Schulz-Flory (ASF) mass distributions and the mean of gallon gasoline equivalent (GGE) versus probability of chain growth (α).

Table 7. ASF product mass distribution ($\alpha = 0.84$) for Fischer-Tropsch benchmark case.

Product Range	Mass Fraction (typical) ¹	Mass Fraction (model) ²
CH ₄	0.026	0.100
C ₂ -C ₄	0.158	0.150
C ₅ -C ₁₁	0.456	0.387
C ₁₂ -C ₂₂	0.411	0.289
C ₂₃₊	0.098	0.074

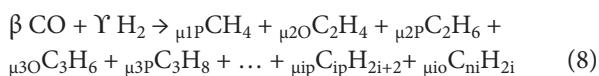
¹Typical ASF mass distribution for $\alpha = 0.84$.

²CH₄ production was adjusted to 10 wt% and normalized the rest of the yields.

reaction product slate, in terms of GGE. Table 7 shows a typical product distribution for $\alpha = 0.84$, outlining the production of methane, light gases, gasoline, jet fuel, diesel, and wax fraction. In the Aspen model, the methane production was adjusted to 10 wt% (from 2.6 wt%) and the rest of the yields were normalized; this was done to account for the variation in product slate occurring due to various reactor configurations and catalyst compositions.

In this formulation, the generic stoichiometry for paraffin and olefin reactions (Eqn (8)) was taken into consideration, with the product yields determined on a mass basis by the adjusted ASF distribution shown in

Table 6. For calculating the olefin to paraffin ratio, an exponential fit to the experimental data of Todic *et al.*⁴⁴ was performed to evaluate a correlation for the olefin to paraffin ratio between a C₃ to C₁₀ range of n-olefins. The carbon, hydrogen, and oxygen balances for the equation involving CO, H₂, n-paraffins, and n-olefins were formulated with the help of the chemical reaction (Eqn (8)). Furthermore, the C₄₊ fraction is redistributed to 74 mol% C₁, 16 mol% C₂, 6 mol% C₃, and 4 mol% C₄ to account for non-ASF effects. A single pass conversion of 85% of CO is assumed, which is in accordance to that observed in slurry reactors.



where,

β = Stoichiometric coefficient for CO

γ = Stoichiometric coefficient for H₂

μ_i = Stoichiometric coefficients for n-paraffins

μ_O = Stoichiometric coefficients for n-olefins

i = Number of carbon atoms

Product recovery and finishing

The FT reactor products are condensed and separated through typical hydrocarbon separation process in a multi-cut distillation column to recover the primary products (naphtha, kerosene/jet, and diesel fractions) as individual streams. Each of the primary hydrocarbon cuts are further processed to yield finished fuel blendstocks for gasoline, jet fuel, and on-road diesel. The product slate was set at 70/30 wt% diesel/naphtha with approximately 2% light ends. The jet and diesel fractions undergo mild hydrotreating to remove any remaining heteroatom contaminants (sulfur, nitrogen, and oxygen) and improve properties for blending. The naphtha-range product from FT synthesis is sent to an isomerization unit to increase branching of the hydrocarbon chains, which improves the quality of the material for gasoline blending (increasing octane value). Capital and operating costs for the product upgrading operations are consistent with costs presented by Gary *et al.*⁴⁵

Results and discussion

Process performance

The process designs feature a processing daily capacity of 2000 metric tonnes (2205 US short tons) of dry biomass

and 90% on-stream time (7884 annual operating hours). The major performance results for the conversion pathways, which include hydrocarbon fuel product yields, are summarized in Table 8. The liquid fuel products include naphtha-, jet-, and diesel-range hydrocarbons. All fuel production and yields are reported in gallon gasoline equivalent (GGE). A lower heating value (LHV) of 116 090 BTU/gal (32.36 MJ/L) for gasoline blendstock is used in the conversion to GGE.¹⁸ Pathways 1A and 1B produce only jet and diesel blendstocks and the product slate is close to evenly split. For Pathways 2A, 2B, and FT benchmark, gasoline blendstock is also produced, with jet fuel being the major blendstock, followed by gasoline and diesel. For pathway performance comparison, all three fuel blendstocks are combined and referred to as a single-fuel product for simplicity. The annual total fuel production ranges from 30.1 MMGGE (Pathway 2B) to 48.0 MMGGE (Pathway 2A). Similarly, the fuel yield profile is identical to the fuel production profile. Pathway 2A exhibits the highest yield (66.2 GGE/dry ton), which is comparable to that of the FT benchmark (65.6 GGE/dry ton). Pathway 2B has the lowest yield (41.6 GGE/dry ton), which is about 63% of the FT benchmark.

In addition to fuel production and yields, Table 8 also lists the carbon conversion efficiency (CCE) for each conversion pathway. CCE is a key process performance metric and is defined as the carbon in the feed that is converted to the product(s). The fuel yields correlate well with the net CCE (biomass-to-fuels), as evident in Fig. 6. In addition to the overall or net CCE from biomass-to-fuels, we also determined the CCE breakdowns for the conversion steps: (i) biomass-to-raw syngas, (ii) raw syngas-to-oxygenates/alcohols, and (iii) oxygenates/alcohols-to-fuels. CCE breakdowns can help researchers to identify the 'hot spot' of the process that presents the highest potential on process improvement in terms of fuel yields. Further, since FT fuels are produced directly from syngas and are not via oxygenated intermediates, the CCE for raw syngas-to-fuels is also quantified for direct comparison.

Using the same design basis, the CCEs associated with the biomass conversion to raw syngas are essentially identical for all pathways, at 71.8%. In contrast, both CCEs for raw syngas-to-oxygenates/alcohols and oxygenates/alcohols-to-fuels are considerably different. For Pathways 1A and 1B, the CCEs are lower for the former than the latter. The reverse is true for Pathways 2A and 2B.

The CCE for the conversion of raw syngas-to-oxygenates/alcohols is 77.7%, significantly higher than syngas fermentation to ethanol (51.6% and 48.5% for Pathways 1B and 2B,

Table 8. Process performance summary for the conversion pathways.

Key Process Targets	Conversion Pathways				Benchmark
	1A	1B	2A	2B	
Oxygenate Intermediate Product from Syngas (lb/hr)	Mixed alcohols ¹ 59,833	Ethanol 66,283	Mixed oxygenates ² 101,250	Ethanol 65,121	N/A ³
Fuel Production (MMGGE/yr):					
Naphtha range	-	-	11.5	7.23	17.0
Jet range	19.5	21.7	31.6	19.84	18.2
Diesel range	21.6	23.1	4.80	3.03	12.3
Total Fuel Product	41.1	44.8	48.0	30.1	47.5
Fuel yield (GGE/dry ton biomass):					
Naphtha range	-	-	15.9	10.0	23.5
Jet range	26.9	30.0	43.7	27.4	25.1
Diesel range	29.8	31.8	6.70	4.18	17.0
Total Fuel Yield	56.7	61.9	66.2	41.6	65.6
Carbon Conversion Efficiency:					
Biomass to raw syngas	71.8%	71.8%	71.8%	71.8%	71.8%
Raw syngas to alcohols/oxygenates ³	41.2%	51.6%	77.7%	48.5%	46.2%
Oxygenates to fuels	86.6%	85.0%	60.6%	61.0%	N/A ³
Biomass to fuels	28.9%	31.5%	33.8%	22.1%	33.2%

¹Methanol, ethanol, and propanol²Ethanol, ethyl acetate, acetic acid, and some higher oxygenates, some LPG type material, some methanol³For Fischer-Tropsch, direct synthesis of hydrocarbons from synthesis gas

respectively), and MoS₂-catalyzed mixed alcohol synthesis (Pathway 1A, 41.2%). The lower CCE for this step for Pathway 1A is attributed to more carbon loss in the mixed alcohols synthesis step as a result of low CO conversion (33%) and mixed alcohols selectivity (70%),⁷ compared to 35% CO conversion and 85% mixed oxygenates selectivity for Pathway 2A (Table 3). The difference in conversion efficiencies from syngas to ethanol for the fermentation scenarios (1B and 2B) is a result of different specific process modeling assumptions for downstream conversion configurations and correspondingly different impacts to the production of oxygenated intermediates from process recycle streams and downstream process and heat integration.

Figure 6 clearly shows that Pathways 1A and 1B exhibit higher CCE associated with the oxygenates/alcohols-to-fuels step (more than 85%) than that of Pathways 2A and 2B (around 61%). Based on the recent study, the Zn_xZr_yO_z catalyst activity and selectivity for the isobutene synthesis are assumed to be similar for mixed oxygenates (Pathway 2A) and ethanol (Pathway 2B).³⁶

The major reaction in the oxygenates/alcohols-to-fuels step is Guerbet reaction (Pathways 1A and 1B) and

isobutene synthesis (Pathways 2A and 2B). A sensitivity study reveals that improving the single-pass ethanol conversion for the Guerbet reaction from 45% to 60% only leads to a 3% increase in the overall product yields. This is primarily attributed to the fact that unconverted ethanol is recycled and sent back to the Guerbet reactor, resulting in similar overall ethanol conversion for the low and high single-pass ethanol conversion cases, at 94% and 97%, respectively. On the other hand, simultaneously increasing the isobutene selectivity from 36% to 47% and doubling the Zn_xZr_yO_z catalyst activity (from gas hourly space velocity of 1000 hr⁻¹ to 2000 hr⁻¹) improves the fuel yield by 11%. Thus, further research is warranted to improve the production of the isobutene rich olefin mixture, specifically improving the isobutene selectivity at lower pressure.³⁶

The overall biomass-to-fuels CCE increases in the order of presentation for the evaluated pathways: 2A (33.8%) > FT (33.2%) > 1B (31.5%) > 1A (28.9%) > 2B (21.3%). With similar fuel yields and CCEs, Pathways 2A and 1B can potentially be alternatives to conventional fuel synthesis routes such as FT process.

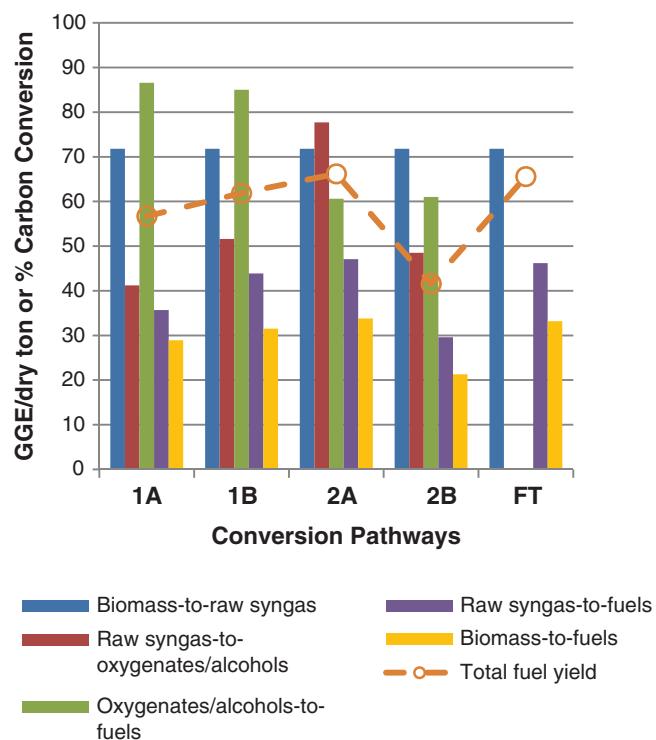


Figure 6. Correlation between carbon conversion efficiencies (CCE) and fuel production yields.

Total capital investment

The capital costs for each plant area are based on data from various sources including NREL design reports and publications and Aspen Capital Cost Estimator software.^{8,13,46} The purchased costs for the equipment and installation factors are used to determine the installed equipment cost. The indirect costs (non-manufacturing fixed-capital investment costs) are estimated using factors based on the total direct cost (TDC). The factors used in this study are adopted from Tan *et al.*¹³ as percentages of total purchased equipment costs (TPEC), TDC, and fixed capital investment (FCI), which is equal to the sum of TDC and total indirect costs. With the calculated total installed cost (TIC) and assumptions for indirect costs and working capital, the FCI and total capital investment (TCI) can be determined. Table 9 presents a summary of these calculations.

Figure 7 gives the breakdown of TIC for each of the pathways analyzed. As shown, clean syngas production is a significant contributor to the capital expenditure (CAPEX) for all pathways. Producing clean syngas is relatively constant for Pathways 1A, 1B, and 2A, and higher for Pathway 2B and FT benchmark. The variation of

CAPEX associated with biomass to clean gas production is largely due to the various flow rates of the recycle of the unconverted syngas and downstream process off-gas to the tar reformer. The cost of the intermediates production step is comparable for the syngas fermentation (Pathways 1B and 2B) and Rh-catalyzed (Pathway 2A) processes, and is highest for the mixed alcohols process (Pathway 1A) at \$202 million. More severe operating conditions for mixed alcohols synthesis in Pathway 1A requires high-pressure syngas compression and more complex heat integration. The capital for the hydrocarbon fuel production step is higher for Pathways 1A (\$87.1MM) and 1B (\$72.4MM) than for Pathways 2A and 2B (both at \$35MM), due to two extra steps (Guerbet reaction and alcohol dehydration) prior to oligomerization, dimerization, and hydrogenation required to produce finished fuel for Pathways 1A and 1B. With the exception of Pathway 1A, TICs for all other pathways are lower than that for the benchmark FT process (\$331.3MM).

Operating costs

Operating costs, including labor costs, materials and feedstock costs, utility costs, and disposal costs, were evaluated for the 2000-dry-metric-tonne/day facility. Details on the variable operating costs, including the annualized costs for catalysts, olivine, and disposal can be found in Table 10. Table 11 demonstrates the breakdown of these operating costs and their contribution to the total production cost. Variable operating costs are determined based on raw materials, waste-handling charges, and by-product credits incurred only during the process operation. Fixed operating costs are generally incurred in full whether or not the plant is producing at full capacity. These costs include labor and various overhead items. Many of the assumptions on fixed operating costs follow NREL's earlier reports^{8,47} and Peters and Timmerhaus.⁴⁸ General overhead equals 90% of total salaries, maintenance equals 3% of FCI, and insurance and taxes equal 0.7% FCI. As shown in Table 11, the fixed operating costs range from \$22.3MM to \$31.6MM per year or \$0.48/GGE to \$0.77 /GGE.

Pathways with oxygenated intermediates produced via biological route (syngas fermentation to ethanol), Pathways 1B and 2B, exhibit lower total annual operating costs (partly due to co-product credits from acetic acid) than those produced via thermochemical conversion (Pathways 1A and 2A). Pathway 2A has the highest total annual operating costs (\$110.8 MM), in which catalyst costs account for \$24.9MM and 64% of it is attributed to the Rh catalyst that is responsible for catalyzing syngas

Table 9. Project cost worksheet (2011 US dollars).

	1A	1B	2A	2B	FT
Total Purchased Equipment Cost (TPEC)	\$212,200,000	\$125,490,000	\$125,200,000	\$131,134,000	\$142,240,000
Installation Factor	1.99	2.19	1.98	2.19	2.33
Total Installed Cost (TIC)	\$422,400,000	\$274,650,000	\$247,300,000	\$287,499,000	\$331,280,000
Other Direct Costs					
Land (Not Depreciated)	\$1,610,000	\$1,610,000	\$1,610,000	\$1,610,000	\$1,610,000
Site Development	4% of ISBL	\$14,576,000	\$9,406,000	\$8,120,000	\$8,874,000
Total Direct Costs (TDC)	\$438,586,000	\$285,666,000	\$257,030,000	\$297,983,000	\$344,299,000
Indirect Costs	% of TDC				
Prorated Expenses	10.00%	\$43,698,000	\$28,406,000	\$25,542,000	\$29,638,000
Home Office & Construction Fees	20.00%	\$87,396,000	\$56,812,000	\$51,084,000	\$59,275,000
Field Expenses	10.00%	\$43,698,000	\$28,406,000	\$25,542,000	\$29,638,000
Project Contingency	10.00%	\$43,698,000	\$28,406,000	\$25,542,000	\$29,638,000
Other Costs (Start-Up & Permits)	10.00%	\$43,698,000	\$28,406,000	\$25,542,000	\$29,638,000
Total Indirect Costs	60.00%	\$262,188,000	\$170,436,000	\$153,252,000	\$177,827,000
Fixed Capital Investment (FCI)		\$700,774,000	\$456,102,000	\$410,282,000	\$475,810,000
Working Capital	5% of FCI (excl. Land)	\$35,039,000	\$22,806,000	\$20,515,000	\$23,791,000
Total Capital Investment (TCI)		\$735,813,000	\$478,908,000	\$430,797,000	\$499,601,000
TCI/TPEC		3.468	3.816	3.441	3.810
FCI Lang Factor = FCI/ISBL TPEC		3.828	4.245	3.992	4.702
TCI Lang Factor = TCI/ISBL TPEC		4.019	4.458	4.192	4.937
					4.715

conversion to mixed oxygenates. In fact, catalyst cost is the second largest cost contributor after the feedstock. On an annual basis, the total operating costs for the pathways increases in this order: 2A (\$110.8MM) > 1A (\$99.5MM) > FT (\$86.2MM) > 1B (\$85.2MM) > 2B (\$82.4MM). While Pathway 2B has the lowest annual operating costs it has the highest total operating costs when normalized on a per GGE fuel production basis, at \$2.74/GGE. The total operating costs for all pathways are higher than the benchmark FT process (\$1.81/GGE); Pathway 1B has the closest total operating costs to the benchmark at \$1.90/GGE.

Minimum fuel selling price

Once the capital and operating costs are determined, a DCFROR calculation was performed to determine the MFSP that meets the economic parameter using the general methodology^{8,35,46,47,49} and the economic parameters.¹³ The discounted cash flow analysis is performed by iterating the selling cost of fuel until the net present value of the project is zero. This analysis requires that the discount rate, depreciation method, income tax rates,

plant life, and construction start-up duration be specified. The MFSP value represents the minimum selling price of liquid fuels assuming a 30-year plant life and 40% equity financing with 10% internal rate of return and the remaining 60% debt financed at 8% interest. Again, the fuel products (gasoline, jet and diesel blendstocks) are combined and referred to as a single-fuel product for simplicity. All MFSP calculations are performed and reported on a combined product basis. The MFSP and contributing costs for the evaluated pathways are shown in Fig. 8. The cost contributions to the MFSP are divided into: (i) capital charges and taxes, (ii) operating costs and co-product credits, and (iii) feedstock costs.

Similar to the overall biomass to fuels carbon conversion efficiency and fuel yields discussed in the section on process performance, the MFSPs for Pathways 1B (\$3.40/GGE) and 2A (\$3.69/GGE) are also comparable (within ±5%) to that of the benchmark FT process (\$3.58/GGE), whereas MFSPs for Pathways 1A and 2B are 37% and 41%, respectively, higher than the benchmark case. When compared to Pathway 1B, the high MFSP (\$4.89/GGE) for Pathway

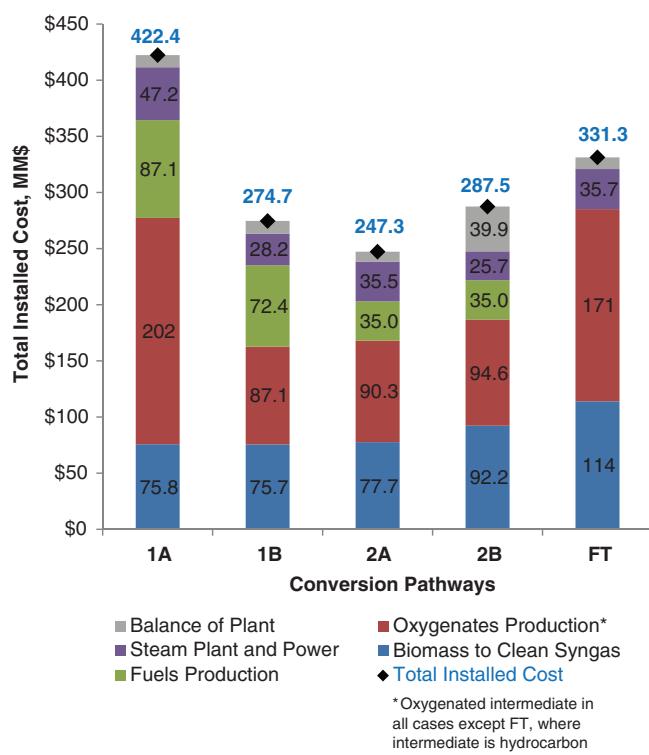


Figure 7. Breakdown of total installed cost by process area for each of the pathways analyzed.

1A is due to the lower carbon conversion efficiency for the syngas to oxygenates step, 41.2% (versus 51.6% for Pathway 1B). Additionally, the CAPEX for the syngas fermentation (Pathway 1B) is significantly lower than that associated with the high pressure mixed alcohols synthesis for Pathway 1B. As a result, the TCI for Pathway 1B is estimated to be \$478.9 MM, compared to \$735.8 MM for Pathway 1A.

The high MFSP for Pathway 2B (\$5.04/GGE) is due to the low fuel yield and overall low carbon conversion efficiency (29.6%) for the combined raw syngas through isobutene synthesis steps. By contrast, for Pathway 2A, the high carbon selectivity of the Rh-catalyzed oxygenates synthesis step compensates for the loss of carbon to CO₂ in the isobutene synthesis step, resulting in a much more favorable overall carbon efficiency for raw syngas to isobutene (47.1%).

As mentioned earlier, the biological conversion of syngas process has the flexibility to yield various co-products (such as acetic acid and 2,3-butanediol) depending on bacterial strain used for conversion.^{31–33} A sensitivity study on Pathways 1B and 2B reveals that the co-production of 2,3-butanediol (2,3-BDO) can noticeably improve the MFSPs, as shown in Fig. 9. To be conservative on the 2,3-BDO co-product credits due to the uncertainty of its market

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

Variable	Information and operating cost
Feedstock	Blended biomass contains 45% pulpwood, 32% wood residues, 3% switchgrass, and 20% construction and demolition waste. Price: \$80.00/dry US ton
Gasifier bed material	Synthetic olivine and MgO. Initial fill then a replacement rate of 0.01 wt% of circulation or 7.2 wt% per day of total inventory. Delivered to site by truck with self-contained pneumatic unloading equipment. Disposal by landfill. Olivine price: \$275/tonne MgO price: \$580/tonne
Tar reformer catalyst (Ni-Mg-K/Al ₂ O ₃)	To determine the amount of catalyst inventory, the tar reformer was sized for a gas hourly space velocity (GHSV) of 2,476/h based on the operation of the tar reformer at NREL's pilot plant demonstration unit. GHSV is measured at standard temperature and pressure. Initial fill then a replacement rate of 0.15 wt% of catalyst inventory per day. Price: \$47.70/kg based on NREL calculations using metals pricing and costs for manufacturing processes.
Mixed alcohols synthesis catalyst (MoS ₂)	Initial fill then replaced every 2 years based on expected catalyst lifetime. Catalyst inventory based on GHSV of 5,000/h. Price: \$31.23/lb (initial load); \$27.12/lb (after initial load)
Guerbet catalyst (MgO-Al ₂ O ₃)	Initial fill then replaced every 4 years based on expected catalyst lifetime. Catalyst inventory based on WHSV of 1.0/h. Price: \$25.00/lb
Dehydration catalyst	Initial fill then replaced every 3 years based on expected catalyst lifetime.

Table 10. (Continued)

(Gamma alumina)	Catalyst inventory based on WHSV of 1.0/h. Price: \$10.30/lb
Oligomerization catalyst (HZSM-23)	Initial fill then replaced every 3 years based on expected catalyst lifetime. Catalyst inventory based on WHSV of 0.21/h. Price: \$30.80/lb
Dimerization catalyst (Nafion)	Initial fill then replaced every 4 years based on expected catalyst lifetime. Catalyst inventory based on WHSV of 1.0/h. Price: \$9.89/lb (Ion Power Inc., New Castle, DE)
Hydrogenation catalyst (Pd/Al ₂ O ₃)	Initial fill then replaced every 3 years based on expected catalyst lifetime. Catalyst inventory based on WHSV of 1.0/h. Price: \$55.20/lb (PEP 2014 Yearbook, 0.4% Pd on Al ₂ O ₃)
Rhodium-based catalyst (RhMnIr/C)	Initial fill then replaced every 4 years based on expected catalyst lifetime. Catalyst inventory based on GHSV of 3,247/h. Price: \$552/lb (PNNL estimate)
Isobutene production catalyst (Zn ₁ Zr _{2.5} O ₂)	Initial fill then replaced every 4 years based on expected catalyst lifetime. Catalyst inventory based on GHSV of 2,000/h. Price: \$30.00/lb (PNNL estimate)
Oligomerization catalyst (Amberlyst 36)	Initial fill then replaced every 1 year based on expected catalyst lifetime. Catalyst inventory based on WHSV of 0.756/h. Price: \$15.62/lb (Dow Chemicals)
Solids disposal	Price: \$18.20/ton (tar reformer catalyst disposal) Price: \$54.00/ton (sand and ash purge)
Diesel fuel	Usage: 38 L/h plant-wide use. Price: \$22.39/GJ (2012 price projection)
Natural gas	Price: \$5.10 per 1,000 standard cubic feet (EIA, 2011 industrial average)
Purchased hydrogen	Price: \$0.684/lb
Co-products	Price: \$608/tonne acetic acid (2013 IHS Chemical Economics Handbook) Price: \$3,230/tonne 1,4-butanediol (2013 IHS Chemical Economics Handbook)
Electricity	Price: \$6.89/kWh (EIA, 2011 industrial average)
Water make-up	Price: \$0.35/tonne
Chemicals	Boiler feed water chemicals–Price: \$6.13/kg Cooling tower chemicals–Price: \$3.67/kg LO-CAT chemicals–Price: \$498.98/tonne sulfur produced from NREL/Harris Group Inc. estimates based on other projects DEPG make-up–Price: \$81.59/million lb acid gas removed Selective amine make-up–Price: \$39.81/million kg acid gas removed.
Wastewater	Most wastewater is cleaned using an RO system and recycled. The balance of the wastewater is sent to off-site treatment facility. Price: \$0.83/tonne
Note: All catalyst costs are assumed to include the disposal cost (base metal catalysts except tar reformer catalyst) and reclamation cost (precious metal catalysts).	

value, the MFSPs are estimated using one of the recent market prices (\$3230/tonne in 2011)⁵⁰ as well as values lower than that. It is evident from Fig. 9 that the Pathway 2B eco-

nomic performance can feasibly be comparable to the benchmark FT process. For example, at 2,3-BDO value of \$2423/tonne (75% of the base price), the MFSP for Pathway 2B is

Table 11. Breakdown of operating cost contribution (2011 US dollars).

	Pathway 1A		Pathway 1B		Pathway 2A		Pathway 2B		Benchmark FT	
	MM\$/year	\$/GGE	MM\$/year	\$/GGE	MM\$/year	\$/GGE	MM\$/year	\$/GGE	MM\$/year	\$/GGE
Feedstock	58.0	1.41	58.0	1.29	58.0	1.21	58.0	1.92	58.0	1.22
Natural gas	--	--	--	--	1.44	0.03	--	--	--	--
Catalysts	8.63	0.21	5.11	0.11	24.9	0.52	3.61	0.12	4.63	0.10
Olivine and magnesium oxide	0.41	0.01	0.54	0.01	0.58	0.01	0.54	0.02	0.54	0.01
Hydrogen	1.64	0.04	1.94	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Other raw materials	0.41	0.01	0.72	0.02	2.40	0.05	1.29	0.04	1.11	0.02
Waste disposal	0.41	0.01	0.88	0.02	0.48	0.01	0.85	0.03	0.60	0.01
Co-product credits	-1.64	-0.04	-4.32	-0.10	--	--	-4.88	-0.16	-4.57	-0.10
Total variable costs	67.8	1.65	62.8	1.40	87.7	1.83	59.4	1.97	60.3	1.27
Fixed operating costs	31.6	0.77	22.3	0.50	23.0	0.48	23.1	0.77	25.9	0.55
Total operating costs	99.5	2.42	85.2	1.90	110.8	2.31	82.4	2.74	86.2	1.81

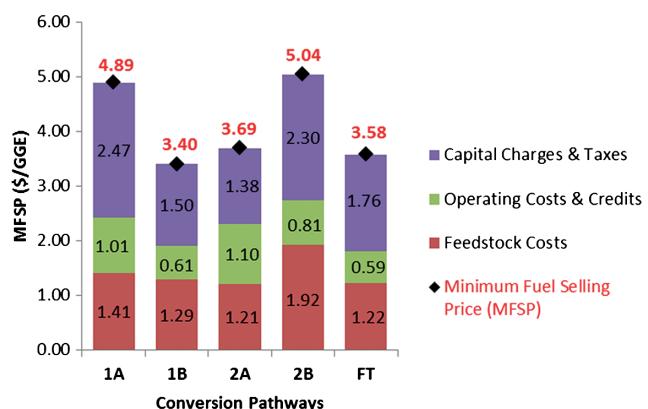


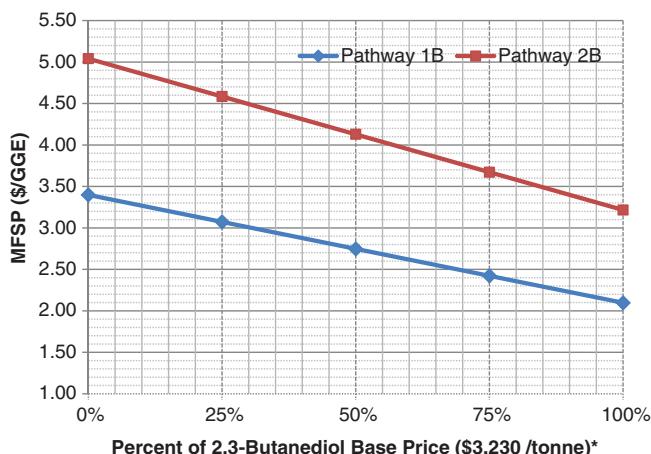
Figure 8. Minimum fuel selling price (MFSP) and cost contribution details.

determined to be \$3.67/GGE, representing a 27% improvement relative to the base case without 2,3-BDO co-product.

Sustainability metrics

Environmental sustainability metrics are estimated for the conceptual processes, as shown in Table 12. Important sustainability metrics considered for the conversion stage are: GHG emissions, fossil energy consumption, fuel yield, biomass carbon-to-fuel efficiency, water consumption, and wastewater generation.

Due to the use of fossil fuel (i.e., natural gas) for the process and the lack of any co-product credits (i.e., export electricity, acetic acid, and 2,3-butanediol), direct biorefinery GHG emissions and fossil energy consumption of Pathway 2A are higher than those of Pathways 1A, 1B, 2B, and the



*It is assumed that 2,3-BDO has the same market value as 1,4-BDO at \$3,230/tonne (\$2,930/U.S. ton) in 2011 U.S. dollars.

Figure 9. Minimum fuel selling price (MFSP) as a function of 2,3-butanediol (2,3-BDO) co-product credit, which in turn is a function of the market price. MFSPs at 0% represent the base cases without the co-production of 2,3-BDO during the syngas fermentation.

benchmark FT process, corresponding to high net GHG emissions (906 kg CO_{2e}/GGE) and fossil energy consumption (12 MJ/GGE). All other pathways have slight excess electricity and do not require natural gas for heat generation (Table 1), the corresponding net GHG emissions and fossil energy consumption associated with the conversion stage are lower, ranging from -0.72 to -0.19 kg CO_{2e}/GGE, and -14 to -2.7 MJ/GGE, respectively. Negative values are attributed to co-product credits. Direct GHG emissions

from these conversion processes are entirely biogenic CO₂, which is not included in GHG emissions quantification per the Intergovernmental Panel on Climate Change global warming methodology.⁵¹ Consequently, the contributions to GHG at the conversion stage are solely from the associated underlying processes (e.g. material inputs/outputs to and from the facility to support process operations).

Table 12 also presents the biomass carbon-to-fuels efficiency of each process and is discussed in the process performance section. An overarching goal of BETO is to enable technologies that produce transportation biofuels in a sustainable way. In addition to fuel yield, biomass carbon-to-fuel efficiency is also an important measure of natural resource utilization and is inherent to biofuel sustainability. Both fuel yield and biomass carbon-to-fuel efficiency are measures of how efficient the technology is at producing liquid fuel. Therefore, when comparing fuel options, it is important to present these metrics alongside GHG emissions as well as other sustainability metrics to provide a more comprehensive representation of the overall performance of a conversion process and the balance between these metrics.⁴⁷ The estimated carbon conversion efficiencies for the evaluated pathways are similar to the earlier indirect liquefaction pathways.^{7,13}

Conservation of water resources is a universal concern. Consumptive water use or water consumption is an important environmental sustainability metric. Water consumption associated with conversion pathways consists of make-up water for the steam and cooling systems. Boiler feed water make-up is needed to replace steam consumed in the reformer. Fresh cooling water is needed to make up for losses at the cooling tower (e.g. evaporation and drift) and blowdown for maintenance of the recirculating cooling system. Water consumed for production of materials used at the biorefinery (e.g. catalysts) and for

life-cycle stages upstream and downstream of conversion is not included in the analysis. It is important to note that steam drum blowdown, cooling tower blowdown, and process condensate are recycled for use for both steam generation and cooling, significantly reducing raw cooling water make-up. The water consumption and wastewater generation for Pathways 1A and 2A are lower than those for Pathways 1B, 2B, and FT benchmark, as shown in Table 12. As a reference, the crude oil refining to gasoline process consumes between 2.8 and 6.6 gal/GGE.⁵²

Conclusions

NREL and PNNL have jointly developed the conceptual biorefinery processes and performed the detailed comparative TEA of five conversion pathways from biomass to gasoline-, kerosene/jet-, and diesel-range hydrocarbons via indirect liquefaction with specific focus on pathways utilizing oxygenate intermediates. The four emerging pathways of interest are compared with a mature pathway, Fischer-Tropsch. We show that the emerging pathways via oxygenated intermediates have the potential to be cost competitive with the conventional FT process (a single-step syngas-to-liquid hydrocarbons process). The evaluated pathways generally exhibit fuel yields in the range of 41.6–66.2 GGE/dry ton biomass and overall carbon conversion efficiencies from 33.8% to 66.2%, compared to those of the FT benchmark, 65.6 GGE/dry ton biomass and 33.2%, respectively. MFSPs for the four developing pathways range from \$3.40 to \$5.04 per GGE. Sensitivity studies show that MFSPs can be improved with co-product credits and are comparable to the FT benchmark (\$3.58/GGE). MFSP is a result of the interplay between product yields, operating cost, and capital investment. Major cost drivers in the integrated processes are tied to achievable

Table 12. Summary of sustainability metrics.

Sustainability Metrics	1A	1B	2A	2B	FT
GHG Emissions*, kg CO _{2e} /MJ (kg CO _{2e} /GGE)	-0.0032 (-0.39)	-0.0016 (-0.19)	0.0074 (0.91)	-0.01 (-0.72)	-0.0053 (-0.65)
Fossil Energy Consumption, MJ fossil energy/ MJ fuels (MJ/GGE)	-0.022 (-2.7)	-0.036 (-4.4)	0.1 (12)	-0.11 (-14)	-0.06 (-6.9)
Total Fuel Yield, GGE/dry ton feedstock	56.7	61.9	66.2	41.6	65.6
Biomass Carbon-to-Fuel Efficiency (C in fuel/C in biomass)	28.9%	31.5%	33.8%	21.3%	33.2%
Water Consumption, m ³ /day (gal/GGE)	1,151 (2.43)	3,342 (2.94)	1,090 (1.9)	3,419 (9.9)	4,250 (7.8)
Wastewater Generation, m ³ /day (gal/GGE)	71 (0.15)	118 (0.23)	617 (1.0)	114 (0.33)	594 (1.1)
Energy Return-on-Investment (EROI)**, MJ/MJ	0.42	0.45	0.46	0.31	0.30

*GHG emissions include all fossil emissions and exclude biogenic CO₂. Negative values are attributed to co-product credits.

**EROI is defined as the ratio of the total energy produced to the total energy input (both direct and indirect) to the biorefinery.

fuel yields and conversion efficiency of the intermediate steps, i.e., production of oxygenates/alcohols from syngas and the conversion of oxygenates/alcohols to liquid fuels. Additionally, co-product values can play an important role in the economics of the processes with oxygenated intermediates (ethanol) derived via syngas fermentation.

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**Eric C.D. Tan, PhD**

Dr Tan is a Senior Research Engineer in the Biorefinery Analysis Group of the National Bioenergy Center at the National Renewable Energy Laboratory (NREL). His current research interests include conceptual process design, economics, and sustainability for conversion of biomass to biofuels and chemicals with particular emphasis on the application of techno-economic analysis and life cycle assessment methods. His prior industry experience spans from Plug Power, Delphi, and Linde.

**Lesley Snowden-Swan**

Lesley Snowden-Swan is a Senior Research Engineer at PNNL working on techno-economic analysis and life cycle analysis of bioenergy systems. She has evaluated emerging technology pathways including hydrothermal liquefaction, fast pyrolysis and bio-oil upgrading, syngas to distillates, and biopower. She holds a Master's degree in Chemical Engineering from Johns Hopkins University.

**Michael Talmadge**

Michael Talmadge is a Senior Process Engineer in the National Bioenergy Center at the NREL. He has 15 years of experience in fuel production technologies including petroleum production and refining process development with ExxonMobil Research and Engineering Company and Valero Energy Corporation. Since joining NREL, he has supported the development of biomass-derived fuel technologies through process modeling and techno-economic analysis of biomass-to-fuels pathways. He has also contributed to the development of strategies to incorporate biomass-derived hydrocarbon intermediates and finished fuel blendstocks into existing petroleum refining infrastructure through the National Advanced Biofuels Consortium.

**Abhijit Dutta**

Abhijit Dutta is a researcher at the NREL. His current work is focused on biorefinery analysis of the thermochemical conversion of biomass. He was previously employed at Aspen Technology and Bloom Energy where he worked in the areas of process simulation and control.

**Susanne Jones**

Susanne Jones is a project manager and team lead for techno-economic analysis at PNNL. She has developed economics for numerous processes including power, hydrogen, Fischer-Tropsch fuels, gasoline and diesel, methanol, higher alcohols, synthetic natural gas, polyols and organic acids from biomass, coal, and natural gas. The scales have ranged from bench-scale systems to large commercial ventures for both private and government clients. Prior to joining PNNL, her industrial experience included chlor-alkali production, petroleum refining and waste acid recovery. She holds a Master's degree in Chemical Engineering from Washington State University.

**Karthikeyan K. Ramasamy**

Dr Ramasamy is involved in the research and process development of producing specialty chemical and infrastructure compatible fuel from the biomass through thermo-catalytic process at PNNL. His current focus is on converting small oxygenates to fuels and chemicals. Prior to joining PNNL he was a Research Engineer at Florida Solar Energy Center, Cocoa, FL. He was involved in process development, laboratory and demonstration scale unit fabrication and optimization for various processes. He holds a PhD in Chemical Engineering from Washington State University.

**Michel Gray**

Michel Gray has over 10 years' experience in biofuels research at PNNL where he works in the Chemical and Biological Process Development Group as a Senior Research Scientist. His research relates to the catalytic conversion of biomass to fuels and chemicals. He has worked on projects that involve synthesis gas conversion to alcohols, gasification, pyrolysis and hydrotreating of biomass, and the conversion of corn ethanol byproducts to chemicals. His strengths are in operations management, project/task management, reactor design and construction, reactor management, and analytics.

**Robert Dagle**

Robert Dagle manages two projects for the Department of Energy's Bioenergy Technologies Office in the area of thermochemical conversions. His research interests lie in the area of heterogeneous catalysis and chemical process development. Experience with multiple catalytic process applications includes steam reforming of hydrocarbons and bio-derived oxygenates, conversion of bio-derived light oxygenates to fuels and chemicals, syngas conversion technologies, and chemical synthesis. He also has development experience with integrating engineered catalysts within novel reactor architectures for process intensification purpose.

**Asanga B Padmaperuma, PhD**

Dr Padmaperuma is a Senior Research Scientist in the Energy & Efficiency Division at the PNNL. His research expertise includes organic multi-step synthesis and characterization, functional molecule design and development, organic electronic device fabrication and testing. His current work focusses on bio-oil characterization and economic analysis, electrochemical and catalytic upgrading of biomass based intermediates to biofuels.

**Asad Sahir, PhD**

Dr. Sahir is currently working on research projects related to conceptual process design, techno-economic analysis, fuel blending and refinery integration in the National Bioenergy Center at NREL. He holds a PhD in Chemical Engineering from the University of Utah, and has previously worked as a Senior Research Engineer at Bharat Petroleum Corporation Limited's Corporate Research and Development Centre.

**Ling Tao, PhD**

Ling has sixteen years' experience in detailed economic, strategic, and engineering analysis on a wide array of biofuels processes, expertise in conceptual process design, techno-economic analysis, separation technologies, process intensification, and R&D process research. Currently, she is a senior modeler and has lead or is still leading several techno-economic analysis projects at NREL. Ling received a BS in Chemical Engineering from Tsinghua University and a PhD from the Department of Chemical Engineering at the University of Massachusetts at Amherst.

**Yanan Zhang, PhD**

At NREL, Yanan undertook multiple projects on the thermochemical process modeling using Aspen Plus and conducted the corresponding techno-economic analyses. She is experienced in gasification and pyrolysis technologies for biofuels production. She holds a PhD in Mechanical Engineering from Iowa State University.

Mark Gerber

Mark Gerber is a retired Chemical Engineer who worked for 34 years at PNNL. Much of his career was spent developing biomass thermo-chemical conversion technologies. He developed and managed several research projects related to biomass gasification technology in the areas of alternative biomass feedstock gasification, catalytic hot-gas clean-up, and mixed alcohol synthesis from syngas using a rhodium-based catalyst.