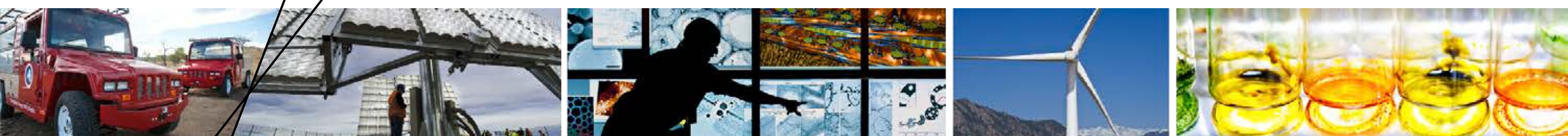
Indirect Liquefaction of Biomass to Transportation Fuels Via Mixed Oxygenated Intermediates



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Modeling and Analysis

Biofpr Biofuels Bioproducts & Biorefining

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

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http://www.eere.energy.gov/biomass

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
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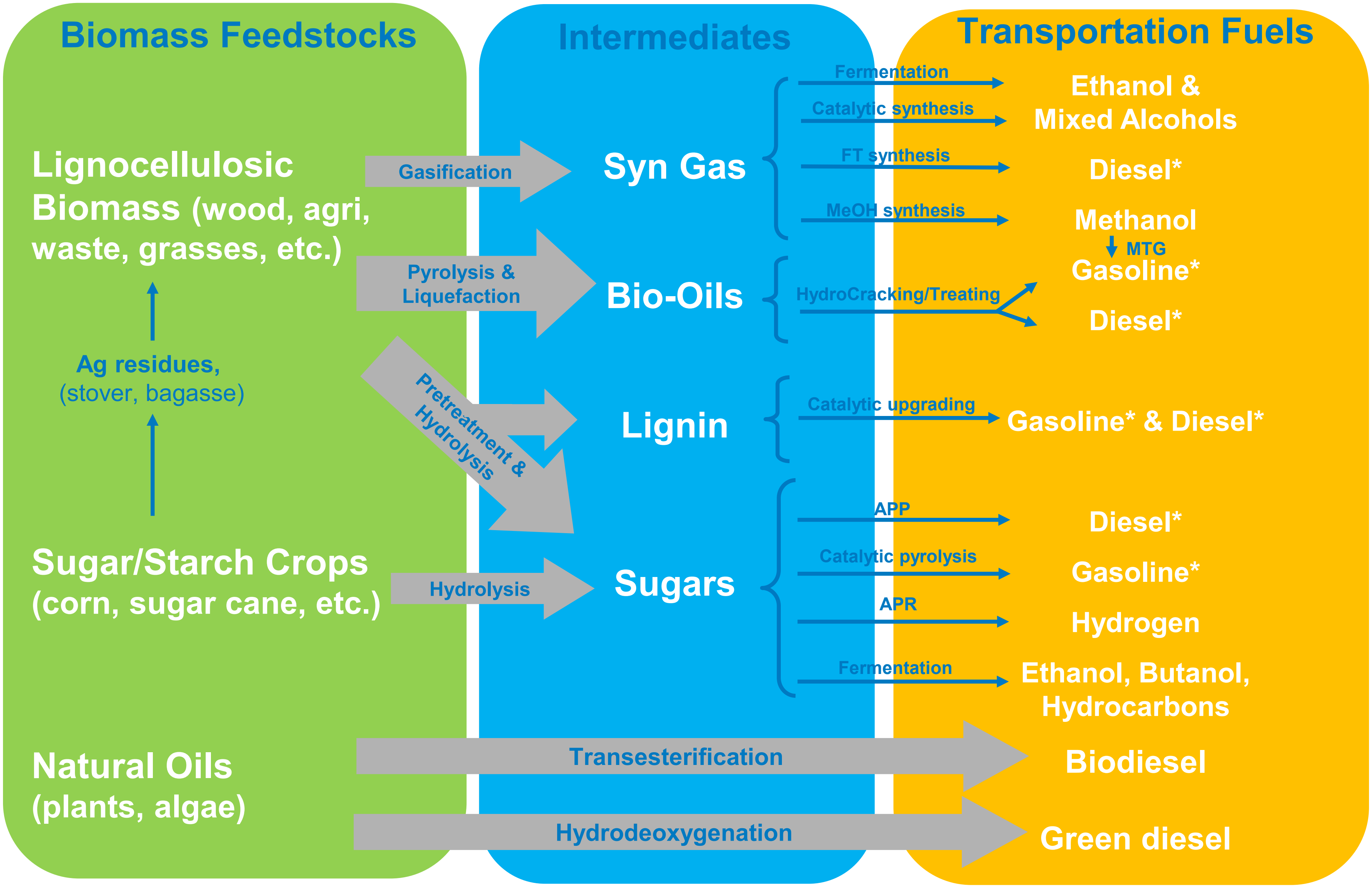
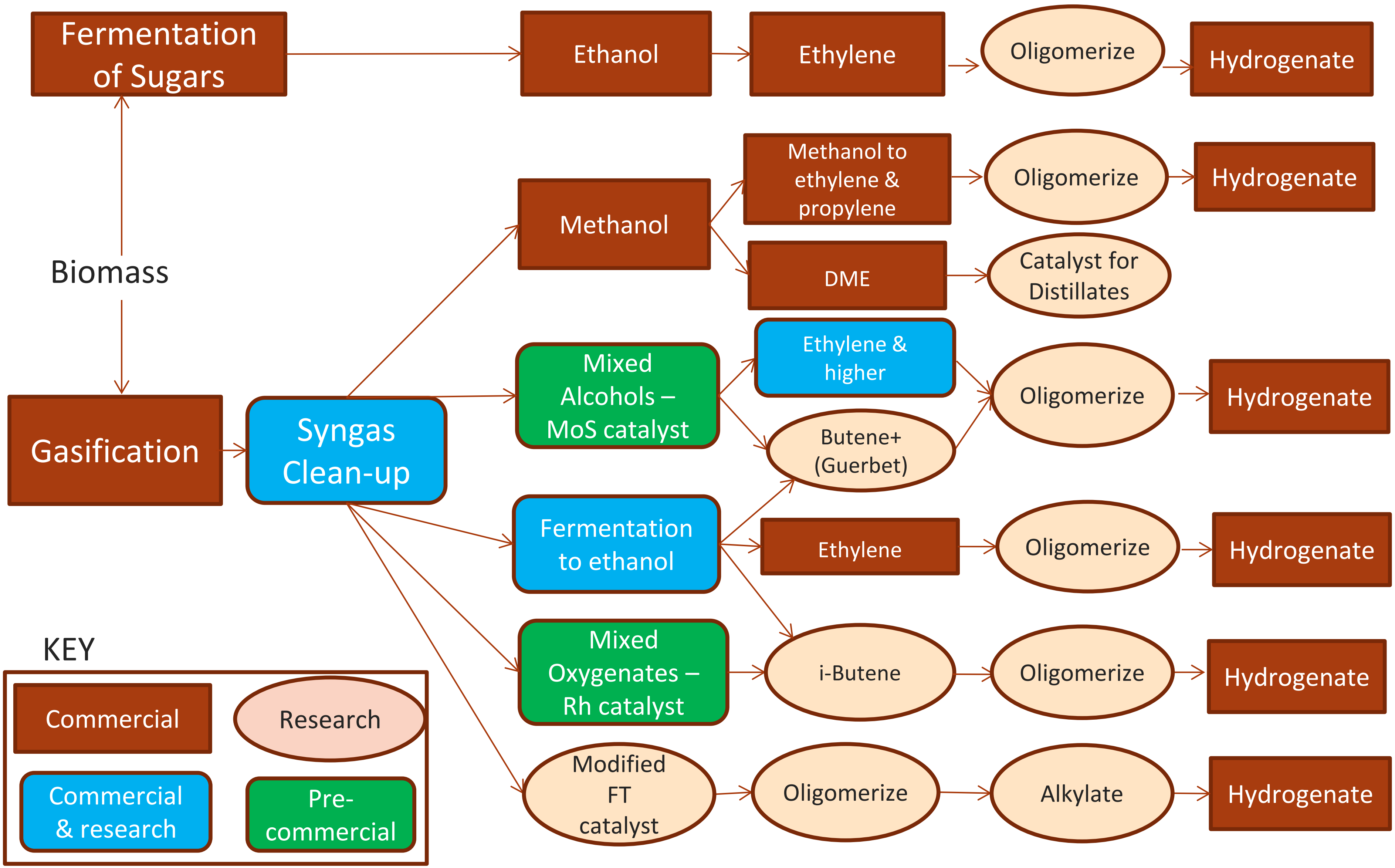
Background – Biofuels Transportation Options

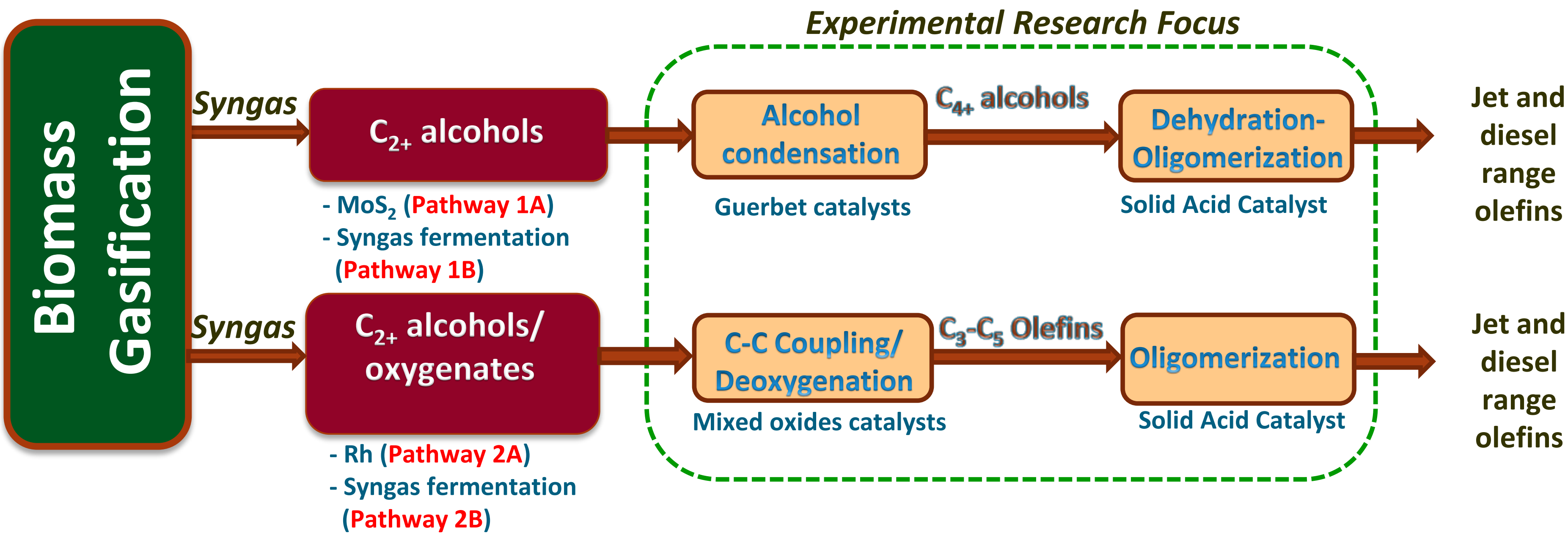


* Blending Products

IDL Opportunities for Distillates

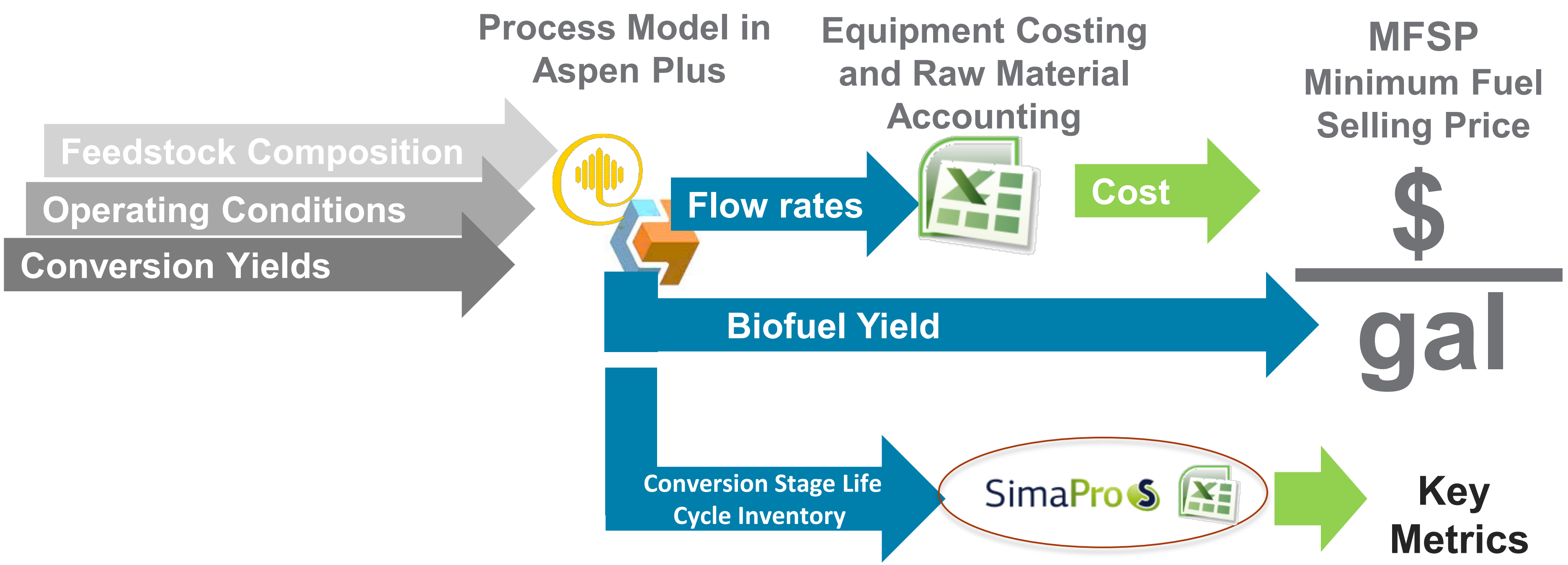


Syngas to Distillates Routes Evaluated



- This study leverages past research performed for BETO to produce oxygenated intermediates, mixed C2+ alcohols and mixed C2+ oxygenates and incorporates the latest developments from current research on the upgrading of oxygenates to hydrocarbon fuels.
- This study also leverages advances in syngas production and clean-up technologies developed for the thermochemical pathway from biomass to mixed alcohols, demonstrated in 2012.

Approach / Methodology



Sustainability Metrics Approach:

a) Partial LCA -- the boundary for the metrics is the biorefinery. The rationale for performing a partial LCA is that the overall focus of this study is the conversion stage. Therefore, to isolate this stage, all others are excluded for quantification of metrics.

b) Systematically quantify and assess key sustainability metrics which allow for conversion pathway evaluation and comparison.

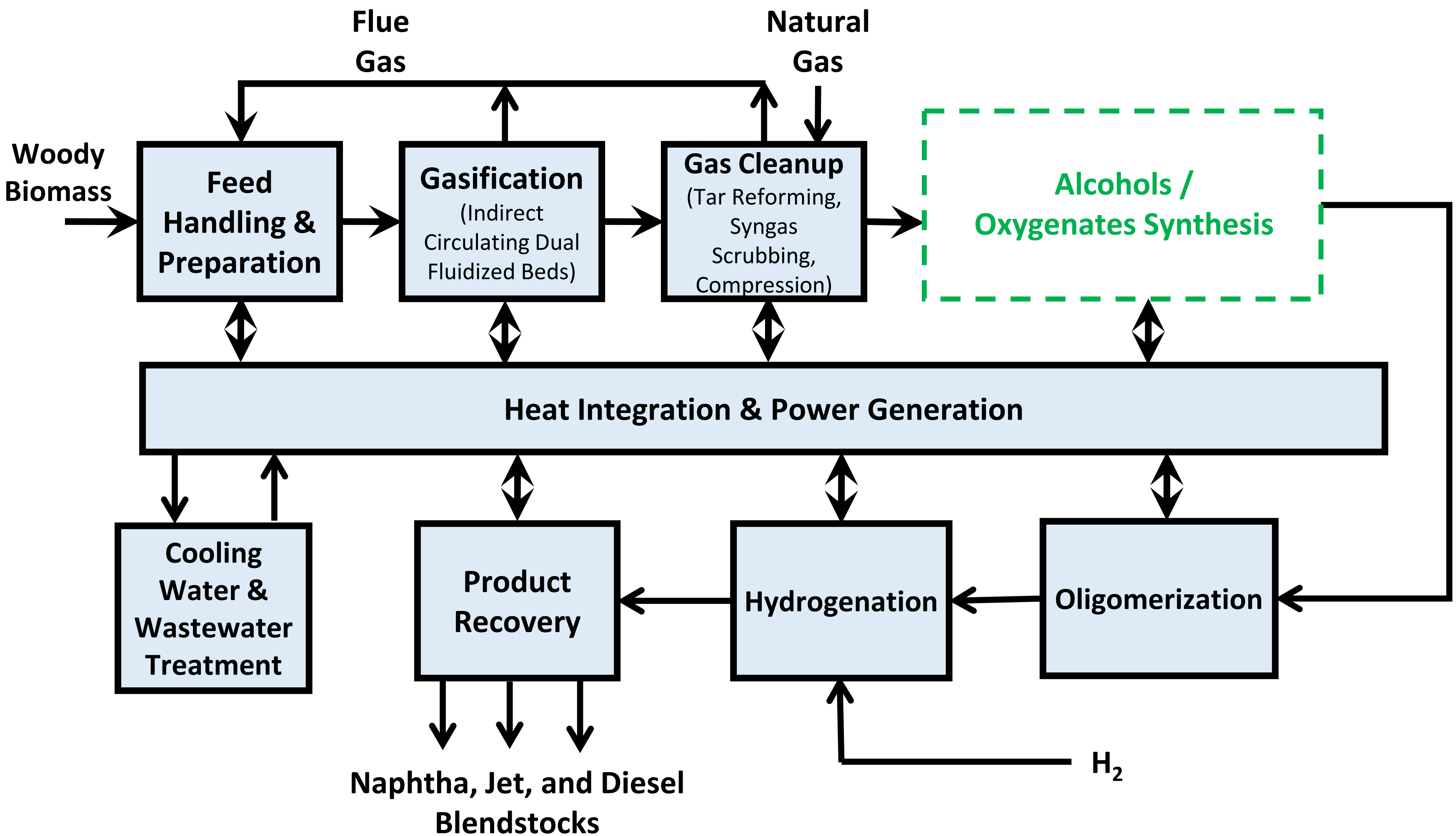
c) For certain pathways, full LCA is performed for sensitivity cases to understand effects on feedstock stages and limitations around RFS thresholds.

- **Fossil GHGs**
- **Fossil Energy Use**
- **Fuel Yield**
- **Carbon-to-Fuel Efficiency**
- **Water Consumption**

n^{th}-Plant TEA Assumptions

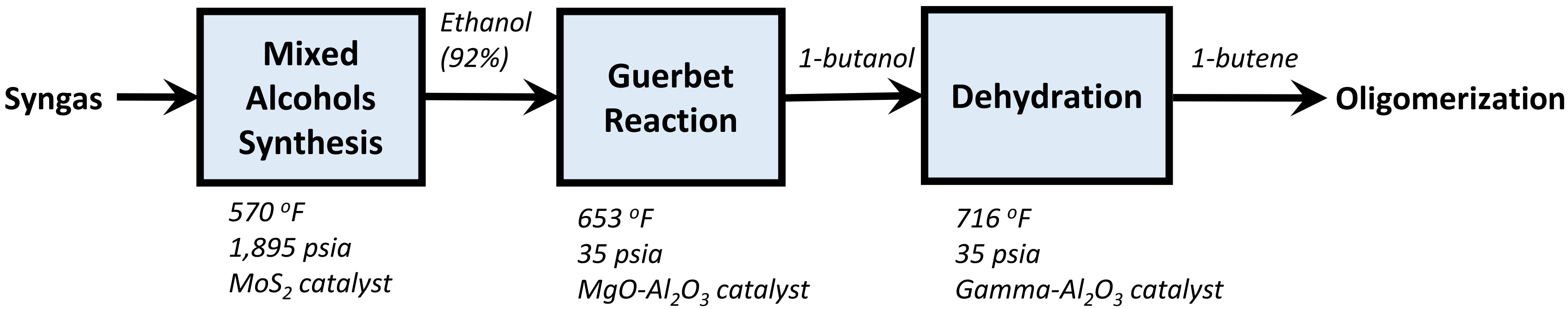
Description of Economic Parameter	Analysis Value / Basis
Delivered Feedstock Cost	$80.00 / US Dry Ton
Internal Rate of Return (IRR)	10.0 %
Plant Financing by Equity / Debt	40% / 60% of Total Capital Investment
Plant Life	30 Years
Income Tax Rate	35.0 %
Interest Rate for Debt Financing	8.0 % Annually
Term for Debt Financing	30 Years
Working Capital Cost	5.0% of Fixed Capital Investment
Depreciation Schedule	Total Plant: 7-Year MACRS
Construction Period (Spending Schedule)	3 Years (8% Y1, 60% Y2, 32% Y3)
Start-Up Time	6 Months
Revenue and Costs During Start-Up	Revenue = 50% of Normal Operation Variable Costs = 75% of Normal Operation Fixed Costs = 100% of Normal Operation
On-Stream Percentage After Start-Up	90% (7,884 Operating Hours per Year)

Main Process Steps

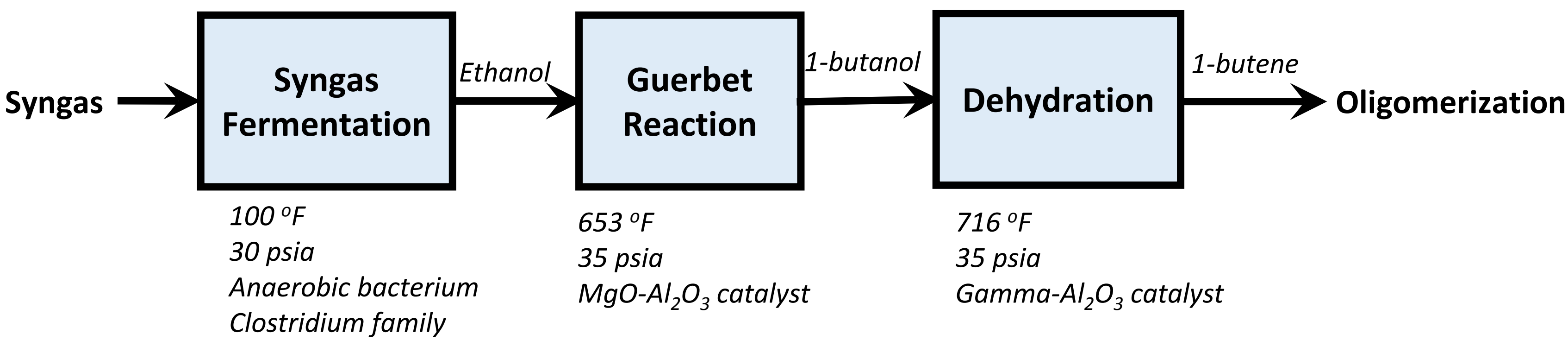


Alcohols / Oxygenates Synthesis

Pathway 1A



Pathway 1B



Pathway 1 – Design Parameters

Guerbet reactor

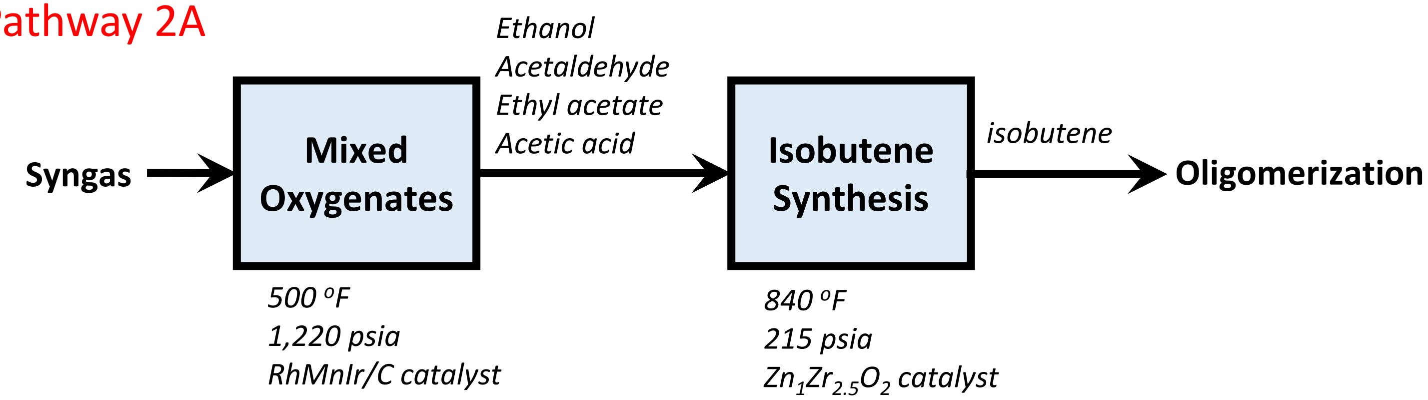
Design Parameters	
Reactor Temperature, °F (°C)	653 (345)
Reactor Pressure, psia (bar)	35 (2.41)
Catalyst	$MgO-Al_2O_3$
WHSV (hr^{-1})	1.0
Single-Pass Conversion	60% (ethanol)
Catalyst Life, yr	4
Oxygenates Selectivities (C), wt%	
Butanol	69.20
Pentanol	8.00
Hexanol	9.30
Heptanol	2.80
2-methyl-1-Butanol	4.20
2-ethyl-1-Butanol	4.20
Octanol	1.00
Others	1.30

Oligomerization reactor

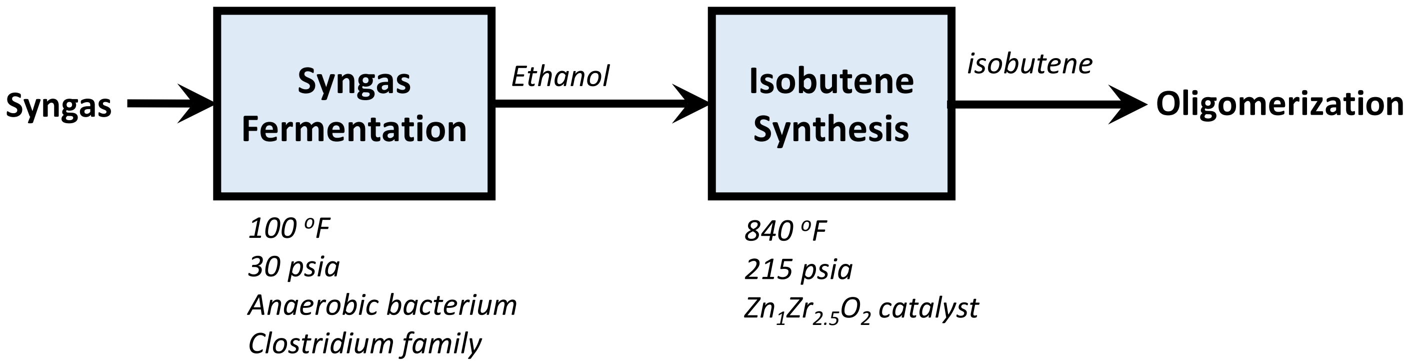
Design Parameters			
Reactor Temperature, °F (°C)			482 (250)
Reactor Pressure, psia (bar)			435 (30)
Catalyst			HZSM-23
WHSV (hr^{-1})			0.21
Single-Pass Conversion			95% (n-butene)
Catalyst Life, yr			3
Product Distribution	C Selectivity (%)	Isomer Selectivity (%)	
C8	26.20	2,3-Dimethyl-1-hexene	20.10
		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

Alcohols / Oxygenates Synthesis

Pathway 2A



Pathway 2B



Pathway 2 – Design Parameters

Mixed oxygenates reactor (Rh catalyst)

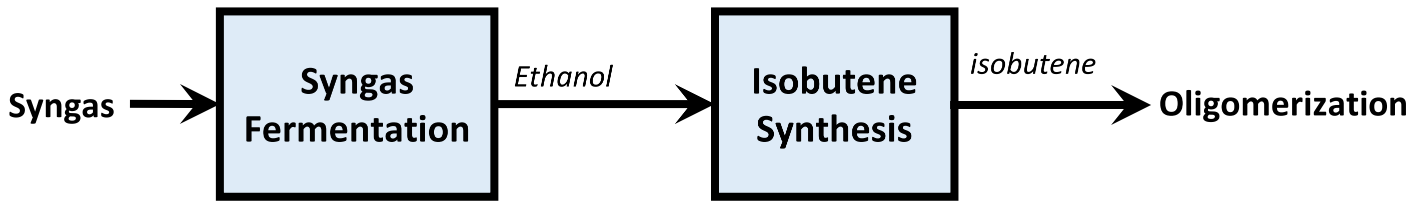
Design Parameters	
Operating Pressure, psia (bar)	1,220 (84.1)
H_2+CO Partial Pressure, psi (bar)	1,000 (68.9)
Operating Temperature, °F (°C)	500 (260)
Catalyst	RhMnIr/C
GHSV (hr^{-1})	3,247
H_2:CO Ratio	1.3
Single-Pass Conversion	35%
Catalyst Life, yr	4
Catalyst Rh Loading, wt%	5.6
C Selectivity to 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

Isobutene reactor

Design Parameter	
Operating pressure, psia (bar)	215 (14.8)
Operating temperature, °F (°C)	840 (449)
Catalyst	$Zn_1Zr_{2.5}O_2$
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

Alcohols / Oxygenates Synthesis

Pathway 2B



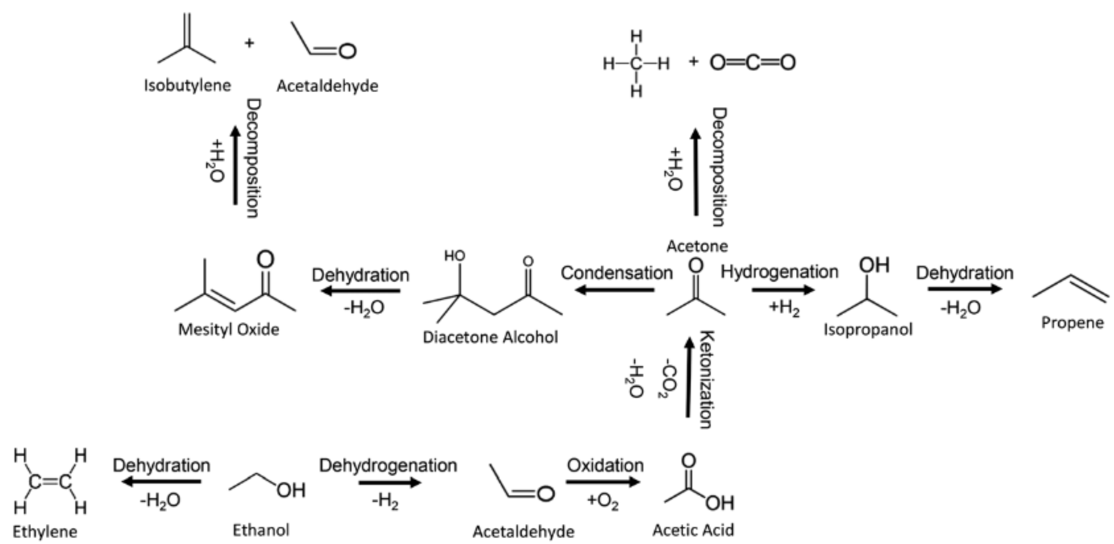
100 °F
30 psia
Anaerobic bacterium
Clostridium family

840 °F
215 psia
$Zn_1Zr_{2.5}O_2$ catalyst

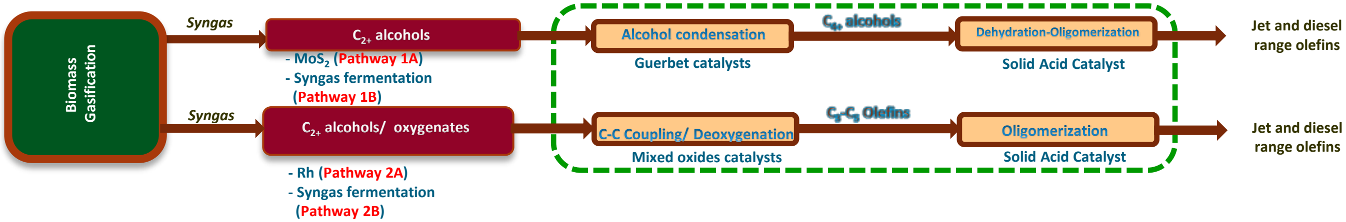
Ethanol to isobutene reaction network

Dagle et al, Green Chem., 2016,18, 1880-1891

$CH_3CH_2OH \rightarrow CH_3CHO + H_2$
$2CH_3CHO + H_2O \rightarrow CH_3COCH_3 + CO_2 + 2H_2$
$3CH_3COCH_3 \rightarrow 2i\text{-}C_4H_8 + CO_2 + H_2O$



Process Performance Summary

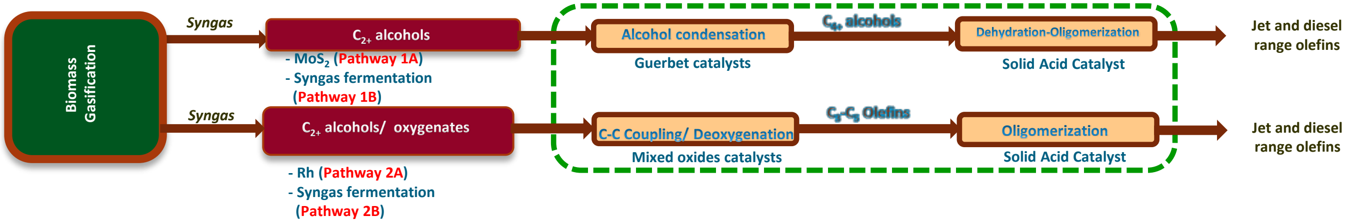


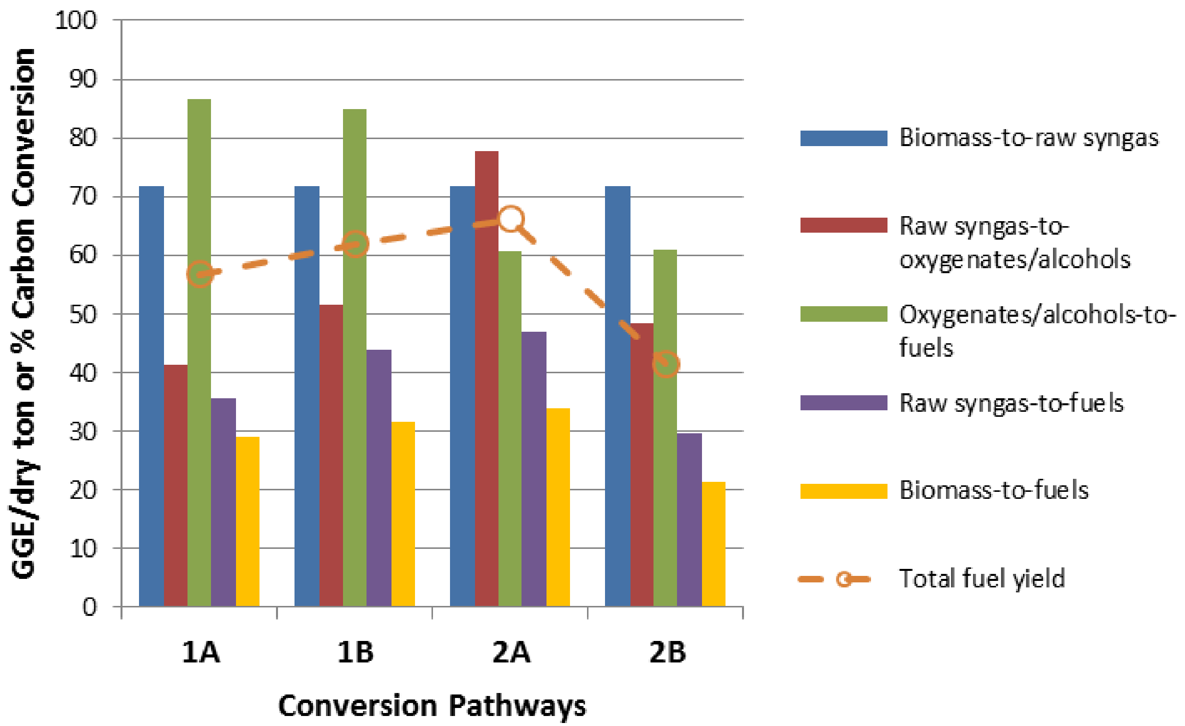
	Conversion Pathways			
Key Process Targets	**1A**	**1B**	**2A**	**2B**
Oxygenate Intermediate Product from Syngas (lb/hr)	Mixed alcohols[1]	Ethanol	Mixed oxygenates[2]	Ethanol
	59,833	66,283	101,250	65,121
Fuel Production (MMGGE/yr):				
Naphtha range	-	-	11.5	7.23
Jet range	19.5	21.7	31.6	19.84
Diesel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

[1] Methanol, ethanol, and propanol

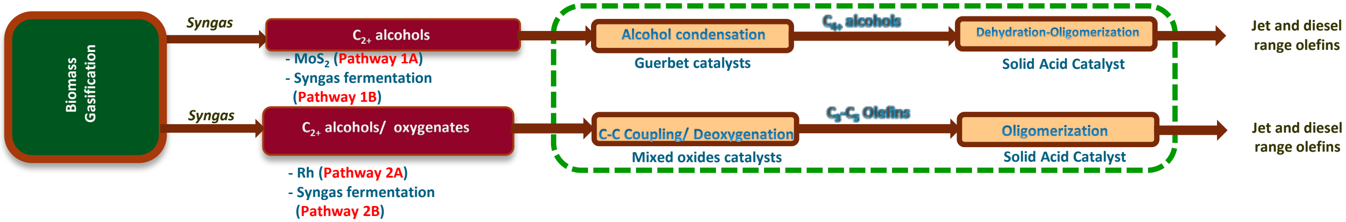
[2] Ethanol, ethyl acetate, acetic acid, and some higher oxygenates, some LPG type material, some methanol

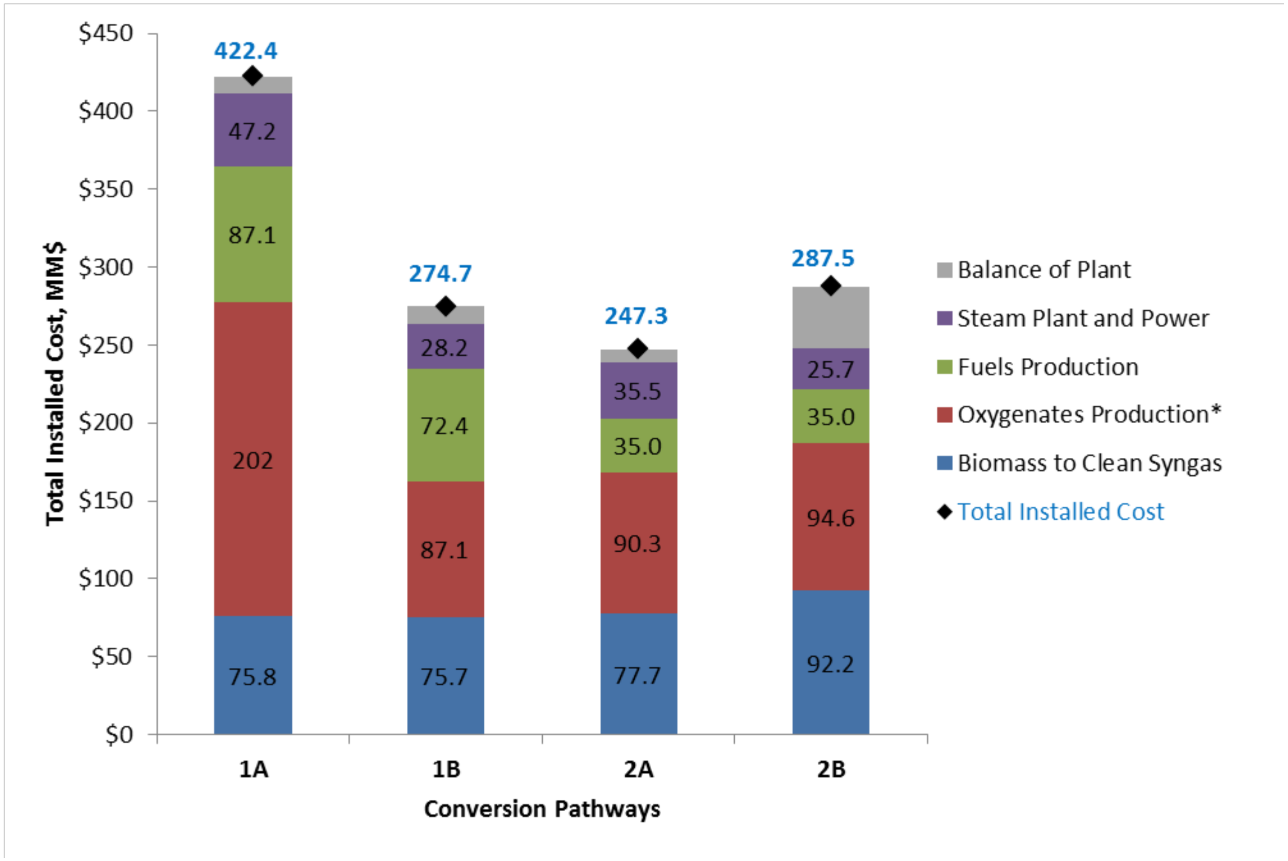
Correlation Between Carbon Conversion Efficiency and Fuel Yield



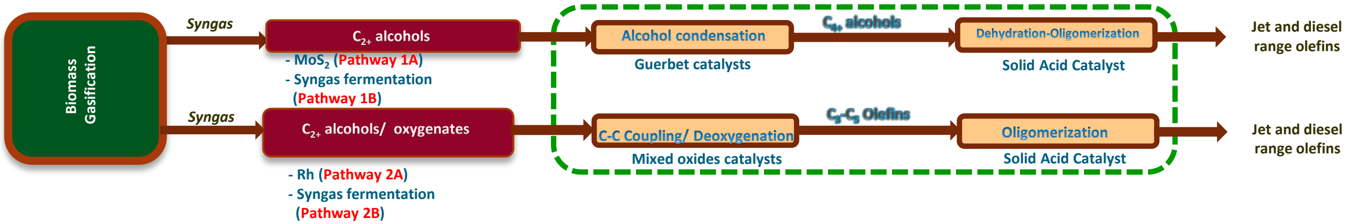


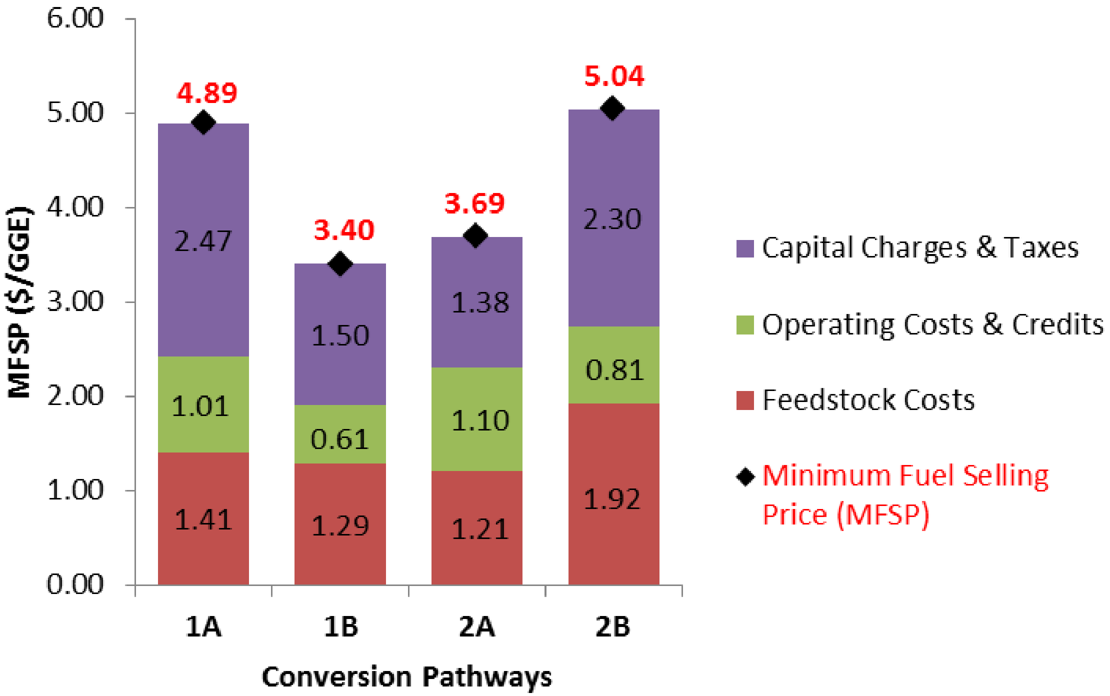
Total Installed Cost (2011$)





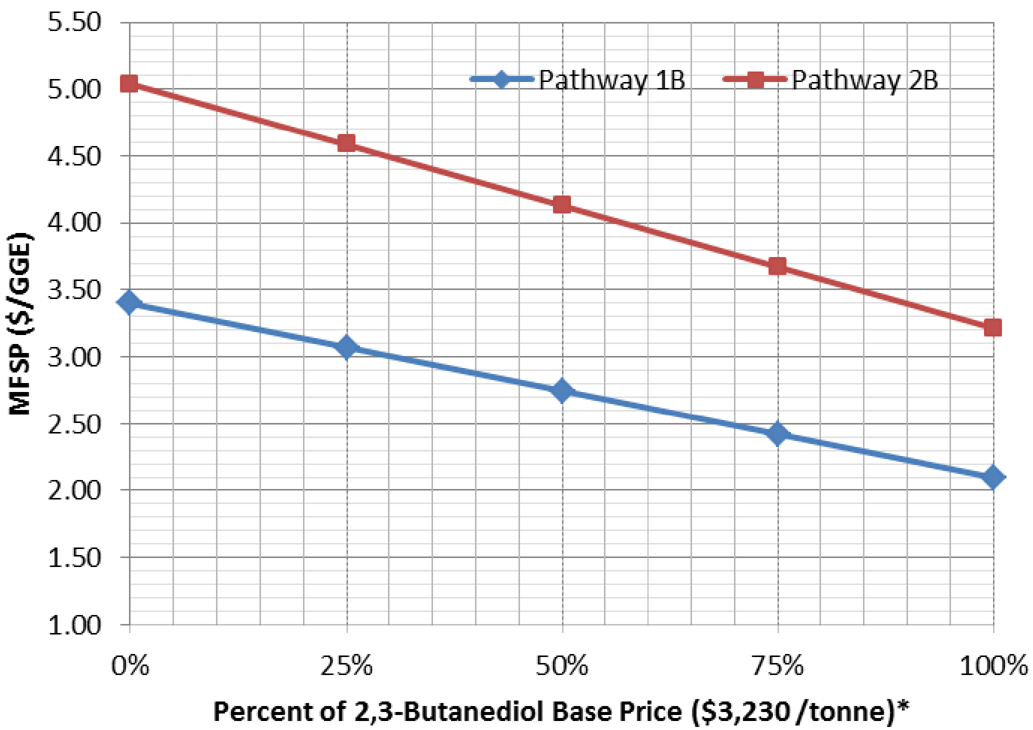
Minimum Fuel Selling Price (2011$)





As a reference, $3.58/GGE for commercial Fischer-Tropsch benchmark.

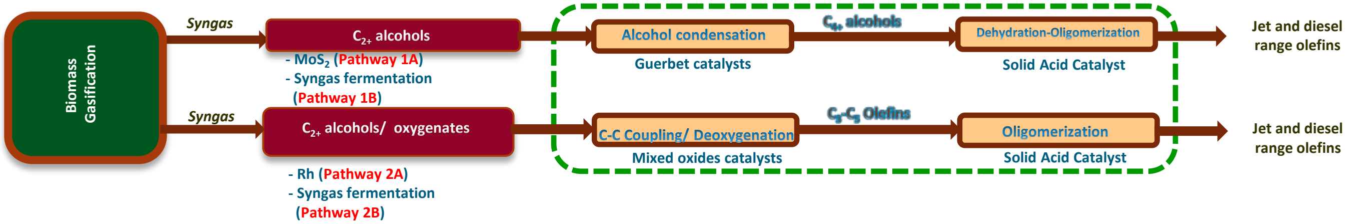
Minimum Fuel Selling Price As A Function of Co-product Credits

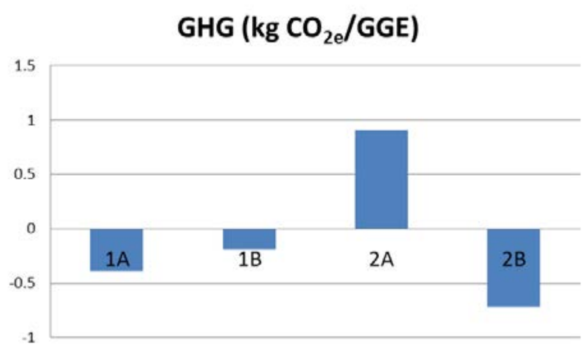


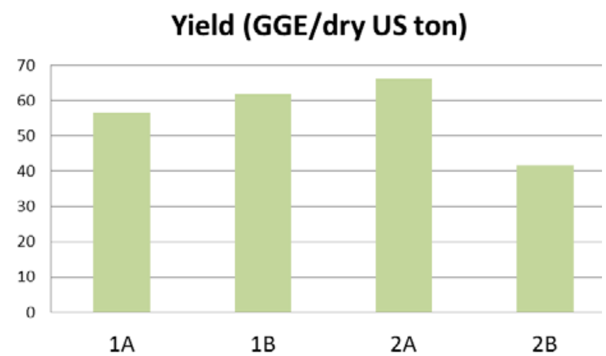
*It is assumed that 2,3-BDO has the same market value as 1,4-BOD at $3,230/tonne ($2,930/US ton) in 2011 US dollars .

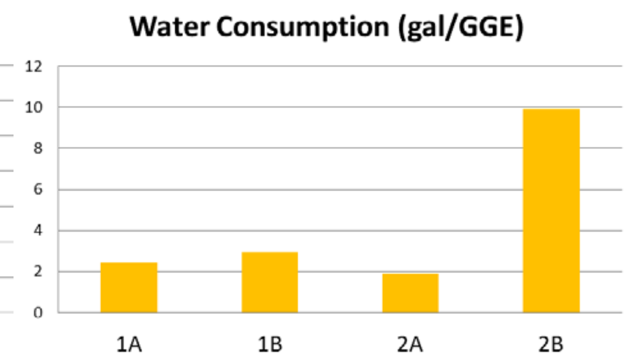
MFSPs at 0% represents the base cases without the co-production of 2,3-BDO during the syngas fermentation.

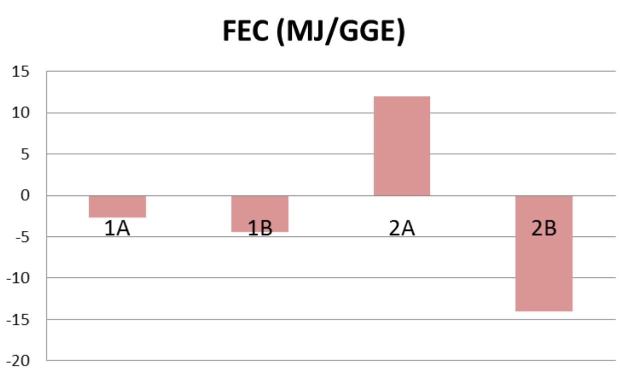
Environmental Sustainability Metrics

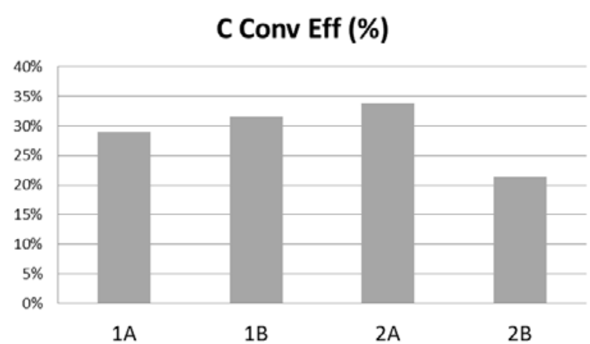


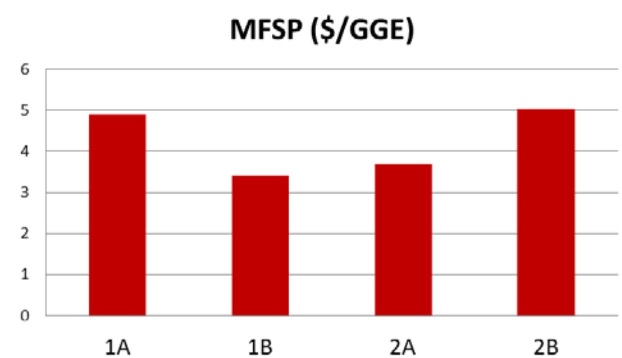












Summary

- This paper presents a comparative techno-economic analysis of four emerging conversion pathways from biomass to gasoline-, jet-, and diesel-range hydrocarbons via indirect liquefaction with specific focus on pathways utilizing oxygenated intermediates.
- The processing steps include: biomass-to-syngas via indirect gasification, gas cleanup, 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: 1) mixed alcohols over a MoS_2 catalyst, 2) mixed oxygenates (a mixture of C2+ oxygenated compounds, predominantly ethanol, acetic acid, acetaldehyde, ethyl acetate) using an Rh-based catalyst, and 3) ethanol from syngas fermentation.
- This is followed by the conversion of oxygenates/alcohols to fuel-range olefins in two approaches: 1) mixed alcohols/ethanol to 1-butanol rich mixture via Guerbet reaction, followed by alcohol dehydration, oligomerization, and hydrogenation, and 2) mixed oxygenates/ethanol to isobutene rich mixture and followed by oligomerization and hydrogenation.
- MFSPs for the four developing pathways range from \$3.40/GGE to \$5.04/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.

Backup Slides

Breakdown of operating cost contribution (2011 $)

	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**
Capital depreciation	23.4	0.57	15.2	0.34	13.4	0.28	15.8	0.53	18.3	0.38
Average income tax	11.1	0.27	7.30	0.16	10.1	0.21	16.4	0.54	19.1	0.40
Average return on investment	67.0	1.63	44.63	1.00	42.72	0.89	37.17	1.24	46.5	0.98
Total	**201.0**	**4.89**	**152.2**	**3.40**	**177.0**	**3.69**	**151.8**	**5.04**	**170.0**	**3.58**

Variable operating costs (2011 $)

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 U.S. 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_2O_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_2O_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 (Gamma alumina)	Initial fill then replaced every 3 years based on expected catalyst lifetime. 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

Variable operating costs (2011 $)

Variable	Information and operating cost
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_2O_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_2O_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_1Zr_{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 makeup	Price: $0.35/tonne
Chemicals	Boiler feed water chemicals–Price: $6.13/kg Cooling tower chemicals-Price: $3.67/kg LO-CAT chemicals-Price: $498.98/tonne sulfur produced from NREL/Harris Group Inc. estimates based on other projects. DEPG makeup-Price: $81.59/million lb acid gas removed Selective amine makeup-Price: $39.81/million kg acid gas removed.
Wastewater	Most wastewater is cleaned using an RO system and recycled. The balance of the wastewater is sent to off-site treatment facility. Price: $0.83/tonne