Biomass and Natural Gas to Liquid Transportation Fuels (BGTL): Process Synthesis, Global Optimization, and Topology Analysis

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Natural Gas and Biomass

Natural Gas

- Abundant supply in the United States
- Low prices
- Utiliz
  gas r
  envir
  dama

- High f

Biomass

- Prices more stable than natural gas
- Reduce greenhouse
  ons in the
  nalysis

stainability of
over long
horizon

A hybrid biomass and natural gas energy system can bring synergistic outcomes

BGTL Important Questions

Q1: Can we produce liquid transportation fuels (gasoline, diesel, kerosene) using only biomass and natural gas?

Q2: Can we address Q1 with a 50% reduction in lifecycle greenhouse gas emissions?

Q3: Can we address Q1 and Q2 without disturbing the food chain?

Q4: Can Q1, Q2, and Q3 be addressed at competitive prices compared to petroleum?

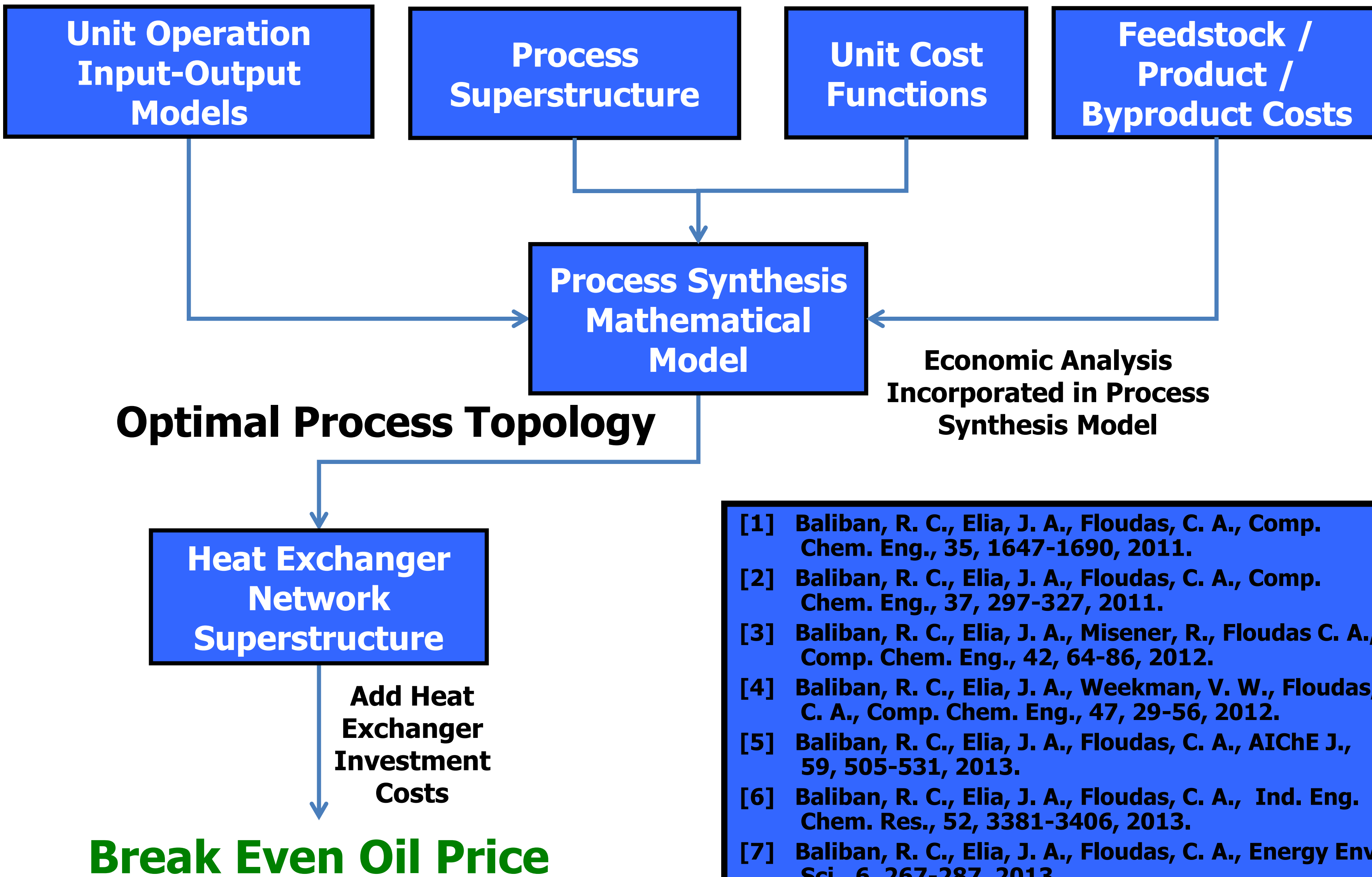
Q5: Can we develop a framework for a single BGTL plant that considers (i) multiple natural gas conversion pathways, (ii) any plant capacity, and (iii) any product combination?

Conceptual Design

- Feed biomass and natural gas to produce gasoline, diesel, and kerosene via a synthesis gas (syngas) intermediate
- Syngas is converted to liquid hydrocarbons via Fischer-Tropsch, MTG, or MTOD
- CO_2 can either be vented, sequestered, or consumed/recycled via the water-gas-shift reaction
- Simultaneous heat, power, and water integration included during synthesis
- Develop input-output mathematical models for each unit in the refinery

Baliban, R. C., Elia, J. A., Floudas, C. A., Biomass and Natural Gas to Liquid Transportation Fuels: Process Synthesis, Global optimization, and Topological Analysis, *Ind. Eng. Chem. Res.*, 52, 3381-3406, 2013.

Process Synthesis Strategy



[1] Baliban, R. C., Elia, J. A., Floudas, C. A., Comp. Chem. Eng., 35, 1647-1690, 2011.

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[4] Baliban, R. C., Elia, J. A., Weekman, V. W., Floudas, C. A., Comp. Chem. Eng., 47, 29-56, 2012.

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[6] Baliban, R. C., Elia, J. A., Floudas, C. A., Ind. Eng. Chem. Res., 52, 3381-3406, 2013.

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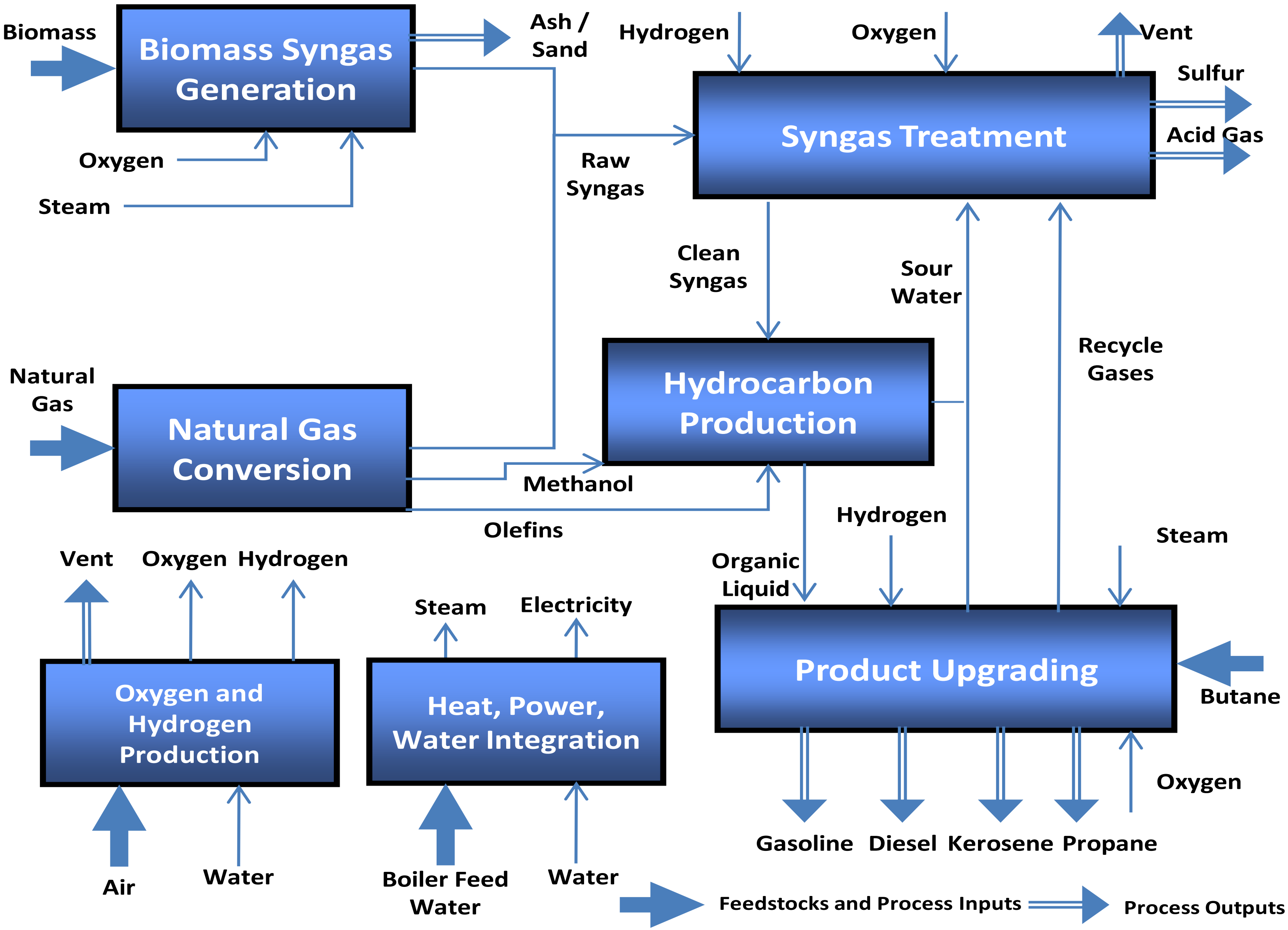
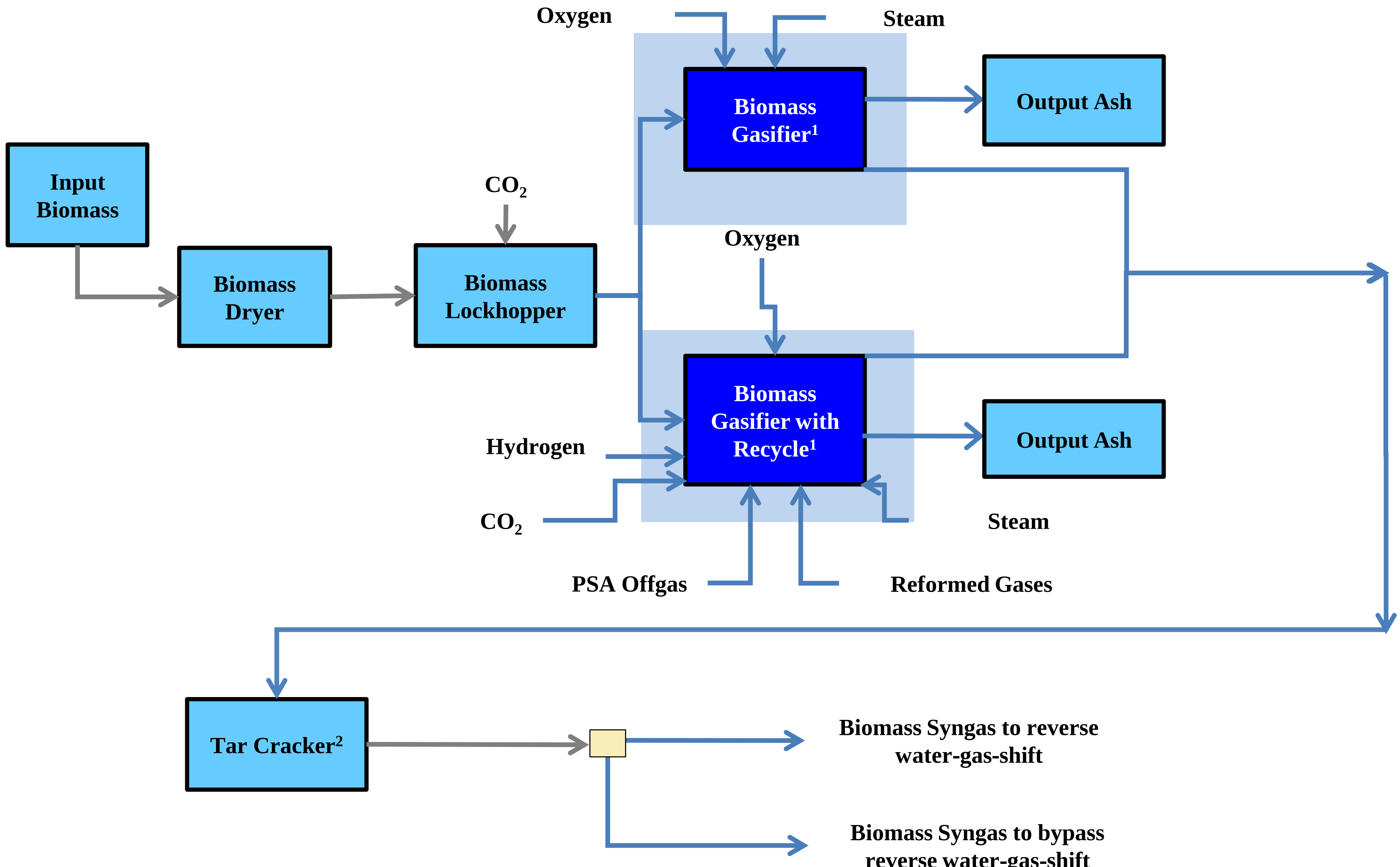
BGTL Process: Biomass and Natural Gas to Liquids



Biomass Syngas Generation



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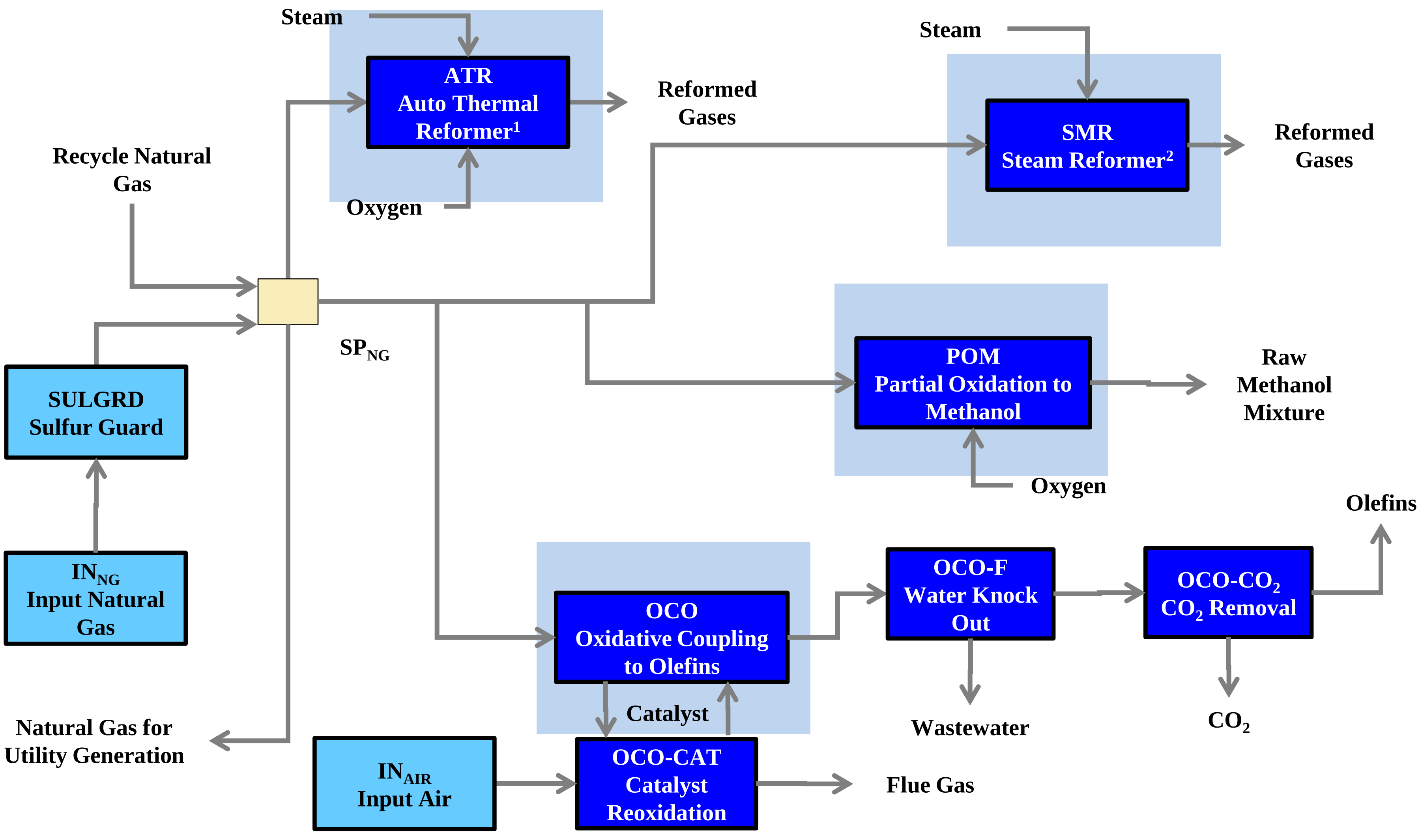
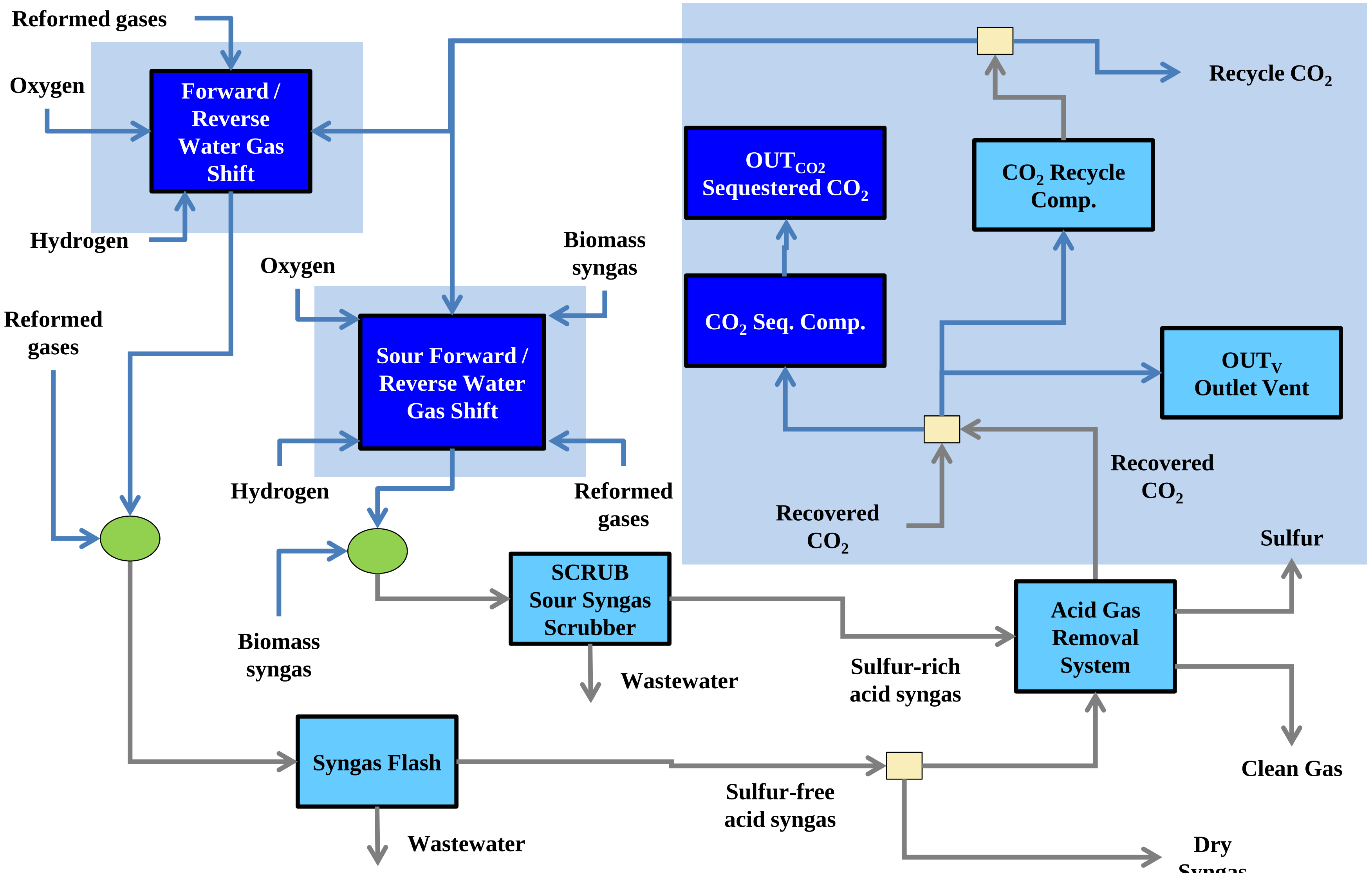
Natural Gas Conversion



Syngas Cleaning and CO_2 Recovery



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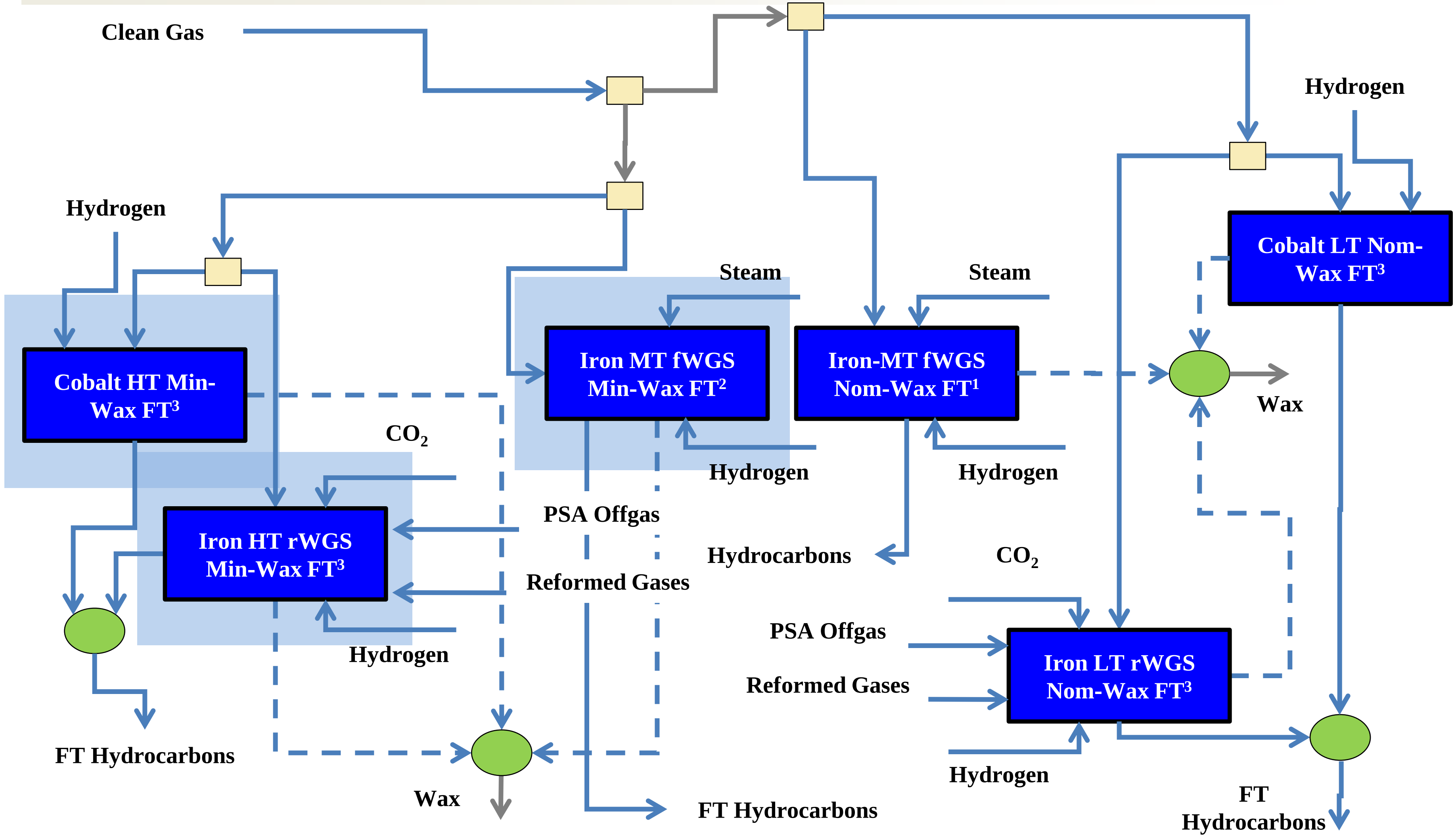
Hydrocarbon Production

- **Purpose of process units**
  - **Convert synthesis gas to raw hydrocarbon product**
  - **Remove aqueous phase and oxygenated species from raw hydrocarbon effluent**
- **Key topological decisions**
  - **Hydrocarbons generated via methanol conversion or Fischer-Tropsch synthesis**
  - **Methanol to Gasoline (MTG) or Methanol to Olefins and Diesel (MTOD)**
  - **Fischer-Tropsch catalyst: Cobalt/Iron**
  - **Low-wax/high-wax Fischer-Tropsch**

Fischer-Tropsch Units

- Catalyst type
  - Cobalt (no water-gas-shift reaction)
  - Iron (water-gas-shift reaction)
    - Forward water-gas-shift (fWGS)
    - Reverse water-gas-shift (rWGS)
- Temperature
  - High-temperature (HT - 320 ºC)
  - Mid-temperature (MT - 267 ºC)
  - Low-temperature (LT - 240 ºC)
- Wax production
  - Minimal (Min-Wax: for maximum gasoline)
  - Nominal (Nom-Wax: to increase diesel)

Fischer-Tropsch Production



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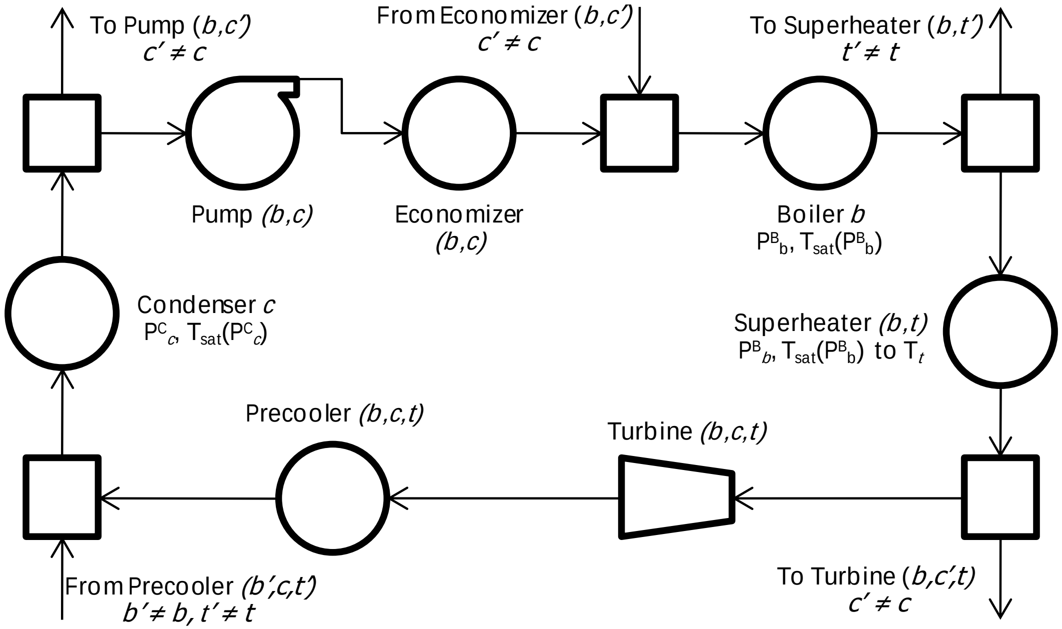
Hydrocarbon Upgrading

- Purpose of process units
  - Convert raw hydrocarbon product to final liquid fuels
  - Recover light gases for treatment
- Key topological decisions
  - Upgrading of Fischer-Tropsch product
    - ZSM5 upgrading
    - Standard upgrading
  - Recycle of light gases
    - Gas turbine
    - Fuel combustor
    - Natural gas conversion

Simultaneous Heat/Power Recovery

- Incorporate **heat engines** with distinct operating conditions into the system to **simultaneously minimize the hot/cold utilities and the recovered electricity**
- Lower amounts of utilities and recovered electricity **reduce the overall cost of the process → increased profitability**



Operating Conditions

- **Condenser Pressures** (c): 1, 5, 15, 40 bar
- **Boiler Pressures** (b): 25, 50, 75, 100, 125 bar
- **Turbine Inlet Temp.** (t): 500, 600, 700, 800, 900° C

[1] Duran, M. A. and I. E. Grossmann, Simultaneous optimization and heat integration of chemical processes, AIChE J., 32, 123, 1986.
[2] Floudas, C. A., A. R. Ciric, and I. E. Grossmann, Automatic synthesis of optimum heat exchanger network configurations, AIChE J., 32, 2, 276, 1986.
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Objective Function

- **Summation representing overall cost of liquid fuels production**
  - **Feedstock costs (*$Cost^F$*)**
  - **Electricity cost (*$Cost^{El}$*)**
  - **CO_2 sequestration cost (*$Cost^{Seq}$*)**
  - **Makeup freshwater cost (*$Cost^{CW}$*)**
  - **Levelized unit investment cost (*$Cost^U$*)**

$$\text{MIN} \sum_{u \in U_{In}} \sum_{(u,s) \in S^U} Cost_s^F + Cost^{El} + Cost^{Seq} + Cost^{CW} + \sum_{u \in U_{Inv}} Cost_u^U$$

- **Overall model size: 16,739 continuous variables, 33 binary variables, 16,492 constraints, and 345 nonconvex terms (nonconvex MINLP)**

Case Studies

- **Three case studies** illustrate optimal topologies for 10,000 barrel/day BTL refinery
  - GDK: Gasoline, diesel, kerosene in US ratios
  - MD: Maximum production (≥75%) of diesel
  - MK: Maximum production (≥75%) of kerosene
- **Four case studies** illustrate effect of capacity for GDK refinery
  - Extra-small capacity (1,000 barrels/day)
  - Small capacity (5,000 barrels/day)
  - Medium capacity (10,000 barrels/day)
  - Large capacity (50,000 barrels/day)
- **50% lifecycle GHG emissions** compared to petroleum-based processes
- **Biomass type**: Forest residues (45 wt% moist.)

Process Results: Topological Analysis

- **Operating temperatures for biomass gasification (BGS), auto-thermal reforming (ATR), and water gas shift (WGS) are selected by the optimization model**
- **Production of liquid fuels via Fischer-Tropsch or methanol conversion**

Operating temperature (°C) selected by MINLP model

Cobalt LTFT unit is used for US ratio and maximum kerosene

***Capacity* 10,000 BPD**

Case Study	Operating Temperatures			FT Unit		FT	Methanol		Gas	CO_2
	BGS	ATR	WGS	Low Wax	Nom. Wax	Upgrading	MTG	MTOD	Turbine	Seq.
US Ratios	900	1000	-	-	Co LTFT	ZSM-5	Y	-	-	-
Max Diesel	900	1000	-	-	-	-	-	Y	-	-
Max Kerosene	900	1000	-	-	Co LTFT	Fract.	-	-	-	-

Methanol synthesis is used for US ratios and maximum diesel

A gas turbine and CO_2 sequestration are not utilized

Process Results: Topological Analysis

- **Topological differences** are highlighted for different capacities
- **Natural gas conversion pathway** is always through auto-thermal reforming

Consistent gasifier temperature as capacity increases

Cobalt LTFT unit is used as refinery capacity increases

Output Fuels
United States demand ratios

Capacity	Operating Temperatures			FT Unit		FT Upgrading	Methanol		Gas Turbine	CO_2 Seq.
	BGS	ATR	WGS	Low Wax	Nom. Wax		MTG	MTOD		
1 kBD	900	1000	-	-	-	-	Y	Y	-	-
5 kBD	900	1000	-	-	Co LTFT	ZSM-5	Y	-	-	-
10 kBD	900	1000	-	-	Co LTFT	ZSM-5	Y	-	-	-
50 kBD	900	1000	-	-	Co LTFT	ZSM-5	Y	-	-	-

MTG is used for all capacity levels

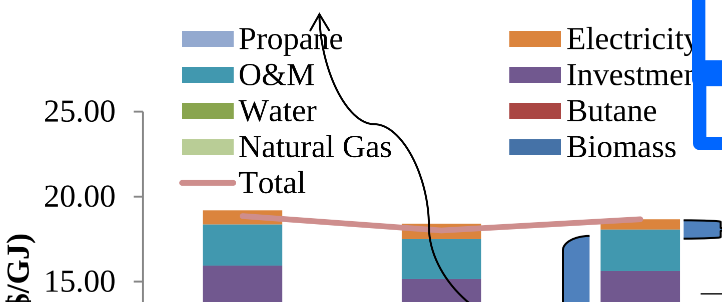
A gas turbine and CO_2 sequestration are not utilized

Overall Fuels Cost

Capacity
10,000 barrels/day

Investment has the highest cost contribution

Contribution to Cost ($/GJ of products)	US Ratios	Case Study: Max Diesel	Case Study: Max Keroesne
Biomass	2.58	2.47	2.34
Natural Gas	3.76	3.82	3.77
Butane	0.58	-0.36	0.00
Water	0.02	0.02	0.02
CO_2 Seq.	0.00	0.00	0.00
Investment	7.81	7.48	7.81
O&M	2.06	1.98	2.06
Electricity	0.60	0.84	0.57
Propane	-0.34	-0.03	0.00
Total ($/GJ)	17.08	16.22	16.57
BEOP ($/bbl)	84.57	79.65	81.67



Break even oil prices between $80/bbl-$85/bbl

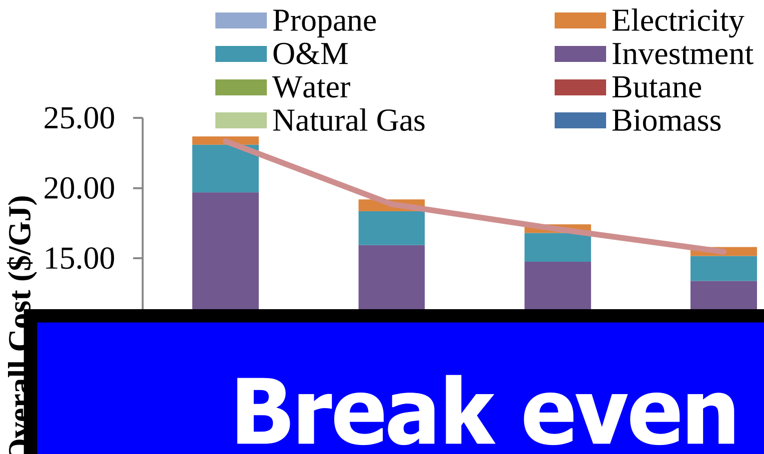
Overall Fuels Cost

Output Fuels

United States demand ratios

Similarity in overall cost of biomass and natural gas

Investment provides largest difference in cost



Contribution to Cost	Capacity			
($/GJ of products)	1 kBD	5 kBD	10 kBD	50 kBD
Biomass	2.61	2.51	2.58	2.34
Natural Gas	3.77	3.70	3.76	3.71
Butane	0.53	0.55	0.58	0.56
Water	0.02	0.02	0.02	0.03
CO_2 Seq.	0.00	0.00	0.00	0.00
Investment	12.78	9.15	7.81	6.75
O&M	3.38	2.42	2.06	1.78
Electricity	0.59	0.84	0.60	0.63
Propane	-0.34	-0.34	-0.34	-0.34
Total ($/GJ)	23.34	18.86	17.08	15.47
BEOP ($/bbl)	120.26	94.69	84.57	75.36

Break even oil prices between $75/bbl-$120/bbl

Life-Cycle Analysis

- **Significant reduction** from fossil-fueled processes
  - GHG emissions avoided from fuels (GHGAF)
  - GHG emissions avoided from electricity (GHGAE)
  - GHG emission index: GHGI = LGHG/(GHGAF + GHGAE)
- No CO_2 Sequestration necessary

Bulk of emissions is from liquid fuels use and process venting

Biomass is critical for emissions reduction

Case Study	Biomass	Natural Gas	Butane	Gasoline	Diesel	Kerosene	LPG	Vented CO2	LGHG	GHGAF	GHGAE	GHGI
US Ratios	-42.19	4.74	0.00	28.52	10.43	5.12	0.40	22.56	29.58	61.22	-2.05	0.50
Max Diesel	-40.48	4.82	0.00	10.61	36.32	-	0.04	19.02	30.32	63.53	-2.89	0.50
Max Kerosene	-38.29	4.75	0.00	10.61	-	34.09	-	18.92	30.09	62.15	-1.98	0.50

Net lifecycle GHG emissions (LGHG) is 50% of fossil based processes

Capacity
10,000 barrels/day

Conclusions

- Developed an optimization framework for thermochemical-based conversion of biomass (perennial crops, agricultural residues, forest residues) and natural gas to liquid fuels
- The process synthesis case studies suggest that liquid fuels can be produced at crude oil prices between \$80-\$85/bbl for a 10 kBD refinery
- A 50% reduction in lifecycle GHG emissions from fossil-fueled processes is achieved in all case studies without CO_2 sequestration
- Results suggest that cost-competitive fuels can be produced using domestic biomass and natural gas with a significant reduction in the lifecycle GHG emissions

Barriers to Consider

- Development of front end engineering design, procurement, and construction of a demonstration or small size plant
- Investment costs for capital expenditure needed
- Continuous supply of sustainable biomass feedstock
- Uncertainty and fluctuations in natural gas prices

Relevant Publications

[1] Baliban, R. C., Elia, J. A., Floudas, C. A., 2010, Toward Novel Biomass, Coal and Natural Gas Processes for Satisfying Current Transportation Fuel Demands, 1: Process Alternatives, Gasification Modeling, Process Simulation, and Economic Analysis, *Ind. Eng. Chem. Res.,* 49, 7343-7370.

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Relevant Publications

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Relevant Publications

[13] Baliban, R. C., Elia, J. A., Floudas, C. A., Gurau, B., Weingarten, M., Klotz, S., 2013, Hardwood biomass to gasoline, diesel, and jet fuel: I. Process synthesis and global optimization of a thermochemical refinery. *Energy & Fuels*, In press (doi:10.1021/ef302003f).

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