Biomass Gasification for the Production of Fuels

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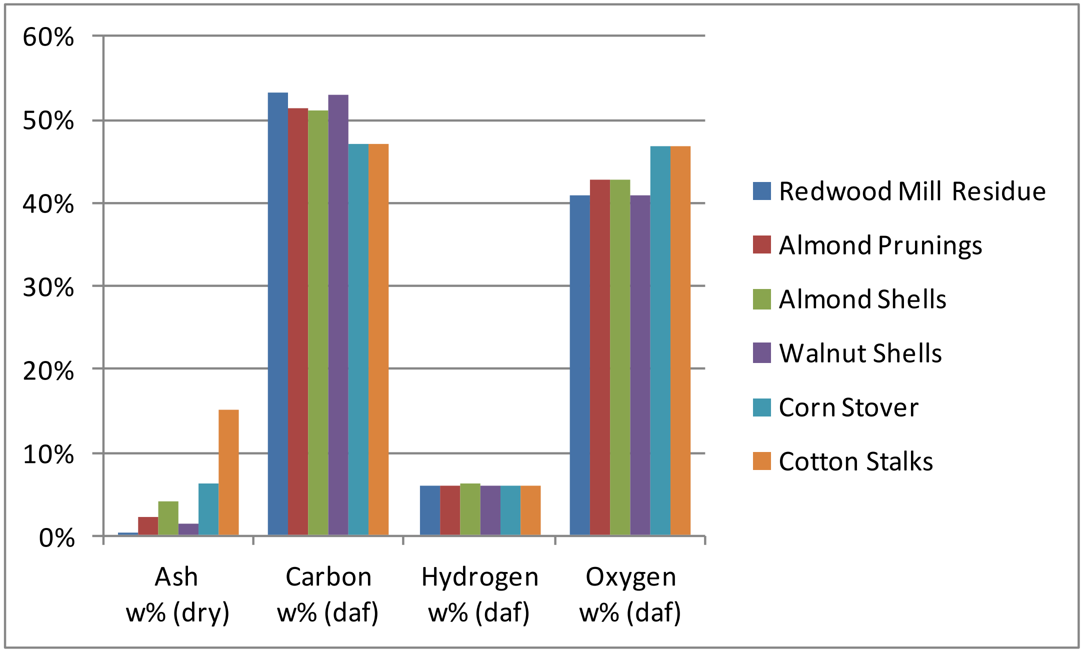
Main Difference between Biomass and Fossil Feedstocks (Crude Oil, Natural Gas, Coal)

- Biomass contains oxygen (~40 w%).
- Biomass contains a different set of minerals (ash).
- Biomass does not occur in highly concentrated reserves but grows geographically distributed.
- Biomass appears as non-uniform solid, from a wide variety of plants (woody, grassy, stalks, leaves, shells, …)
- Biomass is renewable.

Biomass Composition

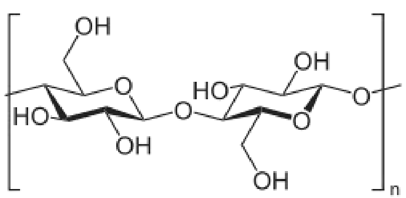


Converted to moles:
$(CH_{1.43}O_{0.65})_n$ (daf)
or ~ $(CH_2O)_n$ (waf)

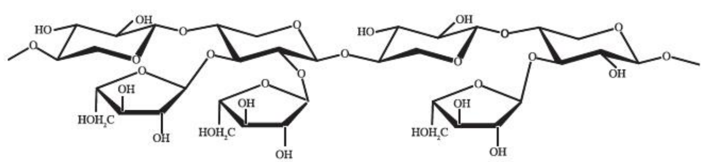
daf…dry and ash free
waf…wet and ash free

Ash: Si, K, Na, Ca, Mg, Al, Fe, and other metals.
Inorganics: N, S.

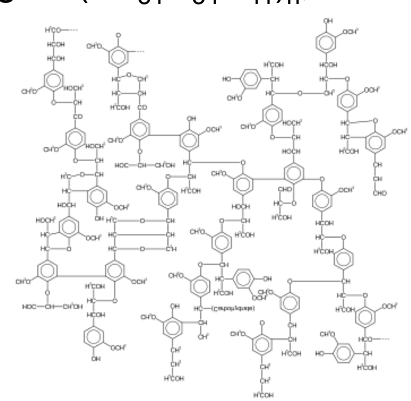
Cellulose $(C_6H_{10}O_5)_n$, 40-50%



Hemicellulose $(\sim C_5H_8O_4)_n$, 20-35%



Lignin $(\sim C_{31}H_{34}O_{11})_n$, 15-35%



Biomass Conversion

Biomass, ~$(CH_2O)_n$

($+C+H_2O$) ←

CO_2 ← → CH_4

$C+CO_2$ ← → CH_3OH

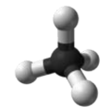
CO_2 ← → C_2H_5OH

CO_2+H_2O ← → ~CH_2

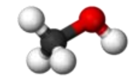
CO_2+H_2O ← → ~CH_2

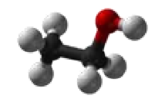
Vehicle Fuels

- Natural Gas

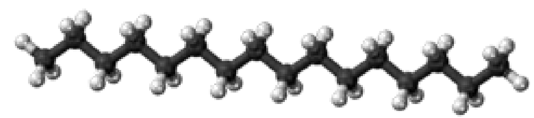
  Methane, CH_4 

- Alcohols

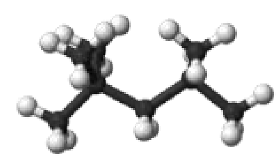
  Methanol, AKI: 99, CH_3OH 

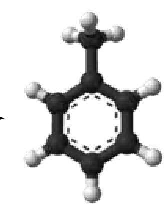
  Ethanol, AKI: 99, C_2H_5OH 

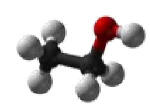
- Diesel components

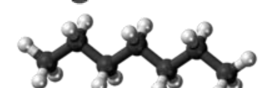
  Hexadecane, $C_{16}H_{34}$ 

- Gasoline components

  Isooctane, AKI: 100, C_8H_{18} 

  Toluene, AKI: 114, C_7H_8 → 

  Ethanol, AKI: 99, C_2H_5OH 

  (***No*** *n*-Heptane, AKI: 0, C_7H_{16}) 

AKI…Anti-knock index, (RON+MON)/2

Definition of Types of Fuels

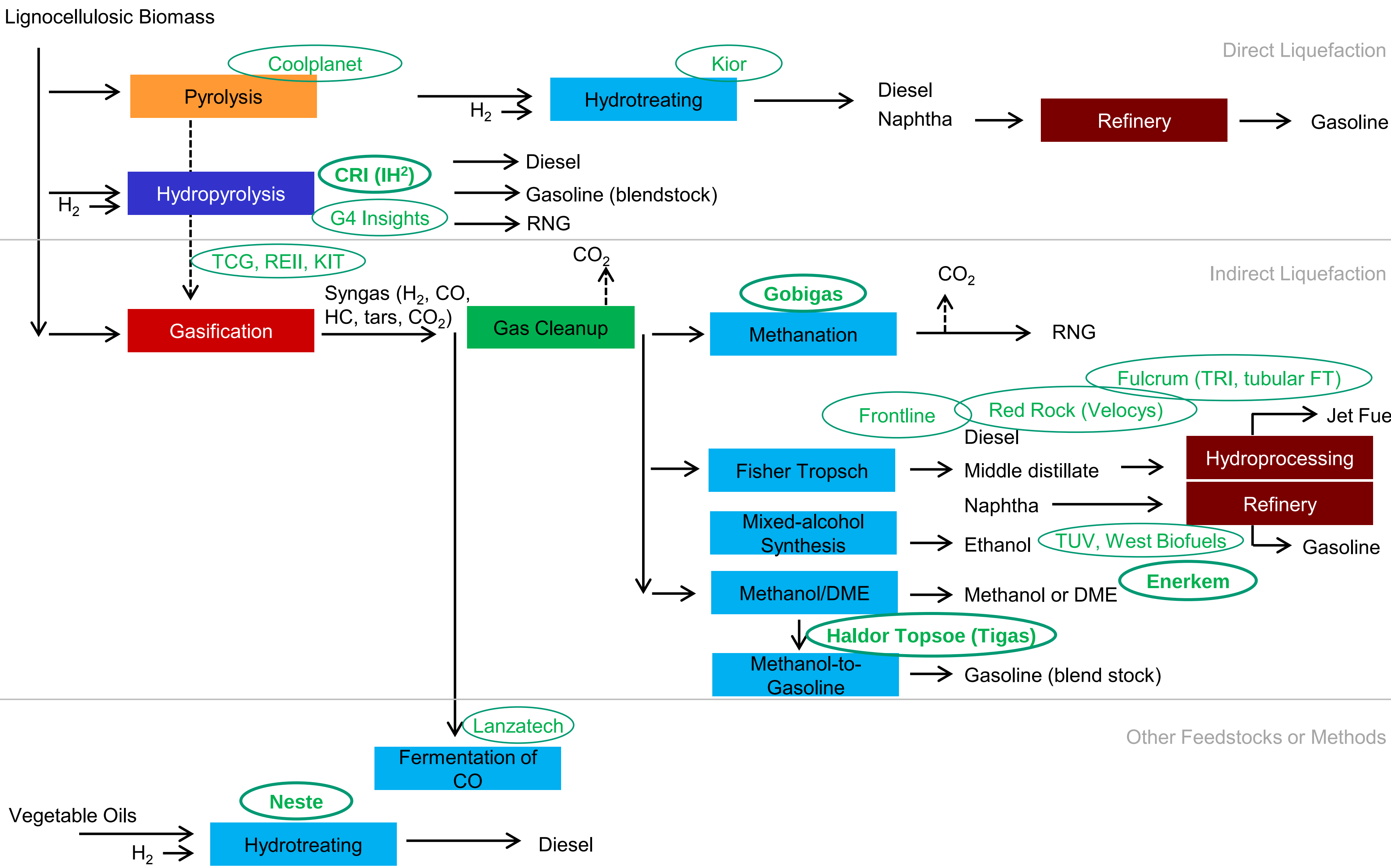
- Co-processing feedstock (refinery-, crude-blendstocks)
  Examples: all types of hydrocarbons outside fuel specifications, hydrotreating of biomass/vegetable oils, biomass/coal.

- Fuel blendstocks (qualify as fuel components but are not widely used fuels themselves)
  Examples: alcohols, aromatics.

- Drop-in fuels (meet or exceed fuel specifications)
  Examples: Fischer-Tropsch diesel, renewable natural gas.

- Alternative fuels (outside main distribution networks)
  Examples: biodiesel, E85, methanol, DME

Conversion Technologies



Gasification – Gas Cleanup – Fuel Synthesis – Fuel Upgrading

Pros:

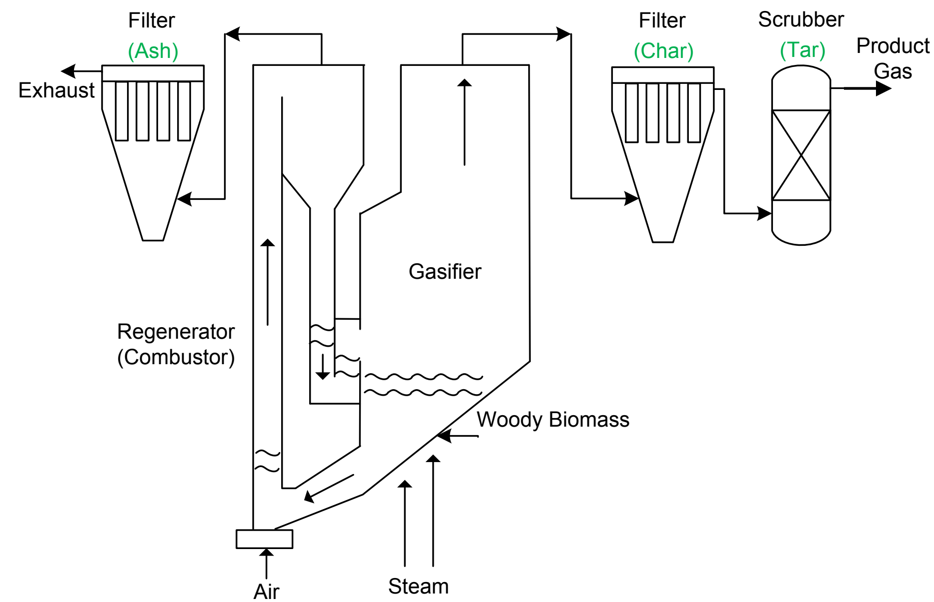
- High temperature – relatively fast process
- Gasification creates a known set of gaseous species
- A variety of fuels and chemicals can be produced by fuel synthesis
- Low level of contaminants in final products

Cons:

- Many process steps – less efficient, more costly
- Often relies on several catalysts – costs and deactivation
- Large size – feedstock availability and product distribution need to match

FICFB Gasifier: Converting Biomass to Producer Gas

- Fast Internally Circulating Fluidized Bed (FICFB)
- Fluidized bed using bed material such as Olivine sand
- Indirectly heated, air-blown, ambient-pressure design.
- Low nitrogen producer-gas, acceptable tar levels.
- Cold-gas efficiency > 70%



Woodland, CA
~1 MW_{fuel}

Research

Burgeis, Italy
~2 MW_{fuel}

CHP

Gussing, Austria
~8 MW_{fuel}

CHP

Senden, Germany
~16 MW_{fuel}

CHP

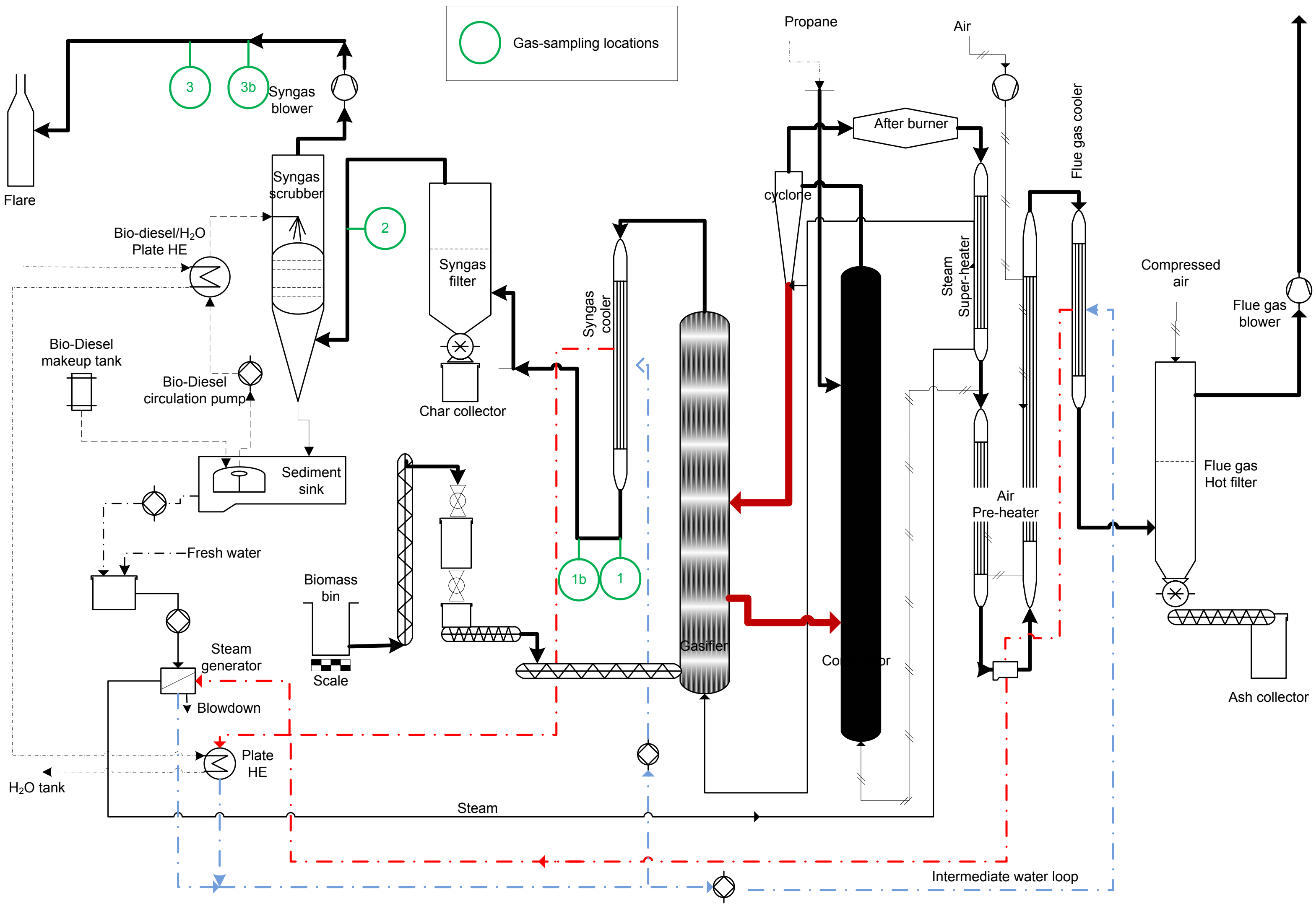
Gothenburg, Sweden
~32 MW_{fuel}

RNG

CHP…Combined Heat and Power, RNG…Renewable Natural Gas

FICCFB Pilot Plant 1MW$_{fuel}$, 5 tons/day

Uses heat recovery for steam generation



Typical Producer-Gas Composition
(after raw-gas cleanup and cool down, e.g. sampling point 3)

Compound	Chemical Formula	Volume Fraction
Hydrogen	H_2	0.38
Carbon Monoxide	CO	0.19
Carbon Dioxide	CO_2	0.22
Methane	CH_4	0.09
Water	H_2O	0.07
Oxygen	O_2	0.002
Nitrogen	N_2	0.02
Ethylene	C_2H_4	0.02
Ethane	C_2H_6	0.002
Acetylene	C_2H_2	0.002
Propylene	C_3H_6	100×10^{-6}
Benzene	C_6H_6	0.003
Toluene	C_7H_8	100×10^{-6}
Naphthalene	$C_{10}H_8$	0.002
Other Tars		0.001
Ammonia	NH_3	150×10^{-6}
Hydrogen Sulfide	H_2S	100×10^{-6}
Hydrogen Chloride	HCl	1×10^{-6}
Carbonyl Sulfide	COS	3×10^{-6}
Thiophene	C_4H_4S	5×10^{-6}
Methyl Mercaptan	CH_3SH	50×10^{-9}
Carbon Disulfide	CS_2	30×10^{-9}
Benzothiophene	C_8H_6S	12×10^{-9}

Depending on steam (water-gas shift), catalysts, residence time.

Decrease with increasing temperature, catalysts, residence time

Oxygen-blown or indirectly-heated gasifier for low N_2 content. Nitrogen content of fuel matters.

Depending on biomass composition

Suitable for gas engine, but for most conversion processes to fuels, gas needs to be further cleaned.

FICFB Gasifier in Comparison to other Gasification Technologies

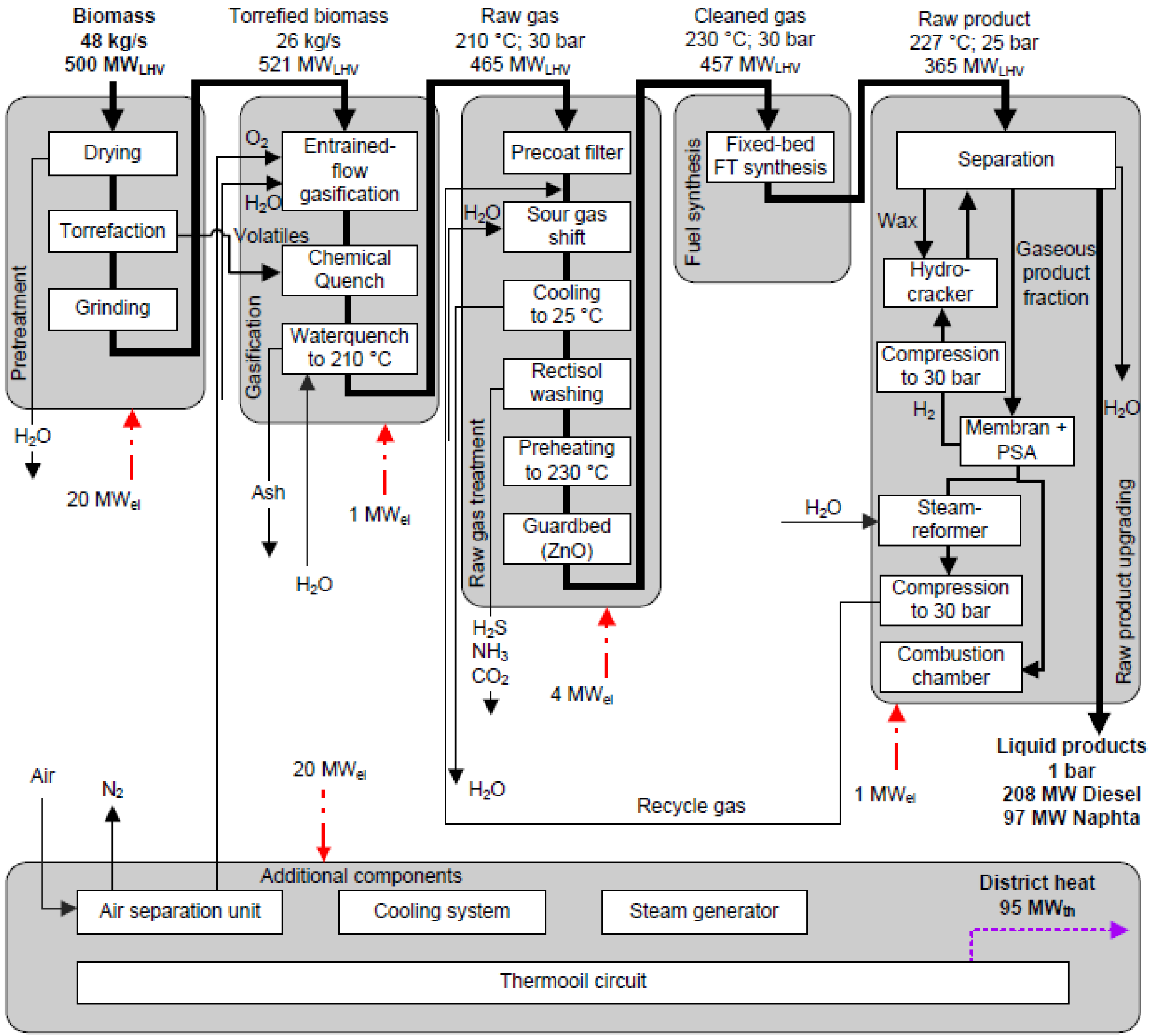
Pros:

- Process works – Güssing plant operated 7000 hours/year for 15 years
- High efficiency to producer gas, few waste streams (char, tar, water internally recycled)
- High hydrogen and methane amount in producer gas
- No oxygen plant required
- Size matches biomass logistics (30-100 MWfuel, ~50 mile radius)

Cons:

- Many process steps – demands on design, operators, and maintenance
  Problems with: refractory lining, feed systems, tars in heat exchangers
- Consumables – bed material, biodiesel for scrubbing, Ca/K additives
- Not zero-emission – exhaust from char combustor

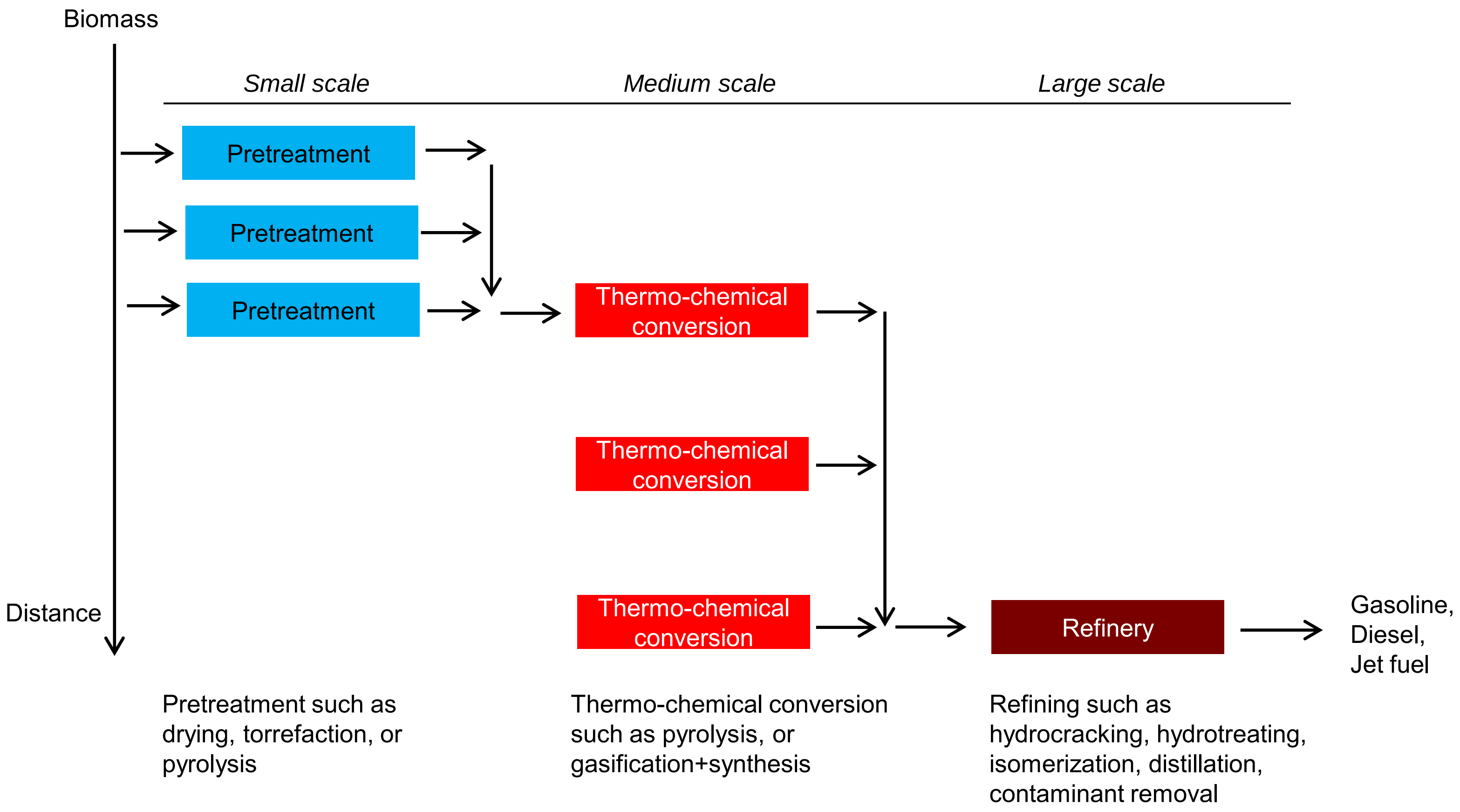
Fischer-Tropsch Synthesis – Larger Scale



Source: DBFZ report, 2009

Feedstock Barrier: Scale and Logistics

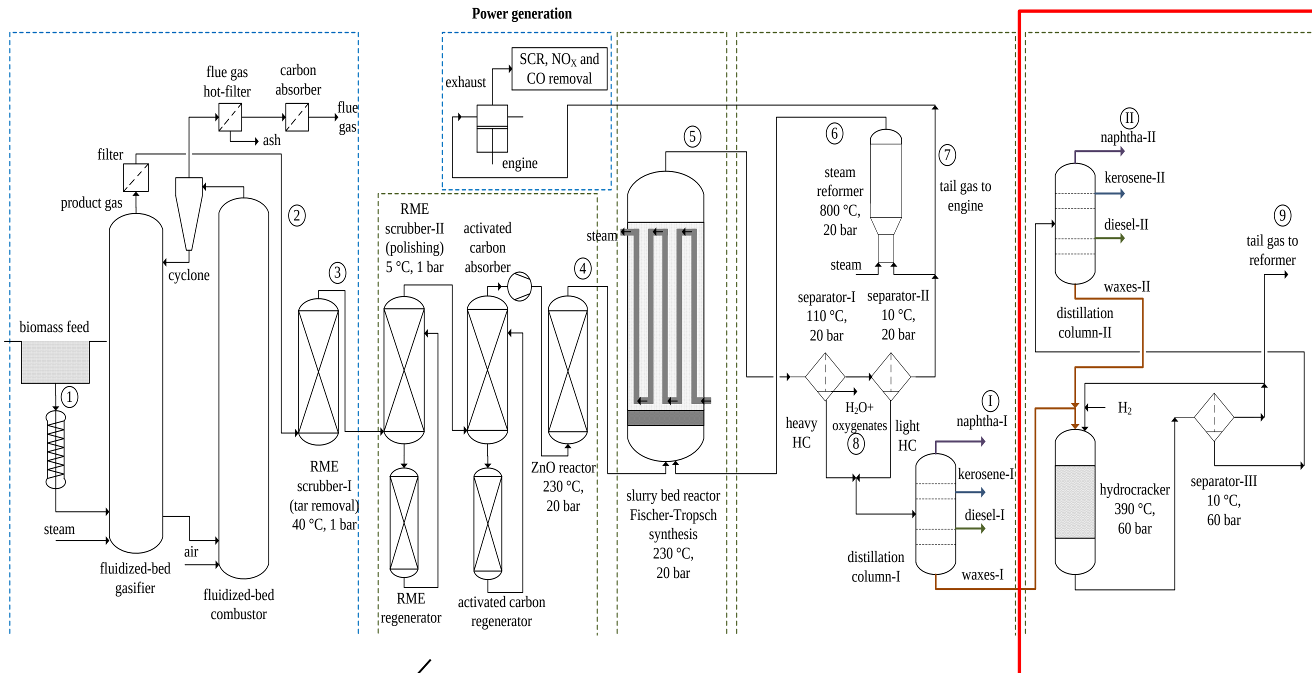
- Biomass is distributed and biomass facilities are small.
- Refineries are concentrated and large. Fuel specifications for gasoline and jet fuel are tight.
- Possibly combine process streams after they are being concentrated in energy:



Fischer-Tropsch Synthesis – Smaller Scale with Centralized Upgrading

Products per 100 MW biomass

Description	Lower heating value [MW]
Products from FT synthesis	
Naphtha	0.24
Jet fuel	6.9
Diesel	22.9
Waxes (further hydroprocessed)	42.8
Total (including waxes)	72.8
Total (liquids)	30.0
Hydrogen to hydrocracker	14.2
Products from hydrocracking	
Naphtha	6.4
Jet fuel	12.8
Diesel	21.4
Total (liquids)	40.7
Tail-gas (not recycled)	
Combined products	
Naphtha	6.7
Jet fuel	19.7
Diesel	44.3
Total final products	70.7



E.g. 5 x 100 MW gasifiers/FT and 500 MW upgrading/refinery

Note:
Naphtha fraction needs to be upgraded in isomerization plant, Jet Fuel fraction is only blend stock

Technologies change with size (types of gasifier, types of gas cleanup,…)

Fischer-Tropsch Synthesis from Producer Gas to Drop-in Fuel (Diesel, Jet Fuel, Gasoline)

Pros:

- Best drop-in diesel fuel.
- Relatively high efficiency.
- Clean paraffinic production of chemicals.

Cons:

- Wide product distribution including naphtha and waxes.
- Gasoline and jet fuel fractions need to be upgraded in isomerization unit.
- Detailed gas cleanup necessary to protect catalyst.
- Large-scale installation needed or co-location with refinery.
- High-pressure equipment.

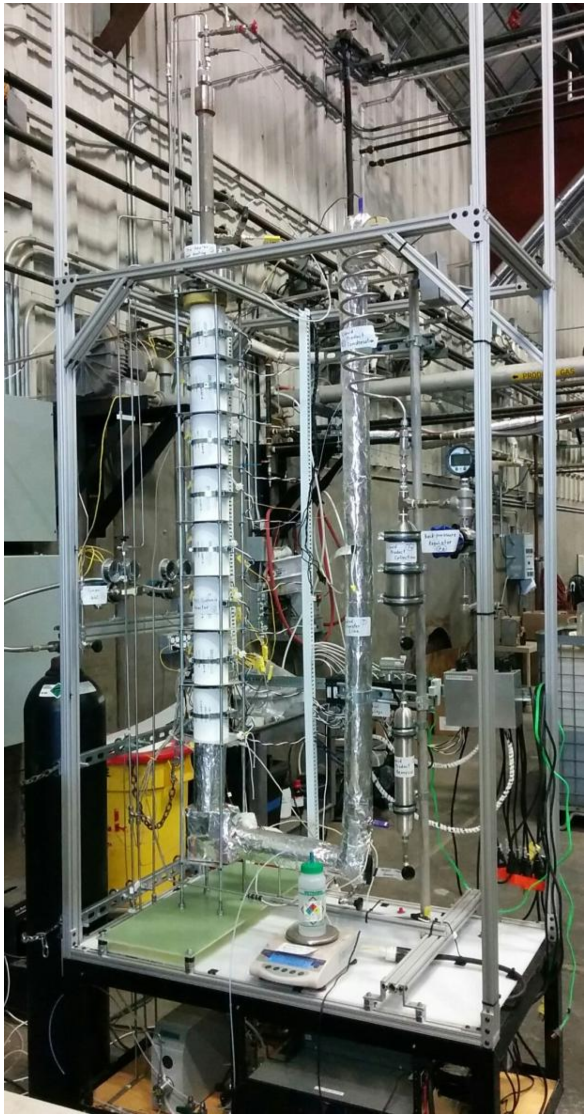
Technical Barrier: Catalyst Deactivation

Contaminant	Methanol Synthesis	FT Synthesis	Mixed Alcohol Synthesis	Fixed-/ Fluidized-bed Methanation
Particulate	< 0.02 mg/Nm3	n.d.		
(soot, dust char, ash)				
Tars (condensible)	< 0.1 mg/Nm3	< 10ppb		
Inhibitory compounds		< 1 ppm		< 1/1000ppm
(class 2-heteroatoms, BTX)				
Sulfur	< 1 mg/Nm3	< 10ppb	< 300ppm	< 10/10ppb
(H2S, COS)				
Nitrogen	< 0.1 mg/Nm3	< 20ppb		
(NH3, HCN)				
Alkali		< 10 ppb		
Halides (primarily HCl)	< 0.1 mg/Nm3	< 10 ppb		

ppm…parts per million, ppb…parts per billion

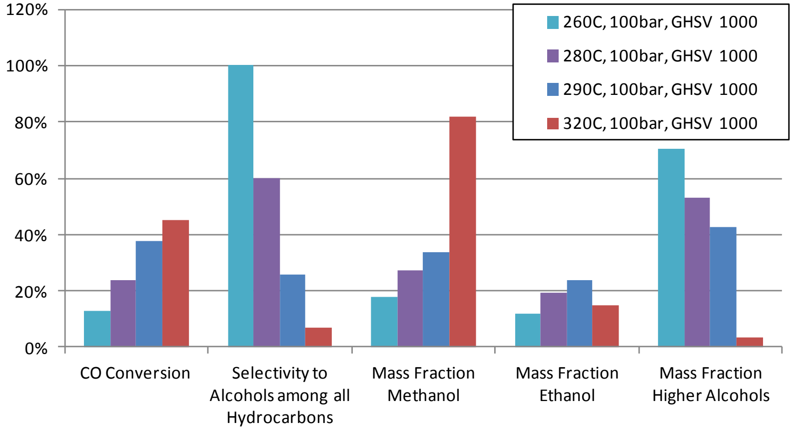
Many thermo-chemical processes employ catalysts and are subject to catalyst deactivation. High demands on gas cleanup.

Mixed-Alcohol Synthesis



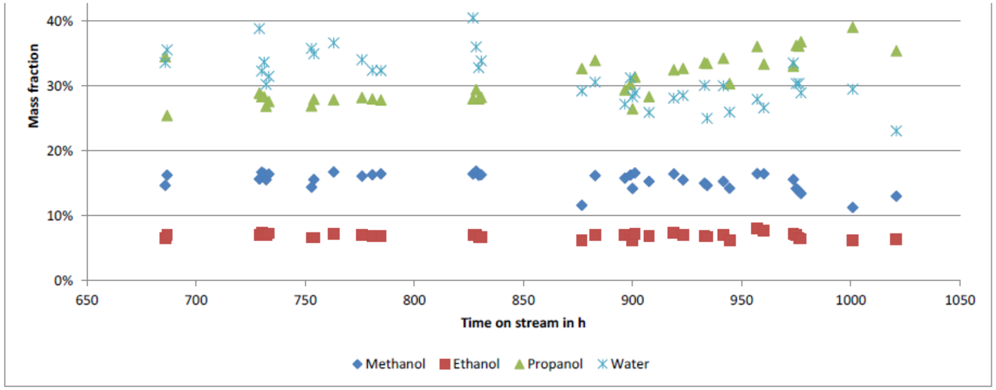
Bench-scale synthesis reactor at the Woodland Biomass Research Center

- MoS_2 based Catalyst from Albemarle. Similar to "Dow" Catalyst, NREL, Range Fuels.
- Allows for 100ppm of H_2S in the feed gas.
- No further producer-gas cleaning necessary.
- Pressures around 100bar are tested.
- Methanol and tail-gas recycling is investigated.
- Commercially, alcohols and water would be separated by distillation.
- Benchscale, laboratory-scale, and pilot-scale unit.
- Collaboration between UCSD, bioenergy2020+ (Austria), and West Biofuels.

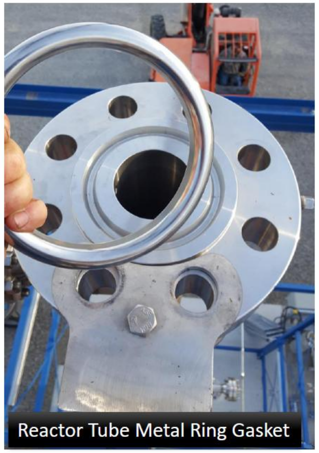


Collaboration with bioenergy2020+ and Albemarle

- Bench-scale reactor in Woodland, CA (UCSD). Testing of process conditions (5slpm feed gas, 8ml/hr alcohols in single pass)
- Laboratory-scale reactor in Güssing. Long-term testing of catalyst (50slpm feed gas)



- Pilot-scale reactor in Woodland, CA (West Biofuels). Testing of thermal management (250slpm feed gas)



Mixed-Alcohol Synthesis from Producer Gas to Fuel Blendstock (Gasoline)

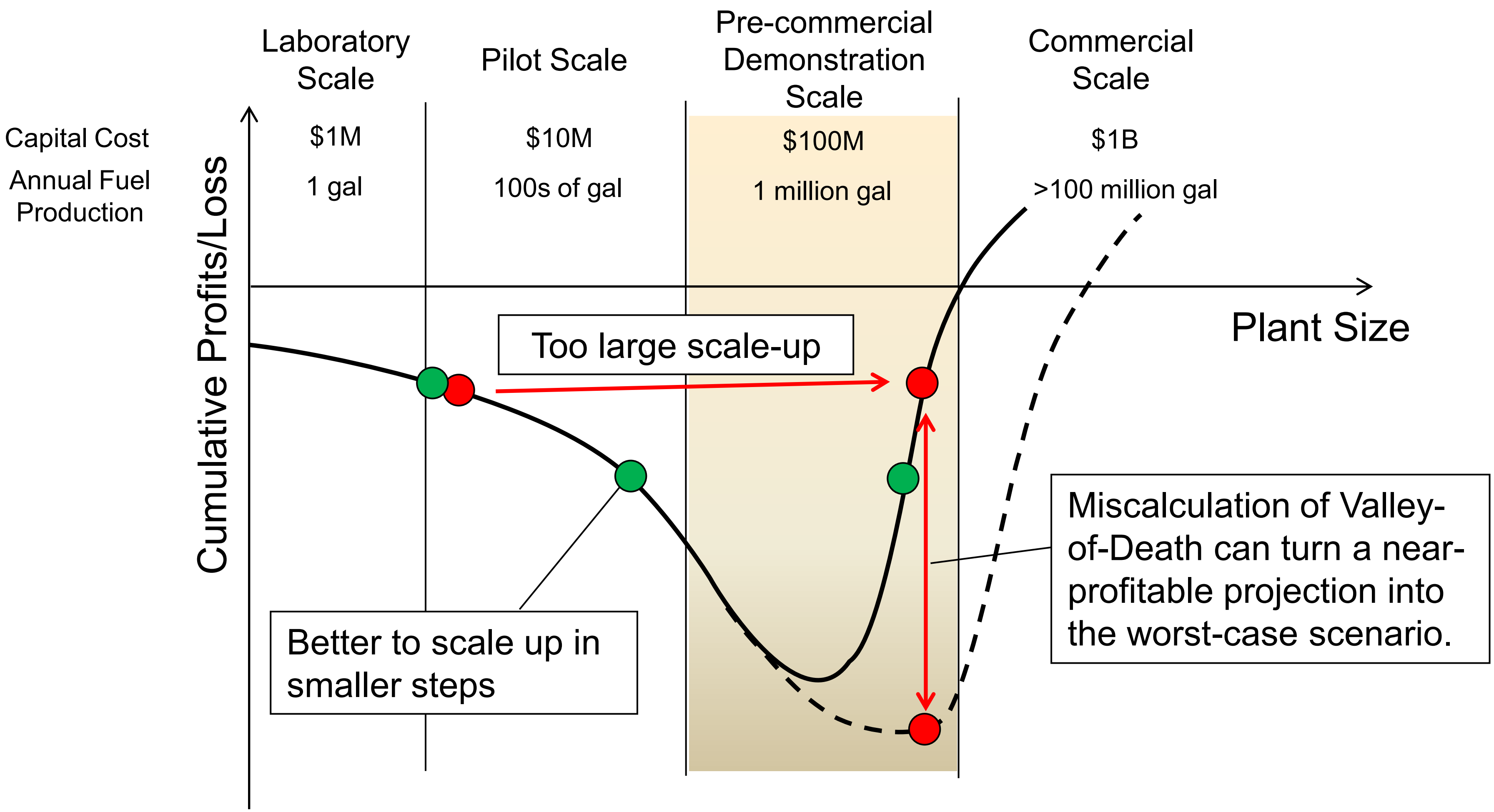
Pros:

- Sulfur tolerant catalyst, virtually no gas-cleanup needed.
- Gasoline blendstock with minimal fuel upgrading.
- Allows for slightly smaller and decentralized plants near biomass source and fuel terminals.

Cons:

- Low conversion efficiency (multi-pass gas recycle necessary).
- High-pressure, H_2S requiring more expensive equipment.
- Mercaptan removal from liquid necessary.

Financial Barrier: Scale-up Risk



Range Fuels: 5 tons/day → 125 tons/day (Phase1) … failed
Kior: 50 times from demonstration to commercial … on hold

Research Center Topics

Guessing, Austria

- Commercial FICFB gasifier
- Electricity production in lean-burn SI-engine
- District heating
- Tar reforming technologies (2x)
- Fischer-Tropsch synthesis (2x)
- Mixed-Alcohol synthesis
- Hydrogen production
- Renewable natural gas production (3x)

Woodland, CA

- Fluidized-bed gasifiers (2x)
- Fixed-bed gasifiers (2x)
- Electricity production in SI-engine with aftertreatment (2x)
- Tar reforming
- Mixed-Alcohol synthesis (2x
- Renewable natural gas production
- Sulfur adsorbent testing

Fluidized-bed Methanation at Various Scales

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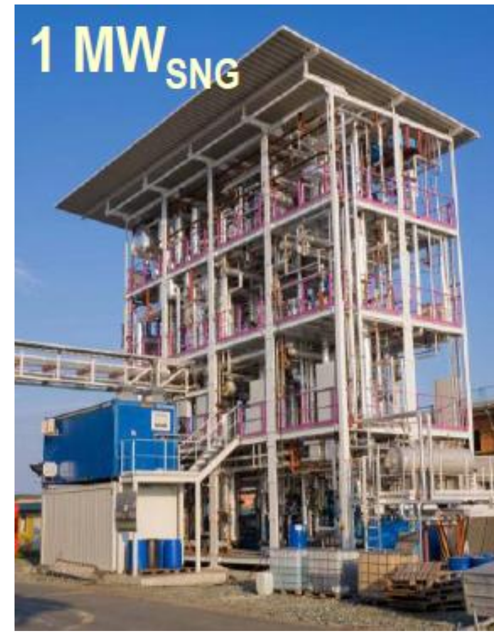
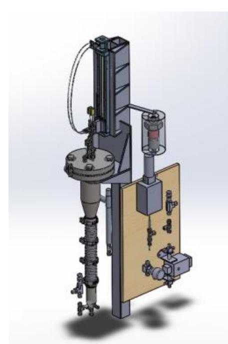
PSI



1-6 slpm

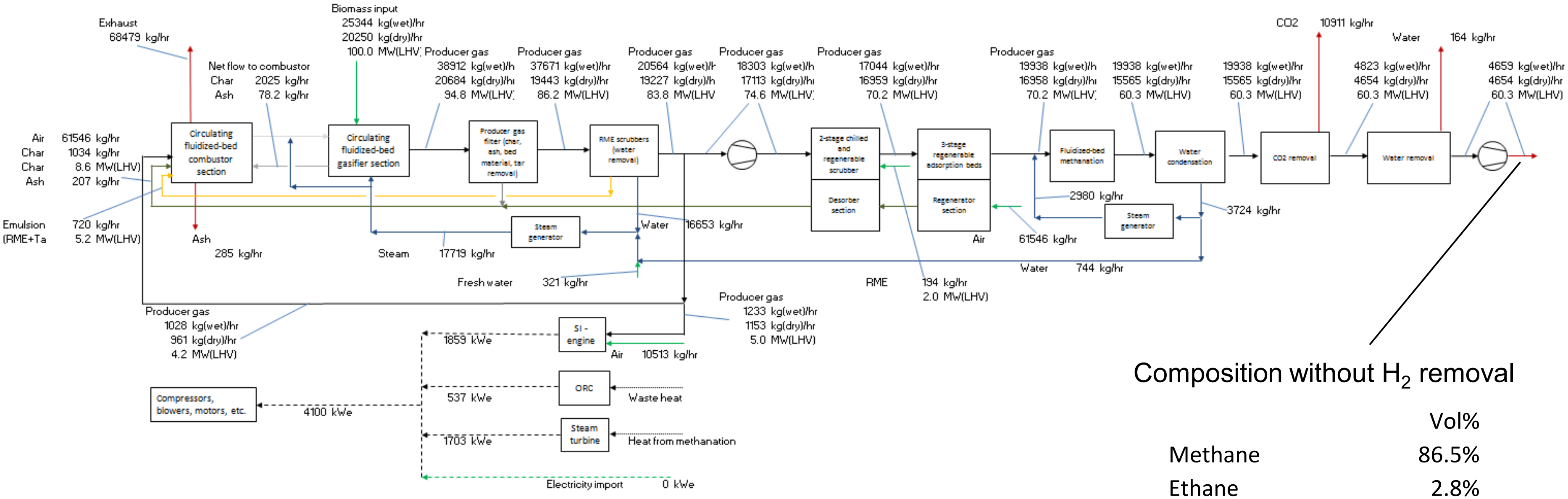
Our research unit

5-20 slpm



Commercial Plant for Renewable Natural Gas

100MW$_{biomass}$ input, 58% efficiency to RNG



Composition without H_2 removal

	Vol%
Methane	86.5%
Ethane	2.8%
Hydrogen	6.4%
Nitrogen	3.2%
Carbon Dioxide	0.7%
Carbon Monixide	0.2%
Moisture	0.1%

- Pipeline specifications (e.g. Rule 21) call for low hydrogen content (pipeline integrity), but hydrogen allowance may increase over time.

Methanation of Producer Gas to Renewable Natural Gas

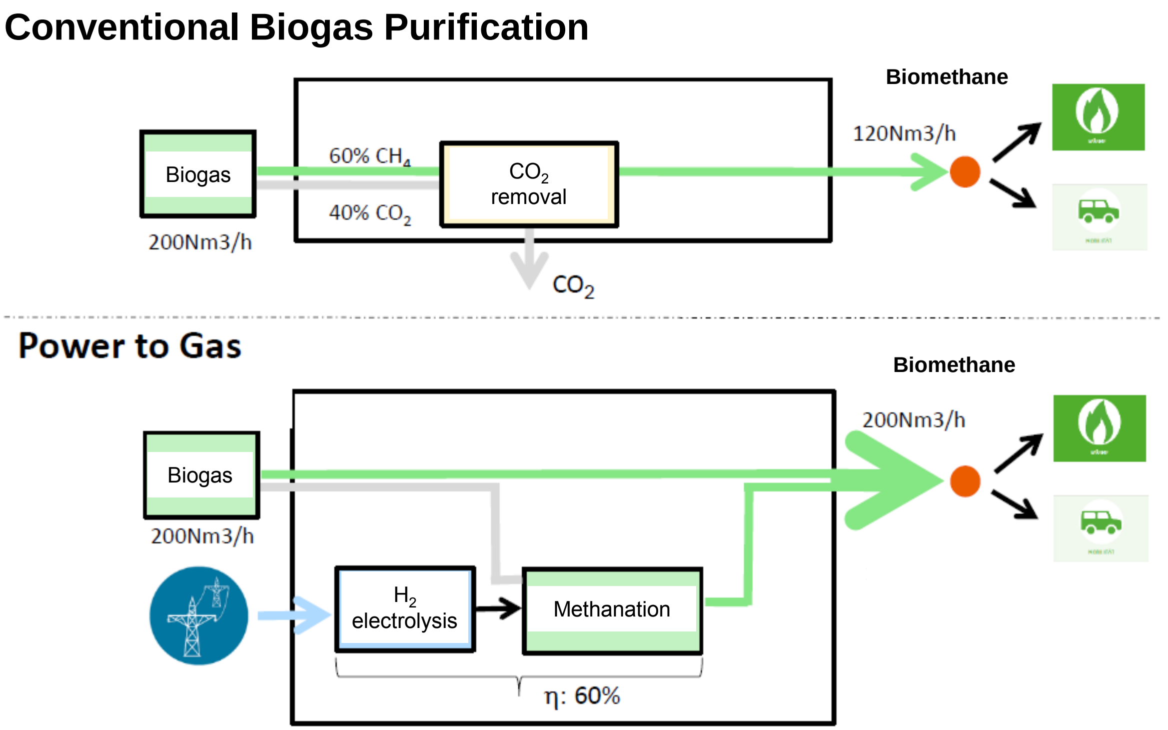
Pros:

- High-conversion with Ni-based catalyst (99.6%)
- High energy efficiency of overall process (60%)
- Methane and ethylene (conversion to ethane) in the producer gas are utilized
- Pipeline specifications can be met
- Minimal fuel upgrading needed

Cons:

- High demands on gas cleanup (sulfur compounds)
- Natural gas prices relatively low
- Expensive interconnection (pipeline injection)

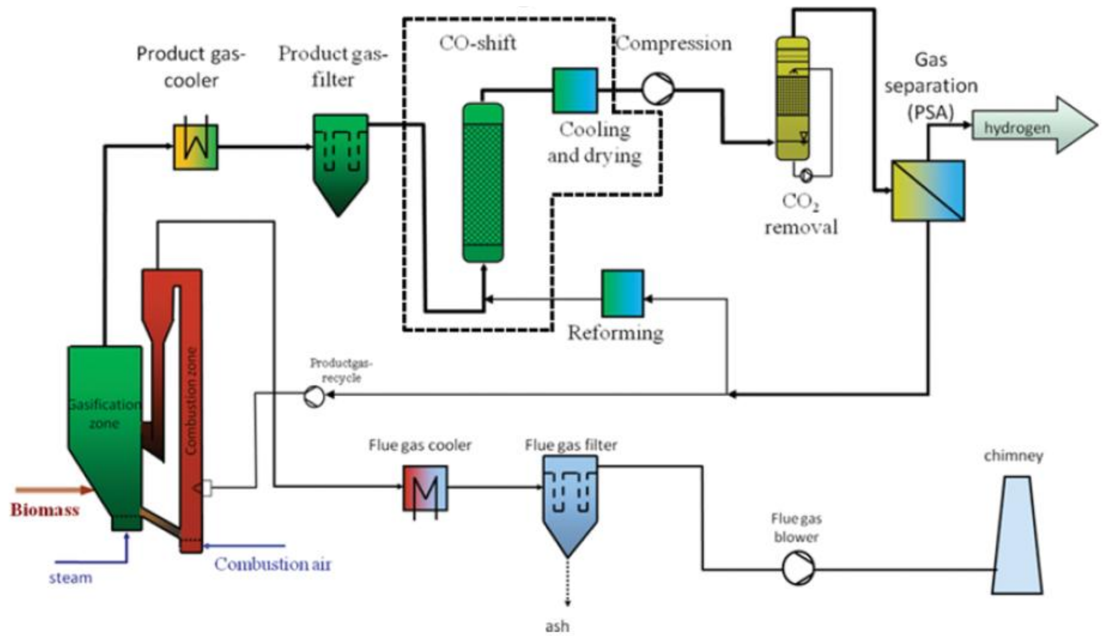
Intermediate Step for Scaling up Fluidized-bed Methanation Technology



Source: PSI, 2017

- Instead of removing CO_2 biogas, convert it to more methane.
- Uses hydrogen from electrolysis during times when electricity is cheap
- Increases biomethane output by ~60% for better economy of scale
- Smaller plant size than methanation of producer gas

Hydrogen Production from Biomass for use in Fuel Upgrading



Source: Loipersböck, 2017

- Makes direct use of hydrogen in producer gas
- High overall efficiency
- Replaces fossil natural gas otherwise used in steam reforming

Acknowledgments

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bioenergy2020+

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