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Innovation for Our Energy Future
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Office of Energy Efficiency & Renewable Energy

An Introduction to Biomass Thermochemical Conversion

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Presentation Outline

- Objective & Definitions
- Biomass Properties
- Combustion
- Gasification
- Pyrolysis
- Other
- Research Areas

Fuels, Chemicals, Materials, Heat and Power from Biomass

Biomass Feedstock

– Trees
– Forest Residues
– Grasses
– Agricultural Crops
– Agricultural Residues
– Animal Wastes
– Municipal Solid Waste

Conversion Processes

- Gasification
- Combustion and Cofiring
- Pyrolysis
- Enzymatic Fermentation
- Gas/liquid Fermentation
- Acid Hydrolysis/Fermentation
- Other

USES

Fuels:
Ethanol
Renewable Diesel

Electricity

Heat

Chemicals
– Plastics
– Solvents
– Pharmaceuticals
– Chemical Intermediates
– Phenolics
– Adhesives
– Furfural
– Fatty acids
– Acetic Acid
– Carbon black
– Paints
– Dyes, Pigments, and Ink
– Detergents
– Etc.

Food and Feed

Basic Definitions

Biomass is plant matter such as trees, grasses, agricultural crops or other biological material. It can be used as a solid fuel, or converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or fuels.

Black Liquor is the lignin-rich by-product of fiber extraction from wood in Kraft (or sulfate) pulping. The industry burns black liquor in Tomlinson boilers that 1) feed back-pressure steam turbines supplying process steam and electricity to mills, 2) recover pulping chemicals (sodium and sulfur compounds) for reuse.

Basic Definitions

Combustion

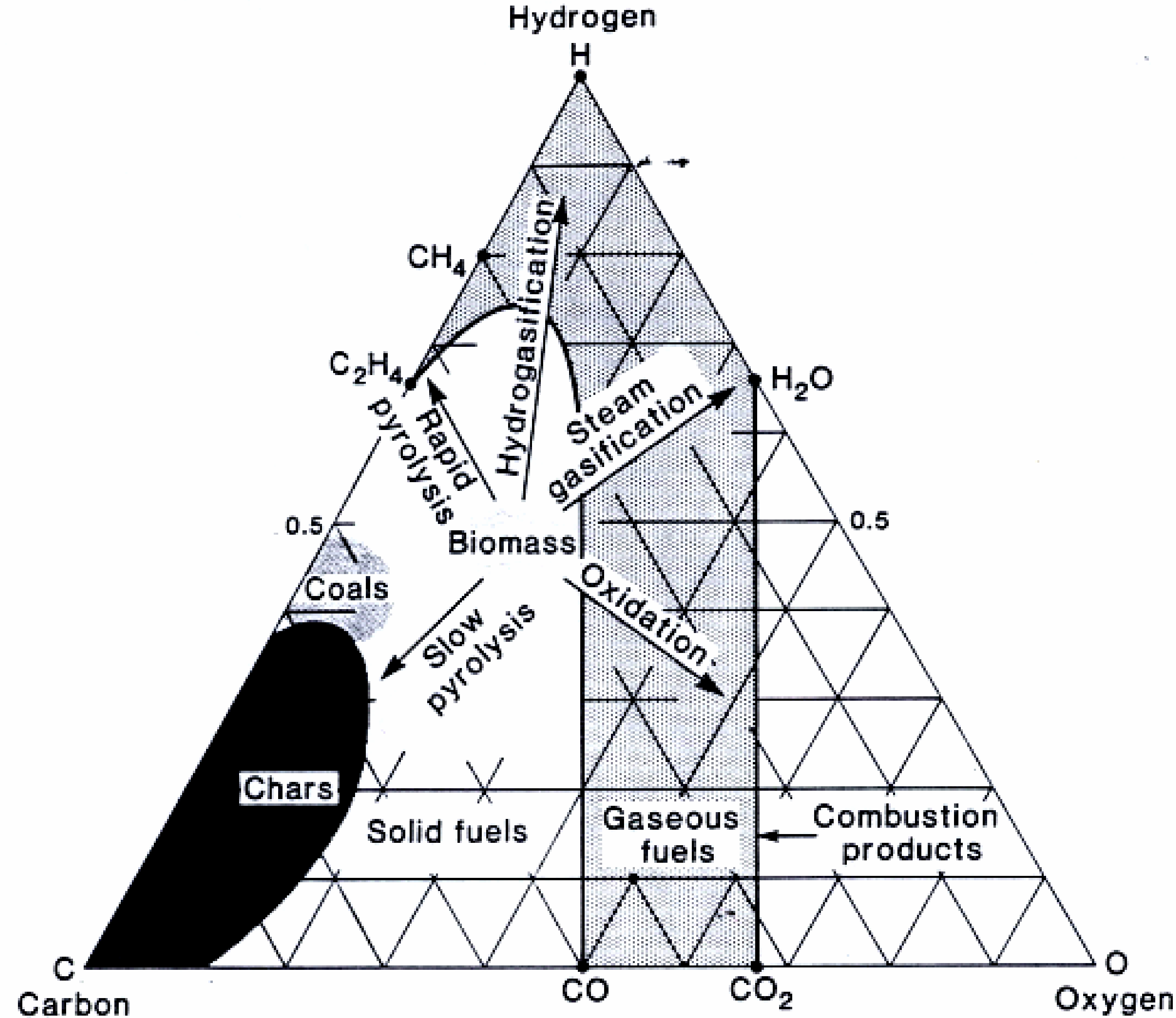
- Thermal conversion of organic matter with an oxidant (normally oxygen) to produce primarily carbon dioxide and water
- The oxidant is in stoichiometric excess, i.e., complete oxidation

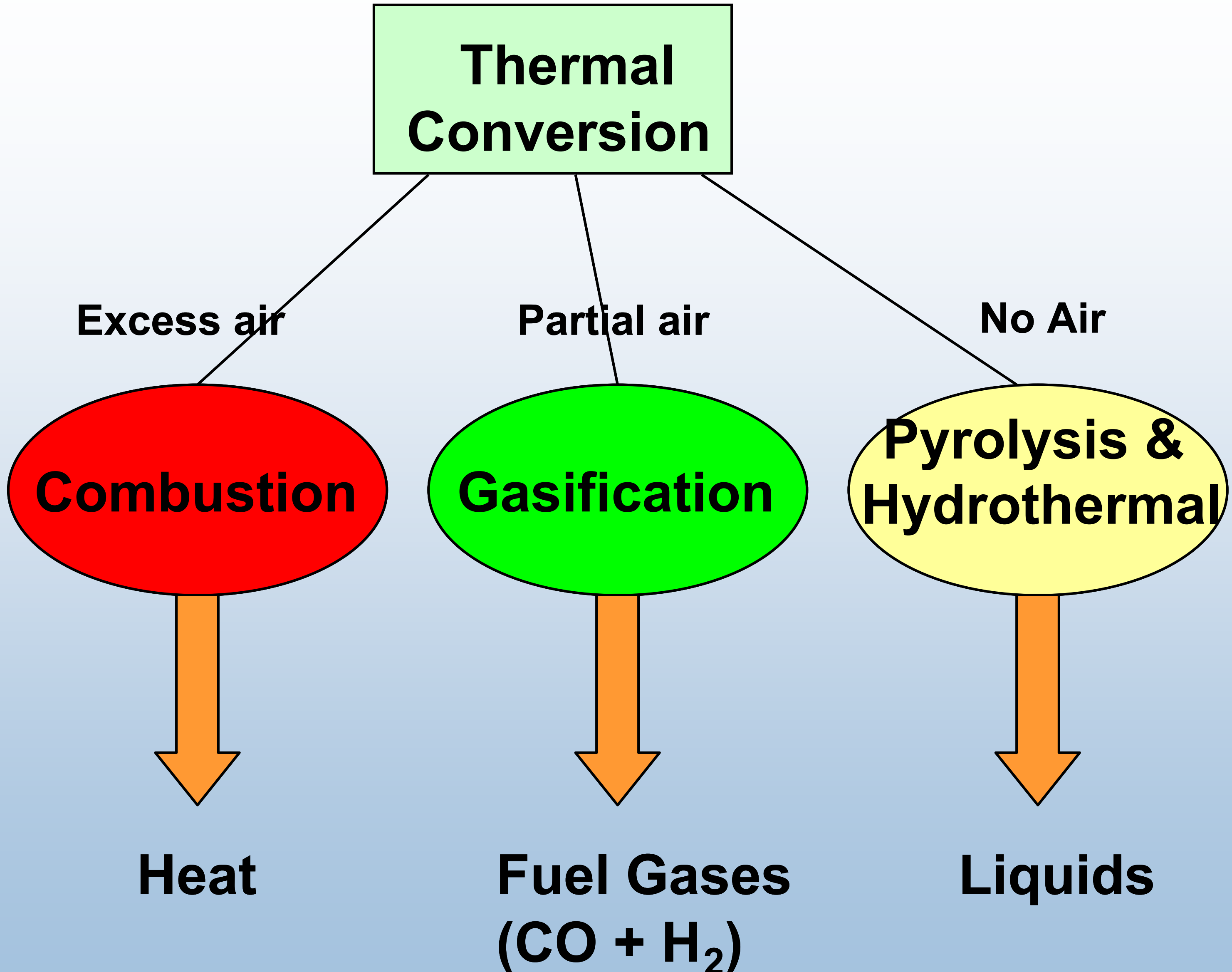
Pyrolysis

- Thermal conversion (destruction) of organics in the absence of oxygen
- In the biomass community, this commonly refers to lower temperature thermal processes producing liquids as the primary product
- Possibility of chemical and food byproducts

Gasification

- Thermal conversion of organic materials at elevated temperature and reducing conditions to produce primarily permanent gases, with char, water, and condensibles as minor products
- Primary categories are partial oxidation and indirect heating


Hydrogen
H
CH4
C2H4
H2O
Hydrogasification
Rapid pyrolysis
Steam gasification
0.5
0.5
Biomass
Coals
Slow pyrolysis
Oxidation
Chars
Solid fuels
Gaseous fuels
Combustion products
C
Carbon
CO
CO2
O
Oxygen



Thermal Conversion
Excess air
Partial air
No Air
Combustion
Gasification
Pyrolysis & Hydrothermal
Heat
Fuel Gases ($CO + H_2$)
Liquids

POTENTIAL BIOMASS PRODUCTS

- Potential Biomass Products
  - Biomass
  - Syngas
  - Hydrogen
  - Pyrolysis Oil – Whole or Fractionated
  - Hydrothermal Treatment Oils
- Biomass
  - Solid
  - $CH_{1.4}O_{0.6}$
  - HHV = 16 – 17 MBTU/ton (MAF)
- Syngas
  - Major components – CO, H_2, CO_2
  - CO/H_2 ratio set by steam rate in conditioning step, typical range 0.5 – 2
  - HHV: 450-500 BTU/scf
- Pyrolysis Oil
  - $CH_{1.4}O_{0.5}$
  - Chemical composition: water (20-30%), lignin fragments (15-30%), aldehydes (10-20%), carboxylic acids (10-15%), carbohydrates (5-10%), phenols (2-5%), furfurals (2-5%), ketones (1-5%)
  - Other (ca.): pH - 2.5, sp.g. - 1.20, viscosity (40°C, 25% water) – 40 to 100 cp, vacuum distillation residue – up to 50%
- Hydrothermal Treatment Oils
  - Water plus alkali at T = 300-350°C, P high enough to keep water liquid. Use of CO is option
  - Yield > 95%
  - Distillate (-500°C): 40 – 50%
  - Distillate Composition: Hardwood (300°C) – $CH_{1.2}O_{0.2}$, Manure (350°C) – $CH_{1.4}O_{0.1}$
  - Qualitative: long aliphatic chains, some cyclic compounds containing carbonyl groups, and a few hydroxy groups, ether linkages, and carboxylic acid groups
  - HHV = 28 – 34 MBTU/ton

Biomass Properties Relevant to Thermal Conversion

Representative Biomass & Black Liquor Compositions

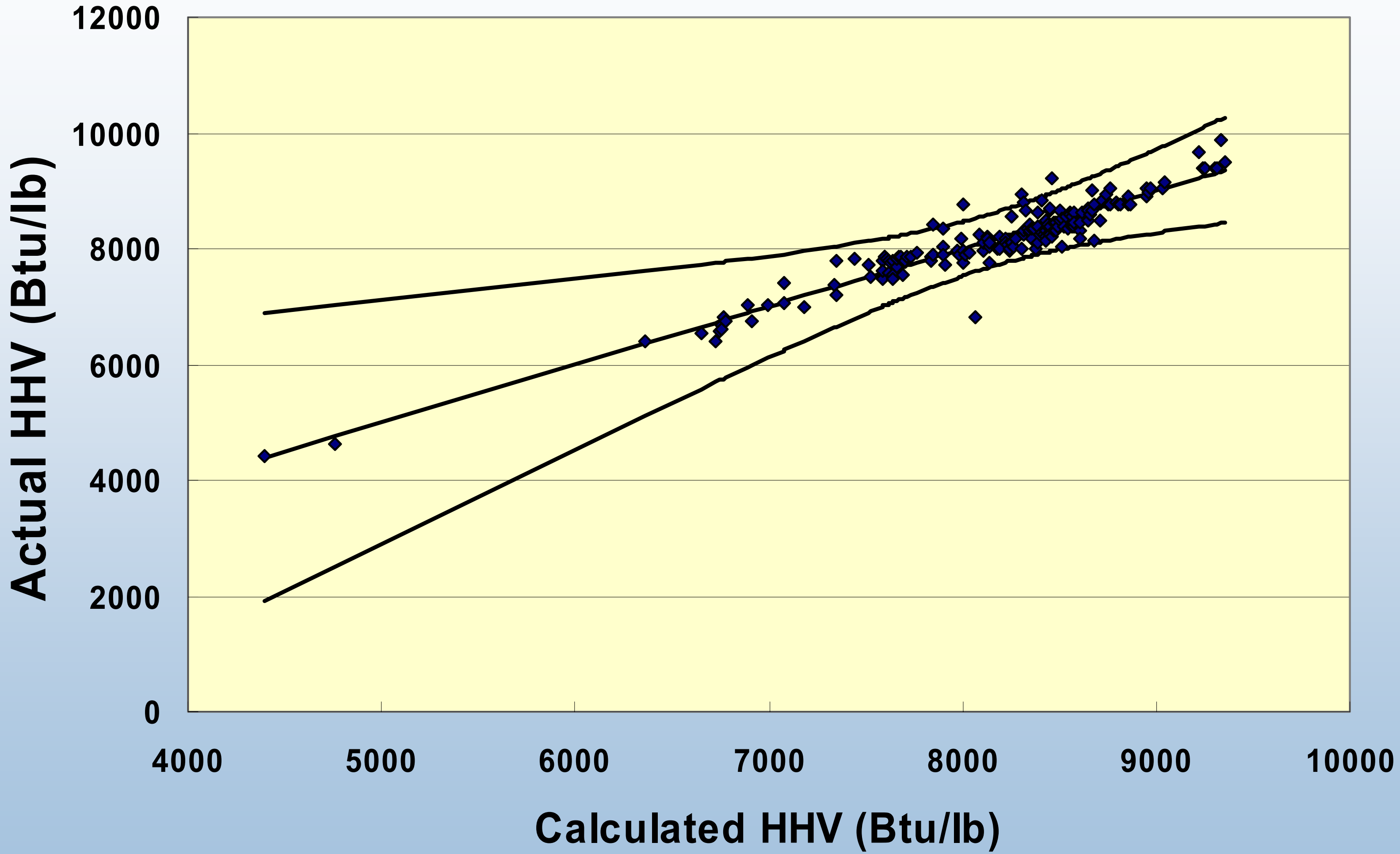
	Poplar	Corn Stover	Chicken Litter	Black Liquor
Proximate (wt% as received)				
Ash	1.16	4.75	18.65	52.01
Volatile Matter	81.99	75.96	58.21	35.26
Fixed Carbon	13.05	13.23	11.53	6.11
Moisture	4.80	6.06	11.61	9.61
HHV, Dry (Btu/lb)	8382	7782	6310	4971
Ultimate, wt% as received				
Carbon	47.05	43.98	32.00	32.12
Hydrogen	5.71	5.39	5.48	2.85
Nitrogen	0.22	0.62	6.64	0.24
Sulfur	0.05	0.10	0.96	4.79
Oxygen (by diff)	41.01	39.10	34.45	0.71
Chlorine	<0.01	0.25	1.14	0.07
Ash	1.16	4.75	19.33	51.91
Elemental Ash Analysis, wt% of fuel as received				
Si	0.05	1.20	0.82	<0.01
Fe	---	---	0.25	0.05
Al	0.02	0.05	0.14	<0.01
Na	0.02	0.01	0.77	8.65
K	0.04	1.08	2.72	0.82
Ca	0.39	0.29	2.79	0.05
Mg	0.08	0.18	0.87	<0.01
P	0.08	0.18	1.59	<0.01
As (ppm)			14	

Representative Biomass and Coal Properties

	Biomass 1	Biomass 2	Coal 1	Coal 2	Tar Sands
Name	Wood	Red Corn Cob	Grundy, IL. No 4	Rosebud, MT	Athabasca
Classification			HvBb	sub B	Bitumen
Proximate Analysis, wt% Dry					
Moisture	25-60	16	8.16	19.84	
Volatile Matter	77-87	ca. 80	40.6	39.02	
Fixed Carbon	13-21	--	45.47	49.08	
Ash	0.1-2	4	13.93	9.16	
Ultimate Analysis, wt % Dry					
C	50-53	45	68.58	68.39	83.6
H	5.8-7.0	5.8	4.61	4.64	10.3
N	0-0.3	2.4	1.18	0.99	0.4
Cl	.001-0.1	--	0.12	0.02	--
O	38-44	42.5	6.79	16.01	0.2
S	0-0.1	0	4.76	0.79	5.5
Ash	0.1-2	4	13.93	9.16	
H/C Atomic Ratio	1.4-1.6	1.5	0.8	0.81	1.47
HHV, Dry, Btu/lb	8,530- 9,050	7,340	12,400	11,684	17,900

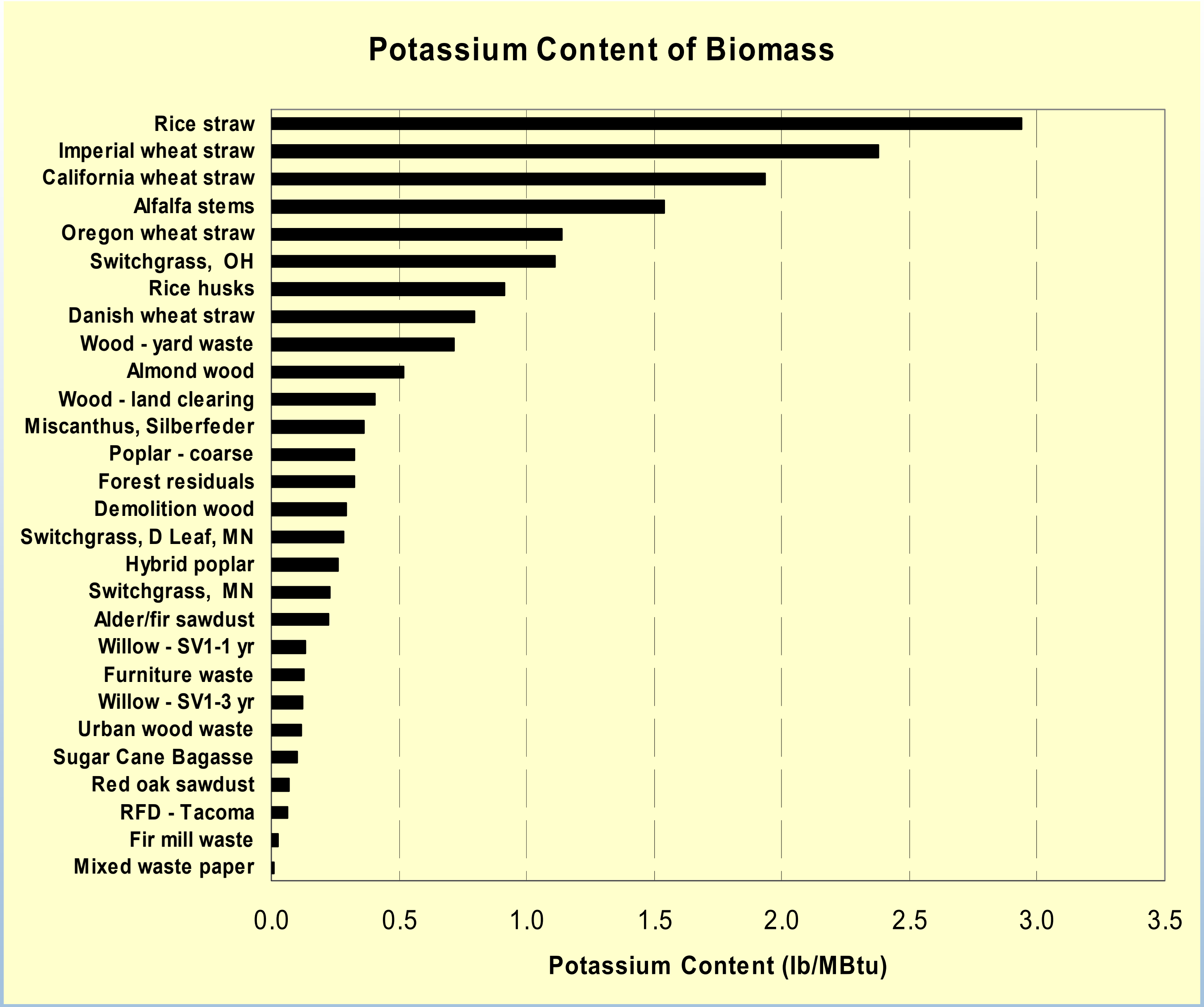
Biomass Higher Heating Value

(with 95% confidence interval)



HHV (Btu/lb) = 85.65 + 137.04 C + 217.55 H + 62.56 N + 107.73 S + 8.04 O - 12.94 A (Eq 3-15) N = 175

Bain, R. L.; Amos, W. P.; Downing, M.; Perlack, R. L. (2003). Biopower Technical Assessment: State of the Industry and the Technology. 277 pp.; NREL Report No. TP-510-33123



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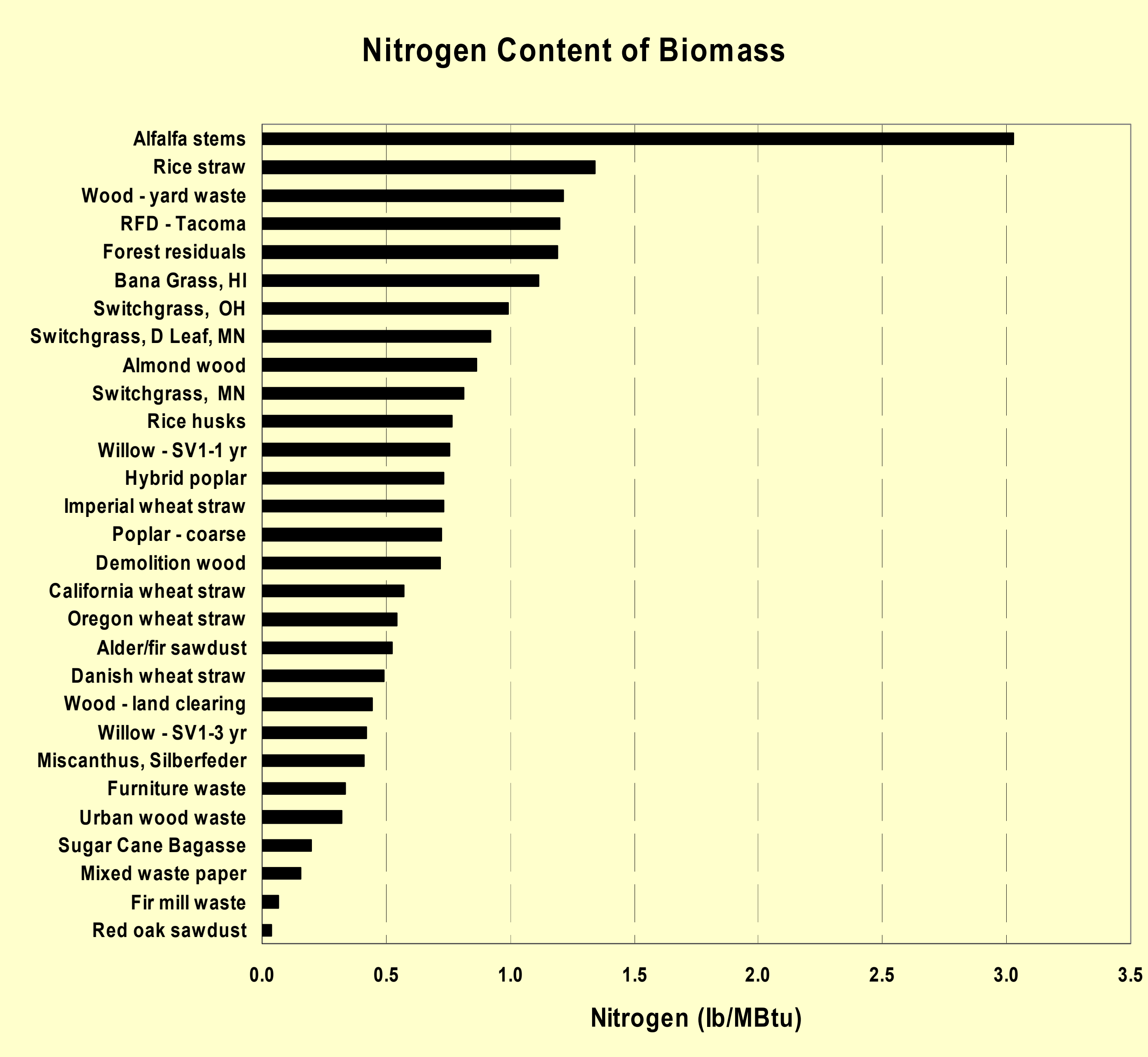

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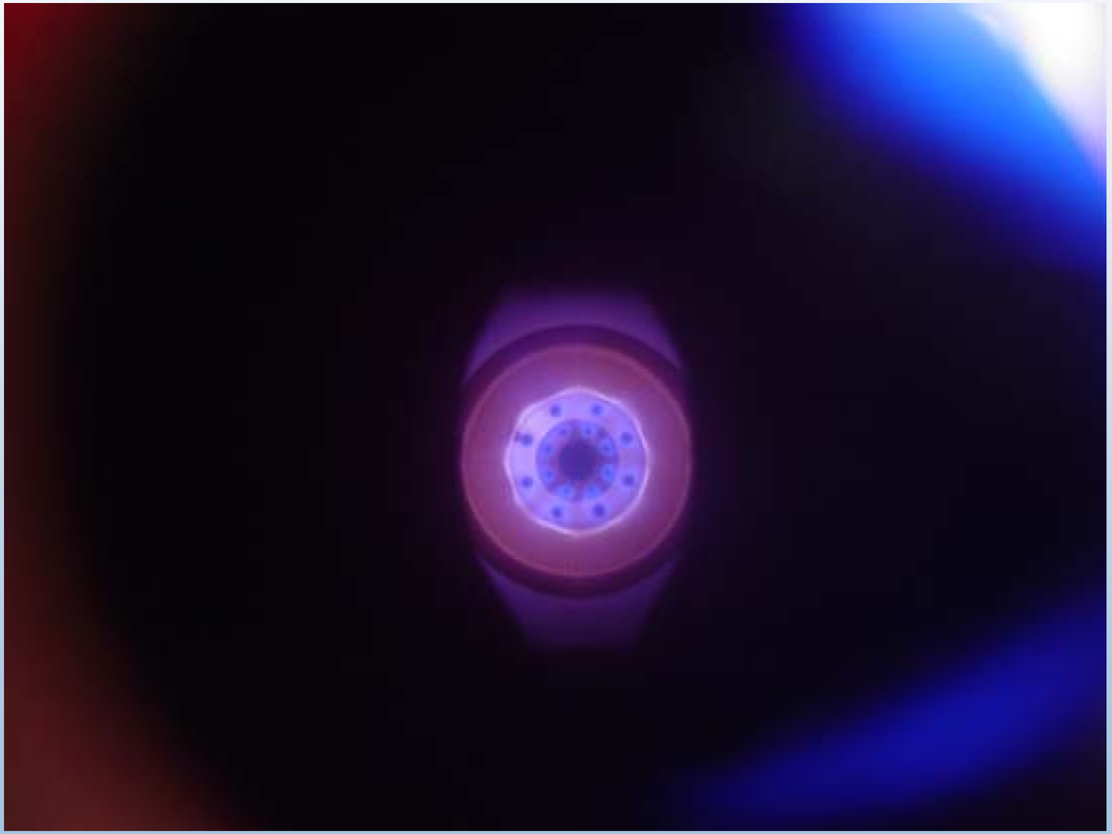
Combustion



Stages of Combustion of Solids

- Drying
- Devolatilization
  - ✓Pyrolysis
  - ✓Gasification
- Flaming Combustion
- Residual Char Combustion

Combustion Reactions

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

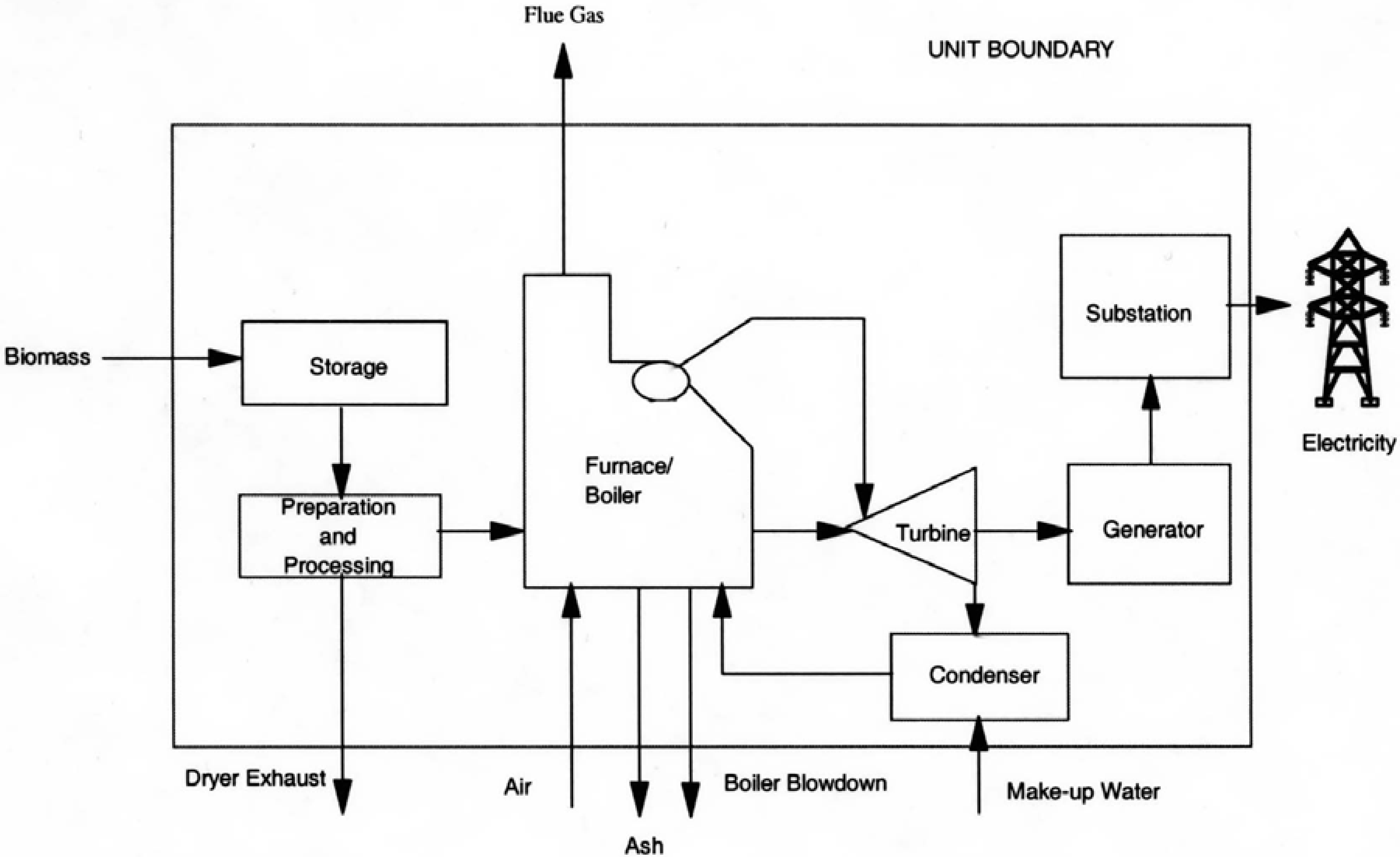
$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

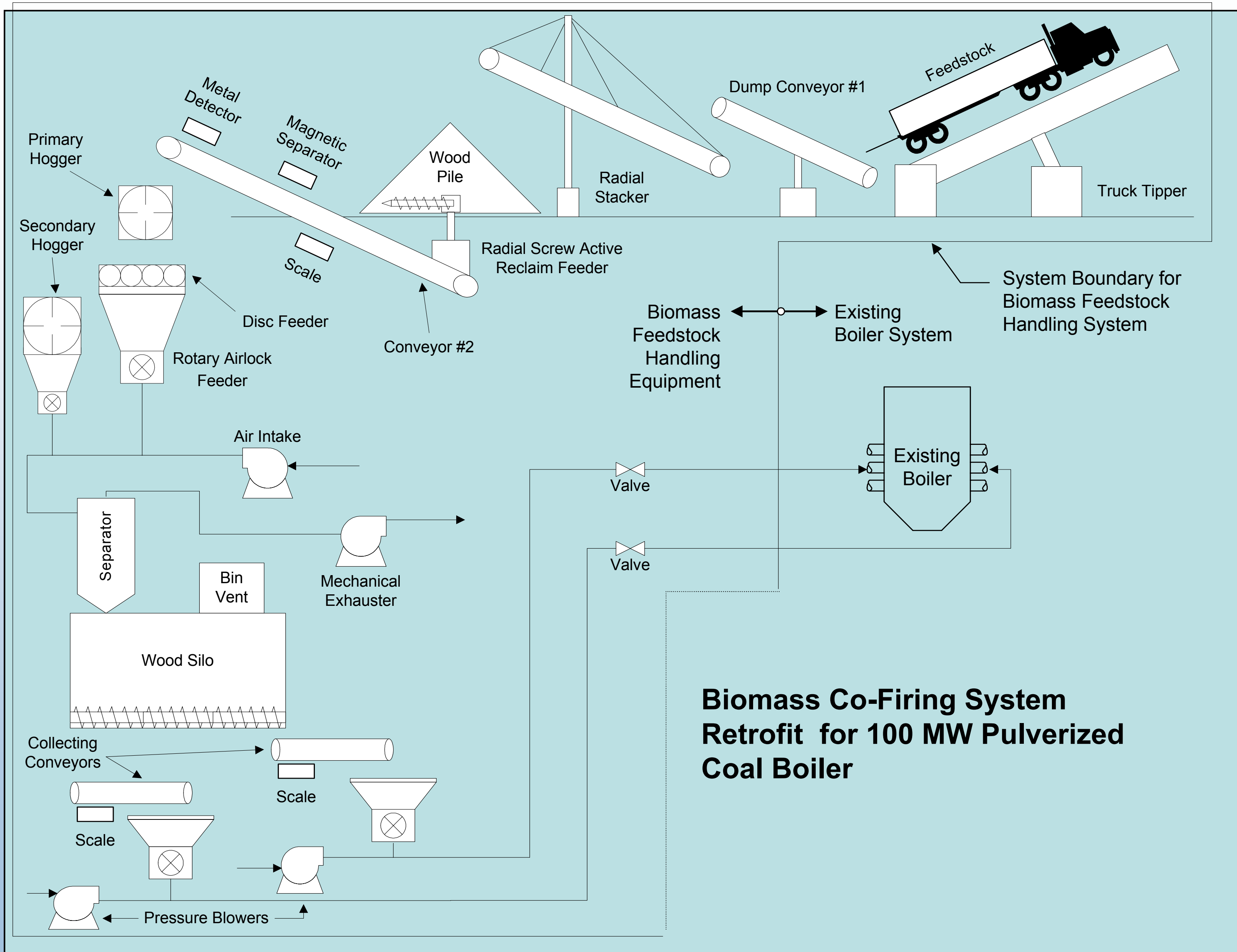
$$CH_4(g) + 2O_2 \rightarrow CO_2(g) + 2H_2O(l)$$

HHV = water as liquid
LHV = water as gas

Combustor Types

- Stoker Grate
- Fluid Bed
- Circulating Fluid Bed
- Entrained Flow

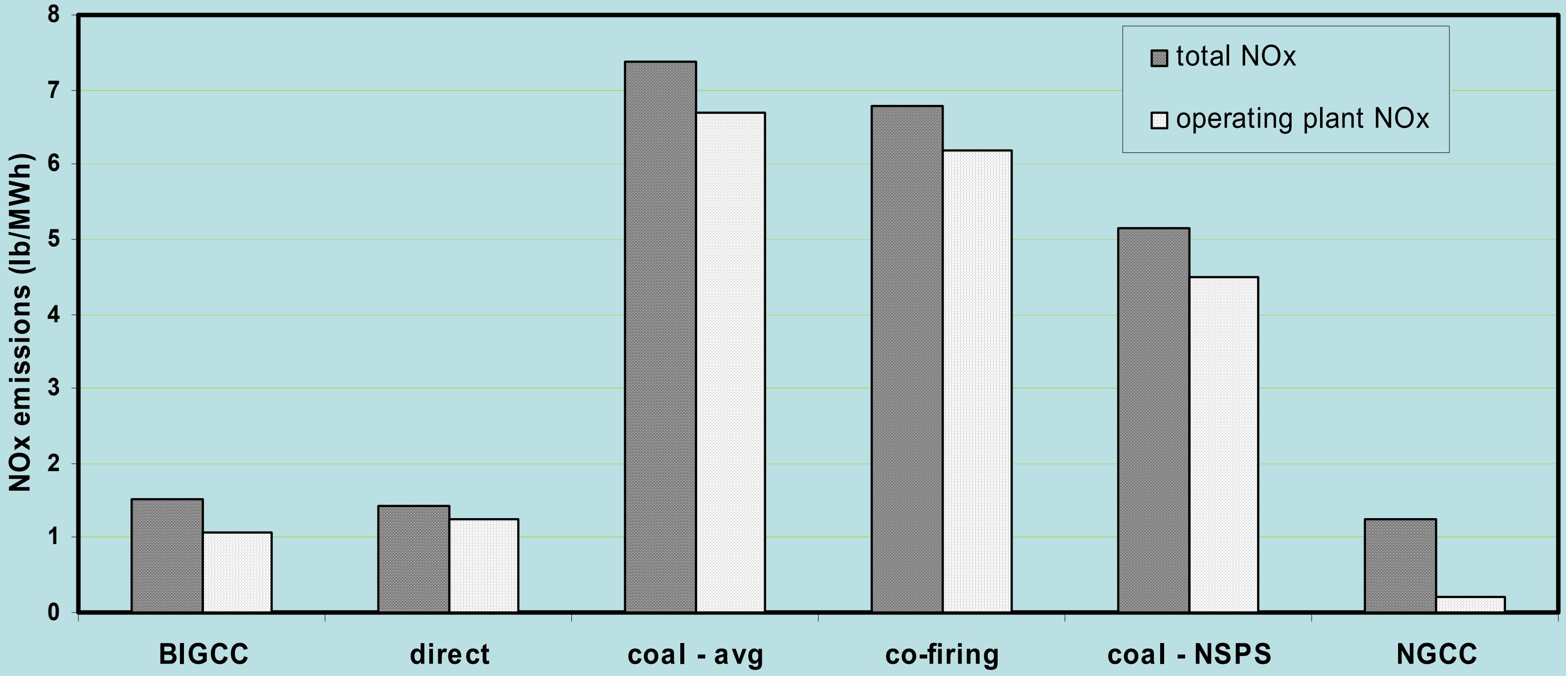

Flue Gas
UNIT BOUNDARY
Substation
Biomass
Storage
Electricity
Furnace/
Boiler
Preparation
and
Processing
Turbine
Generator
Condenser
Dryer Exhaust
Air
Boiler Blowdown
Make-up Water
Ash


Metal Detector
Magnetic Separator
Wood Pile
Radial Stacker
Dump Conveyor #1
Feedstock
Truck Tipper
Primary Hogger
Secondary Hogger
Scale
Radial Screw Active Reclaim Feeder
Disc Feeder
Conveyor #2
Rotary Airlock Feeder
System Boundary for Biomass Feedstock Handling System
Biomass Feedstock Handling Equipment
Existing Boiler System
Air Intake
Separator
Mechanical Exhauster
Valve
Existing Boiler
Valve
Bin Vent
Wood Silo
Collecting Conveyors
Scale
Scale
Pressure Blowers
Biomass Co-Firing System Retrofit for 100 MW Pulverized Coal Boiler

Direct Air Emissions from Wood Residue Facilities by Boiler Type (lb/MWh)

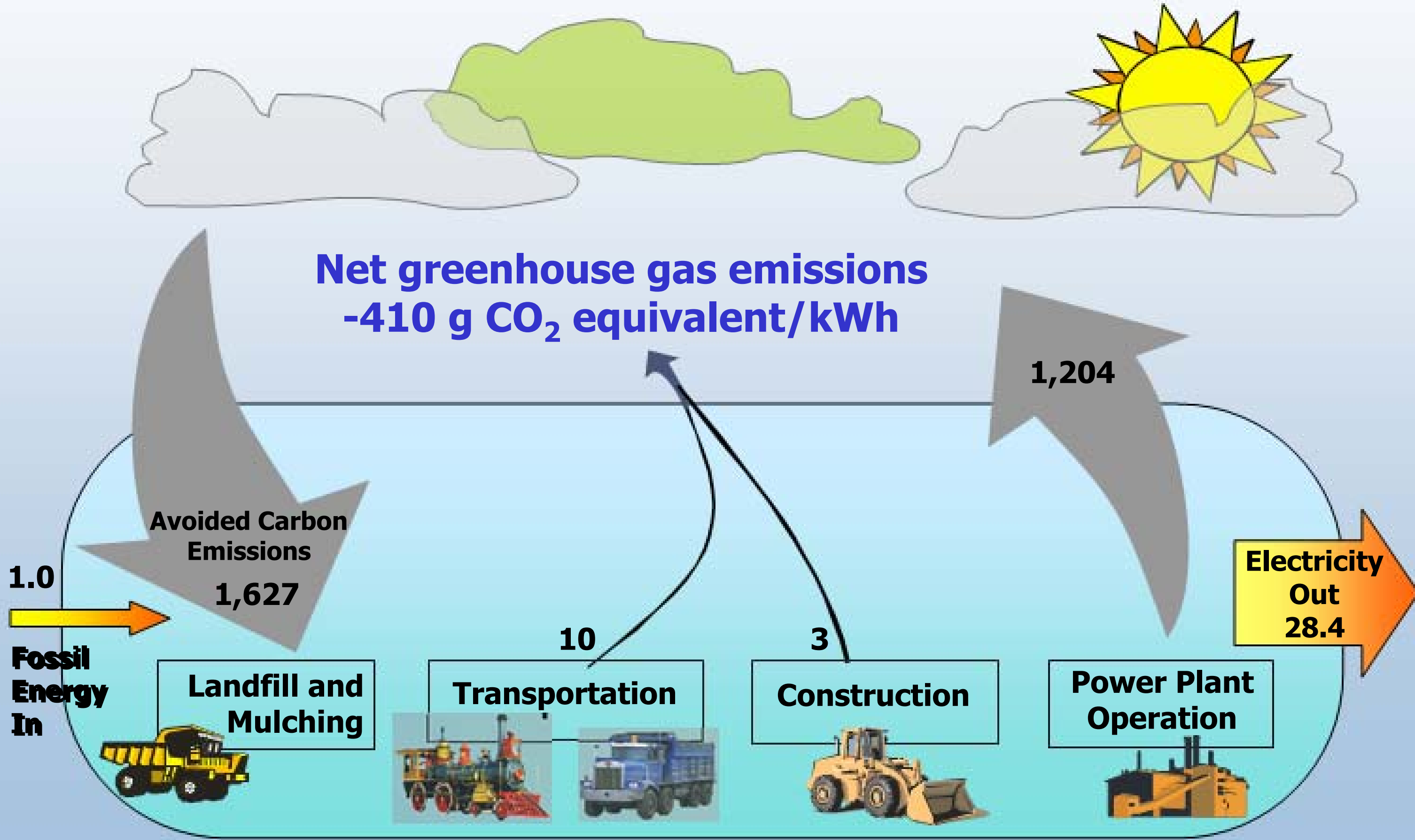
	SO_X	NO_X	CO	PM-10[1]	Comments
Biomass Technology					
Stoker Boiler, Wood Residues (1,4)	0.08	2.1 (biomass type not specified)	12.2 (biomass type not specified)	0.50 (total particulates) (biomass type not specified)	Based on 23 California grate boilers, except for SO_2 (uncontrolled)
Fluidized Bed, Biomass (4)	0.08 (biomass type not specified)	0.9 (biomass type not specified)	0.17 (biomass type not specified)	0.3 (total particulates) (biomass type not specified)	Based on 11 California fluid bed boilers.
Energy Crops (Poplar) Gasification (a,b)	0.05 (**suggested** value based on SOx numbers for Stoker and FBC, adjusted by a factor of 9,180/13,800 to account for heat rate improvement)	1.10 to 2.2 (0.66 to 1.32 w /SNCR; 0.22 to 0.44 w ith SCR)	0.23	0.01 (total particulates)	Combustor flue gas goes through cyclone and baghouse. Syngas goes through scrubber and baghouse before gas turbine. No controls on gas turbine.
Coal Technology					
Bituminous Coal, Stoker Boiler (f)	20.2 1 wt% S coal	5.8	2.7	0.62	PM Control only (baghouse)
Pulverized Coal Boiler (d)	14.3	6.89	0.35	0.32 (total particulates)	Average US PC boiler (typically:baghouse, limestone FGC)
Cofiring 15% Biomass (d2)	12.2	6.17	0.35	0.32 (total particulates)	?
Fluidized Bed, Coal (f)	3.7 (1 w t% S coal Ca/S = 2.5)	2.7	9.6	0.30	Baghouse for PM Control, Ca sorbents used for SO_x
Natural Gas Technology					
4-Stroke NG Reciprocating Engine (g)	0.006	7.96-38.3 (depends on load and air:fuel ratio)	2.98-35.0 (depends on load and air:fuel ratio)	0.09-0.18 (depends on load and air:fuel ratio)	No control except PCC at high-end of PM-10 range
Natural Gas Turbine (e)	0.009 (0.0007 w t% S)	1.72	0.4	.09 (total particulates)	Water-steam injection only
Natural Gas Combined Cycle (c,e)	0.004	0.91 (0.21 w / SCR)	0.06	0.14 (total particulates)	Water-steam injection only

NOx Emissions - Life Cycle Total and Plant Operating Emissions



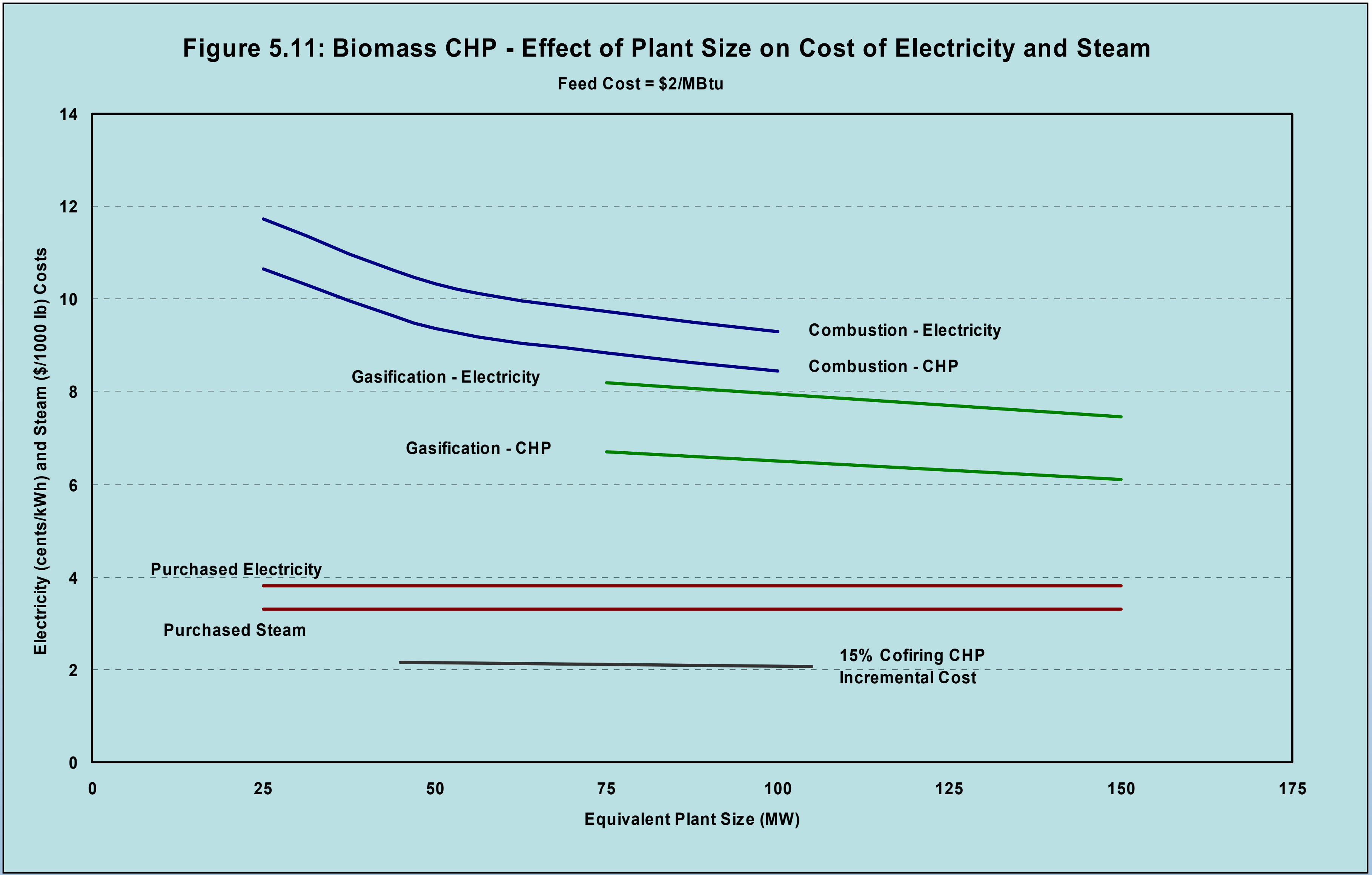
Life Cycle CO2 and Energy Balance for a Direct-Fired Biomass System

Current biomass power industry



Direct-Fired Biomass Residue System

134% carbon closure



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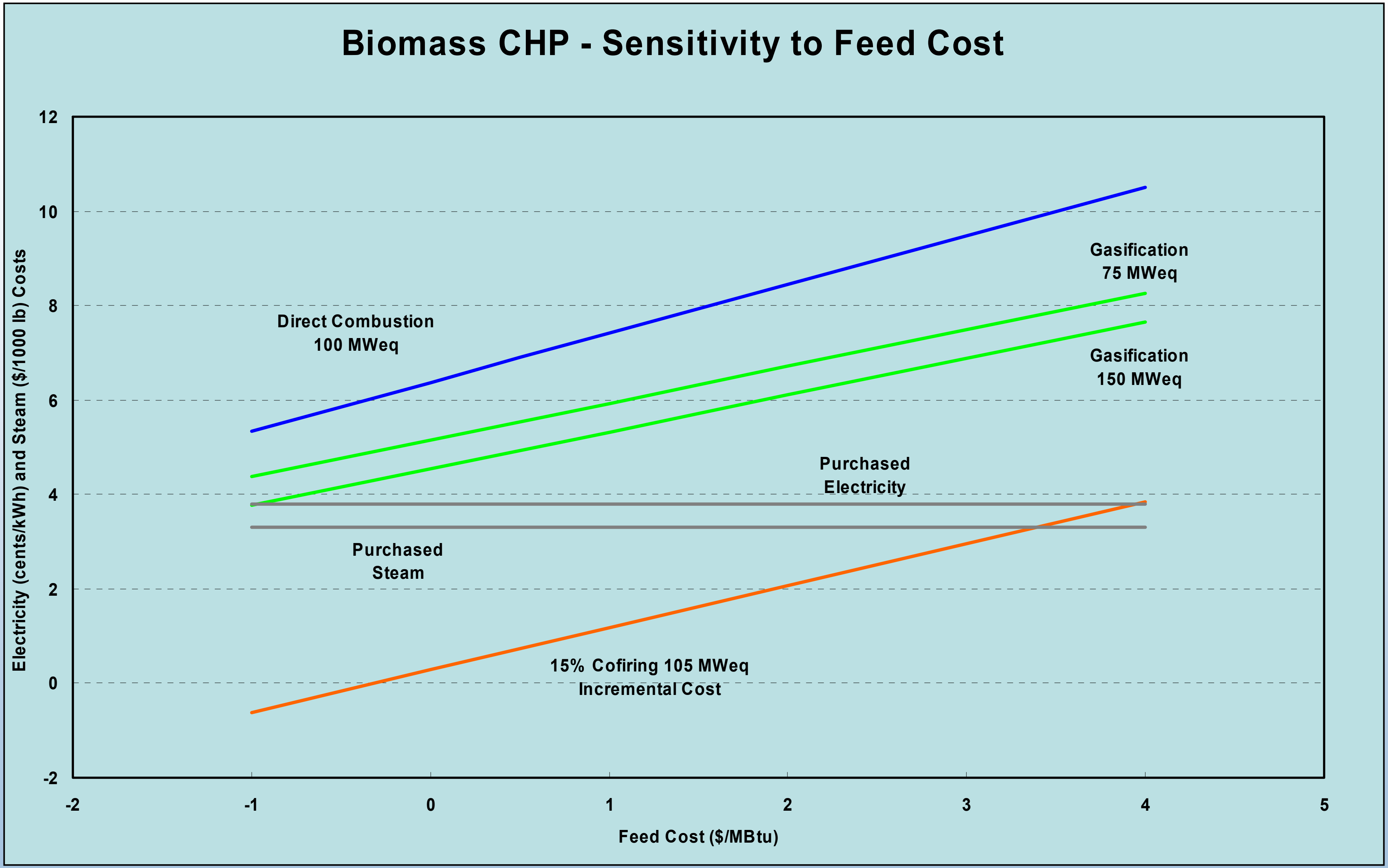

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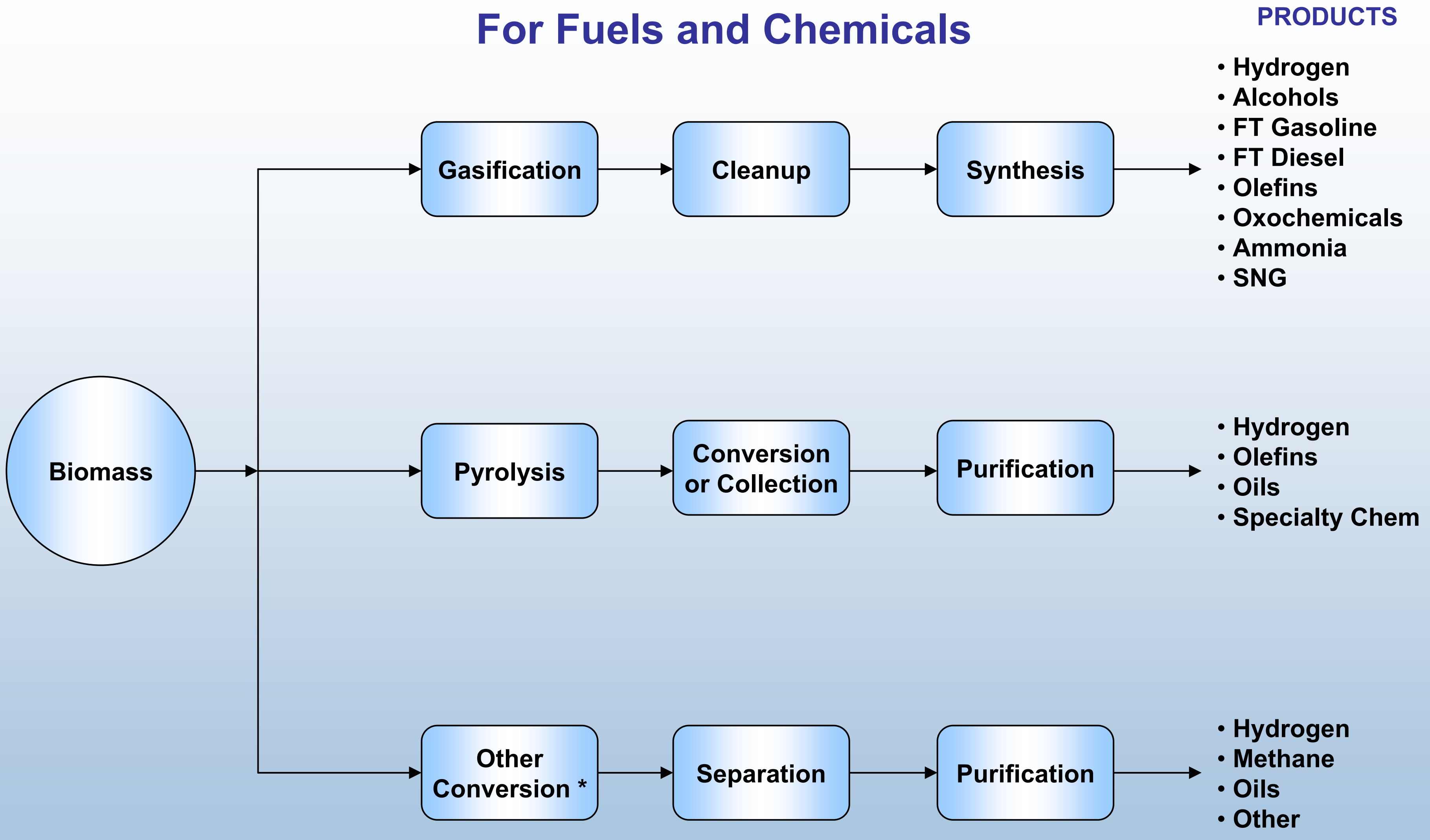
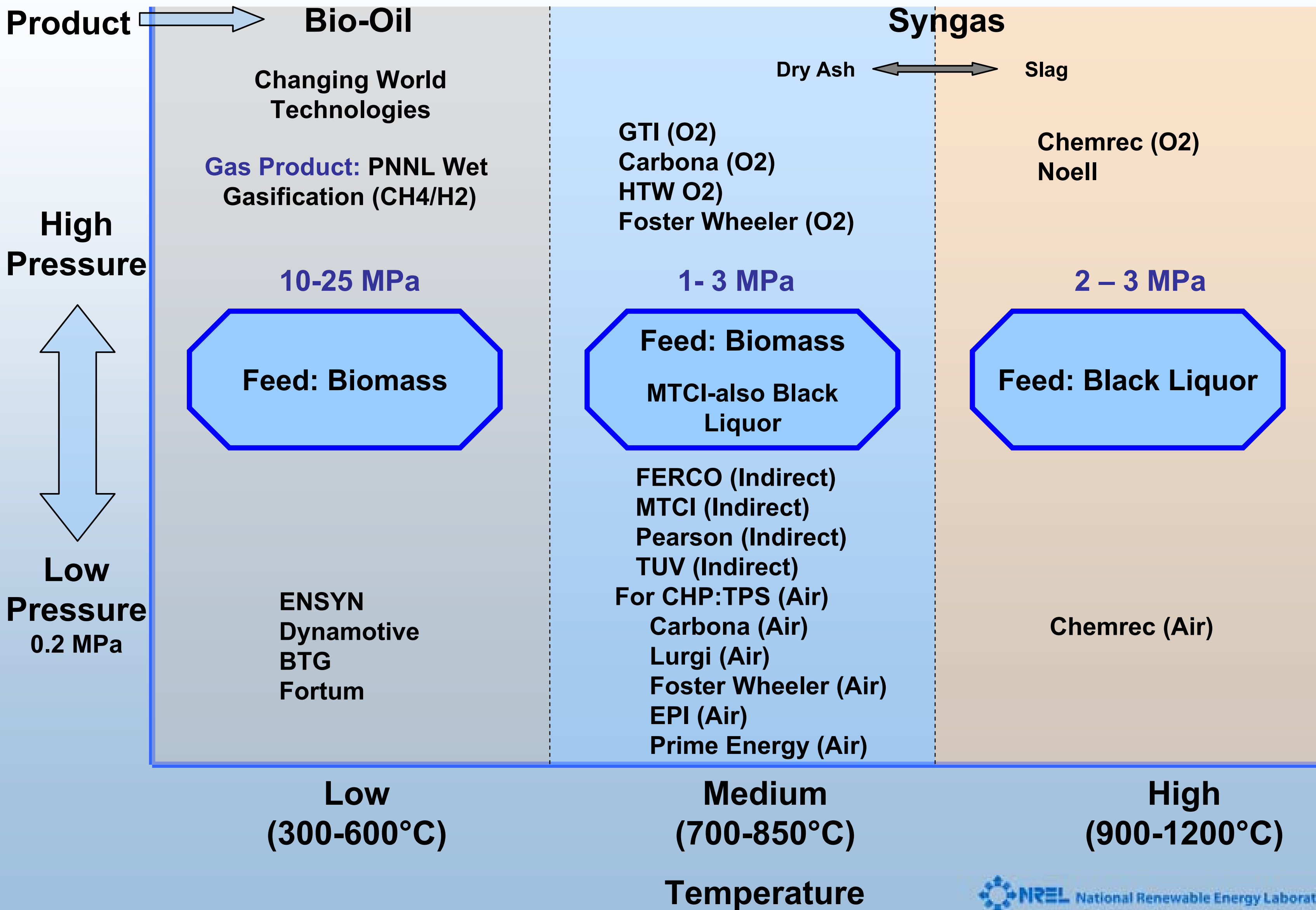
Biomass Thermochemical Conversion For Fuels and Chemicals



* Examples: Hydrothermal Processing, Liquefaction, Wet Gasification

Thermochemical Conversion
Of Biomass and Black Liquor



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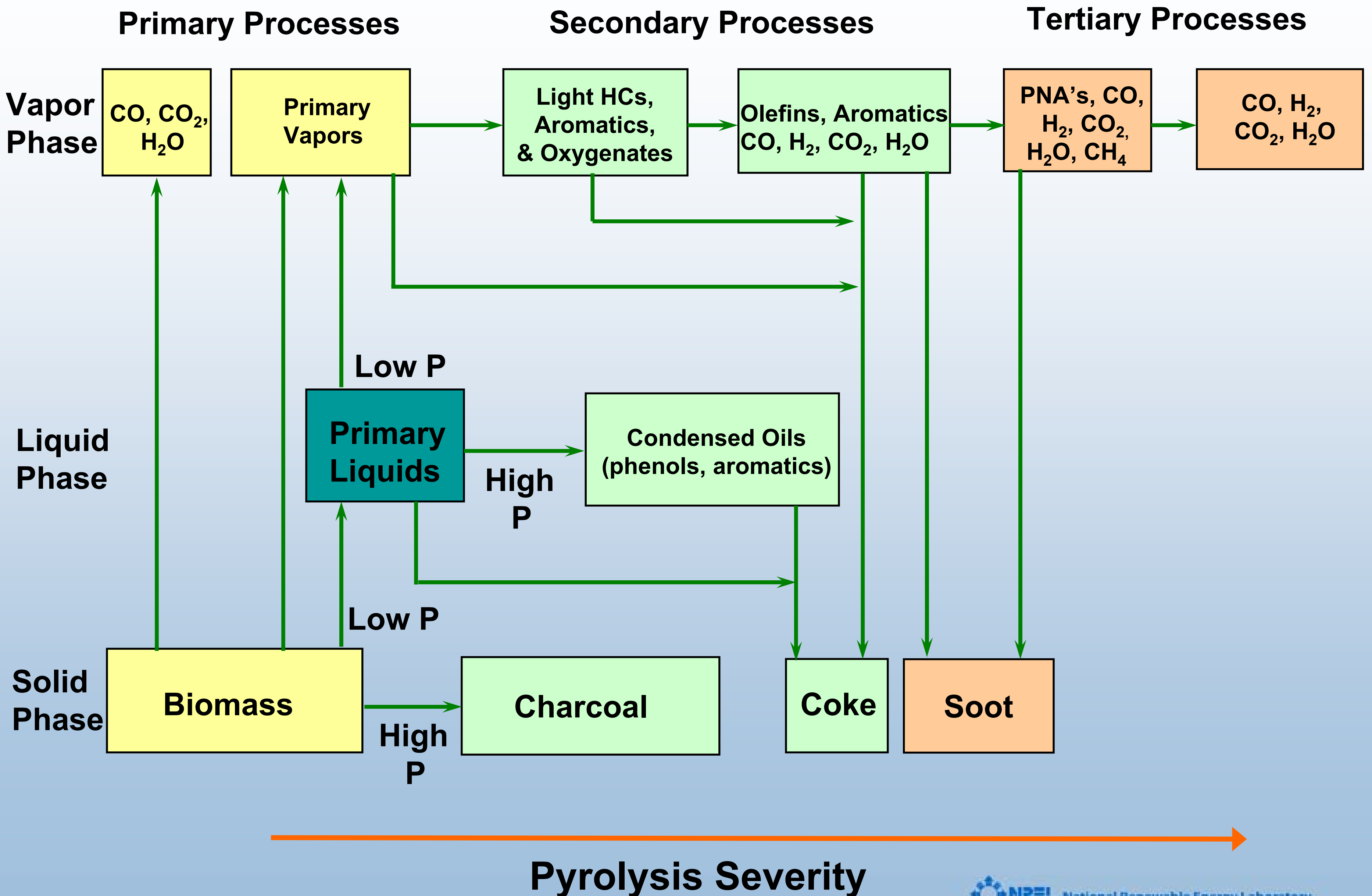


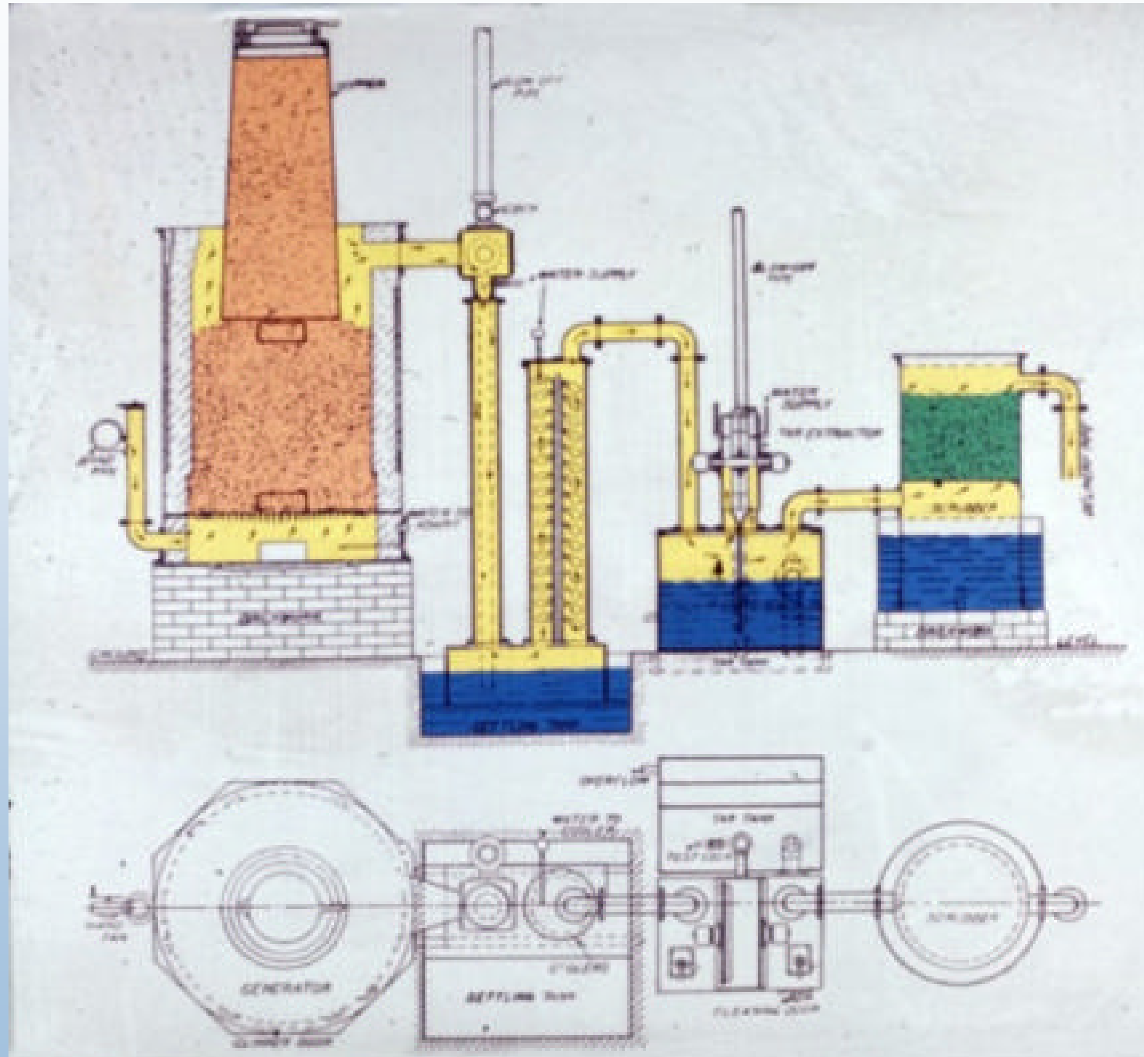
Primary Processes
Secondary Processes
Tertiary Processes
Vapor Phase
CO, CO_2, H_2O
Primary Vapors
Light HCs, Aromatics, & Oxygenates
Olefins, Aromatics CO, H_2, CO_2, H_2O
PNA's, CO, H_2, CO_2, H_2O, CH_4
CO, H_2, CO_2, H_2O
Low P
Liquid Phase
Primary Liquids
High P
Condensed Oils (phenols, aromatics)
Low P
Solid Phase
Biomass
High P
Charcoal
Coke
Soot
Pyrolysis Severity

Mixed Oxygenates (400 °C) → Phenolic Ethers (500 °C) → Alkyl Phenolics (600 °C) → Heterocyclic Ethers (700 °C) → PAH (800 °C) → Larger PAH (900 °C)

Conventional Flash Pyrolysis (450 - 500°C)	Hi-Temperature Flash Pyrolysis (600 - 650°C)	Conventional Steam Gasification (700 - 800°C)	Hi-Temperature Steam Gasification (900 - 1000°C)
Acids Aldehydes Ketones Furans Alcohols Complex Oxygenates Phenols Guaiacols Syringols Complex Phenols	Benzenes Phenols Catechols Naphthalenes Biphenyls Phenanthrenes Benzofurans Benzaldehydes	Naphthalenes Acenaphthylenes Fluorenes Phenanthrenes Benzaldehydes Phenols Naphthofurans Benzanthracenes	Naphthalene* Acenaphthylene Phenanthrene Fluoranthene Pyrene Acephenanthrylene Benzanthracenes Benzopyrenes 226 MW PAHs 276 MW PAHs
* At the highest severity, naphthalenes such as methyl naphthalene are stripped to simple naphthalene.			

Chemical Components in biomass tars (Elliott, 1988)

Gasification

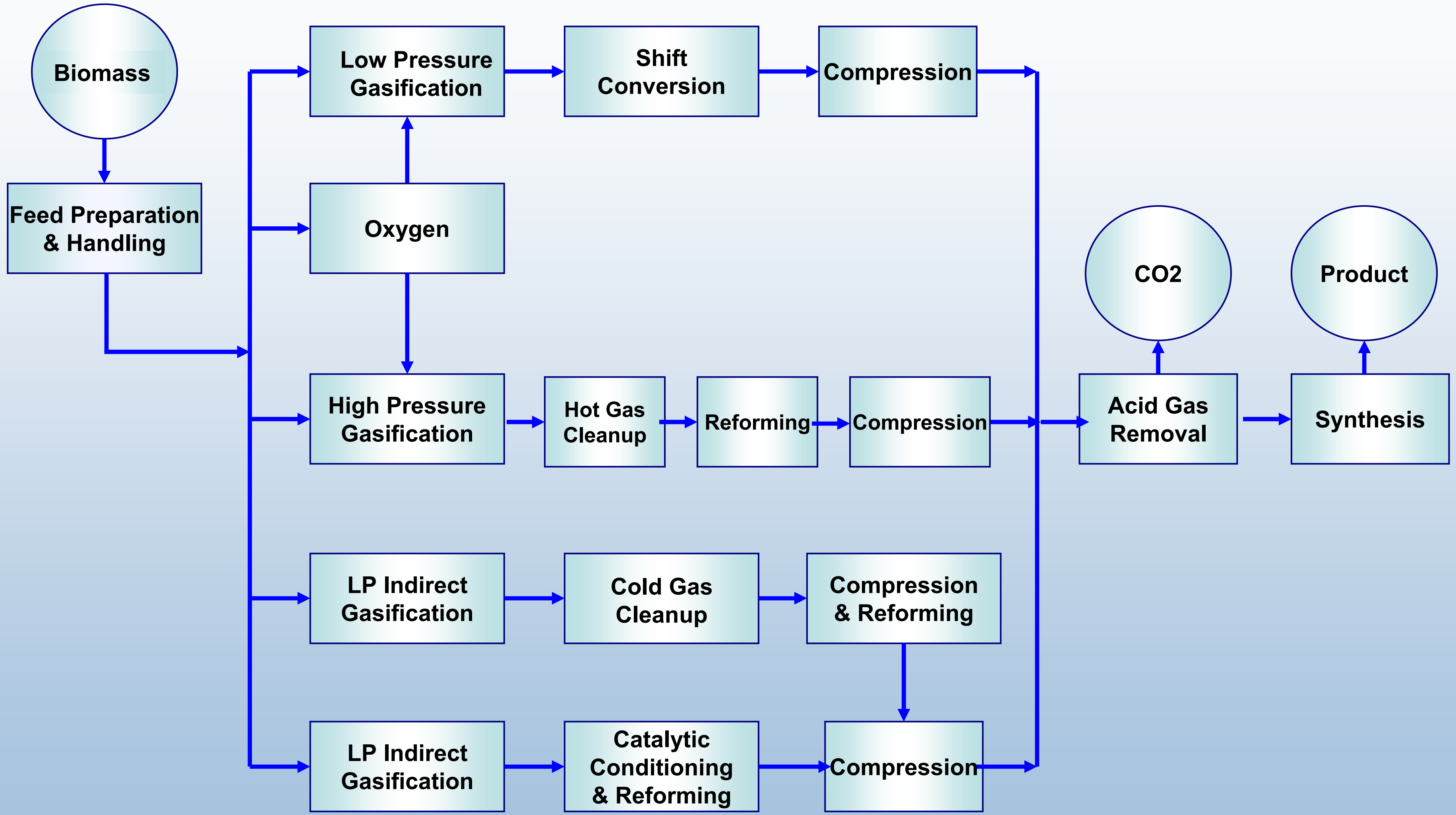


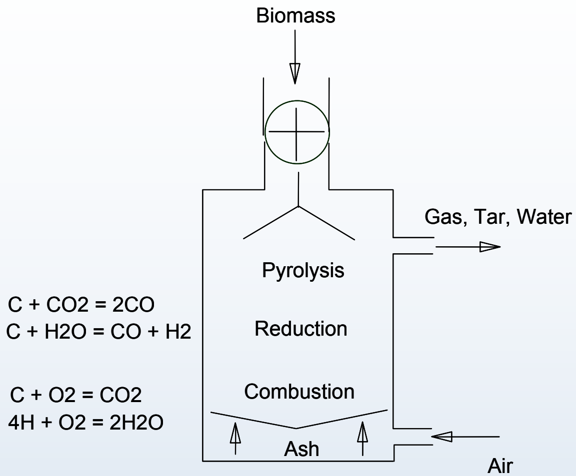
Circa 1898

1792 and all that

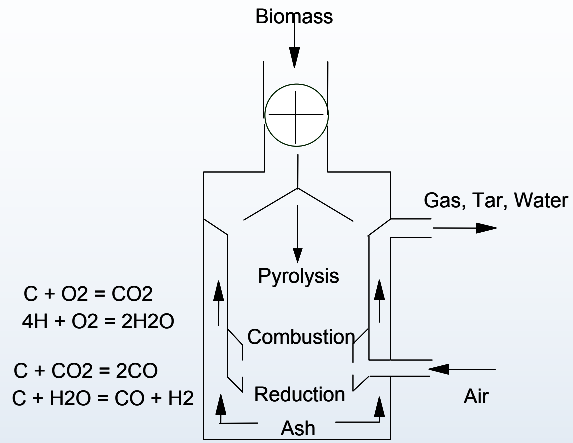
- Murdoch (1792) coal distillation
- London gas lights 1802
- Blau gas – Fontana 1780
- 1900s Colonial power
- MeOH 1913 BASF
- Fischer Tropsch 1920s
- Vehicle Gazogens WWII
- SASOL 1955 - Present
- GTL 1995 – Present
- Hydrogen – Future?

Representative Gasification Pathways

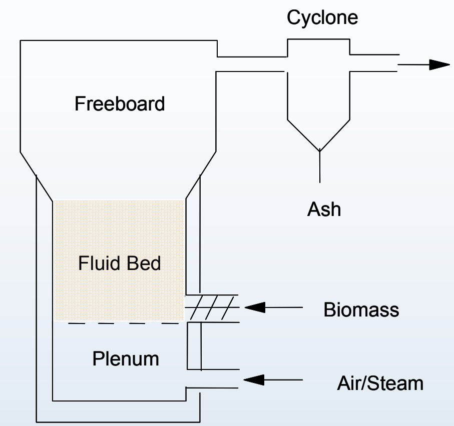




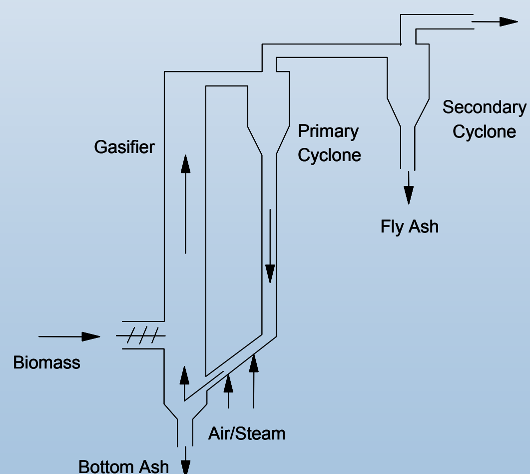
Updraft Gasifier



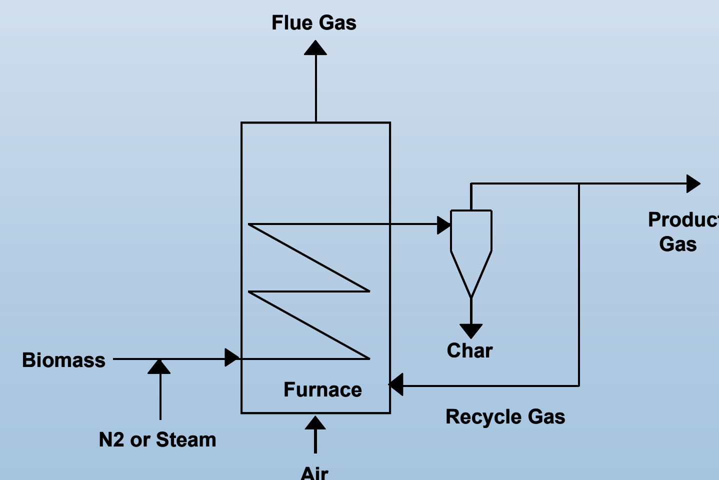
Downdraft Gasifier



Fluid-Bed Gasifier



Circulating Fluid-Bed Gasifier



Entrained Flow Gasifier

Gasifier Types-Advantages and Disadvantages

Gasifier	Advantages	Disadvantages
Updraft	Mature for heat Small scale applications Can handle high moisture No carbon in ash	Feed size limits High tar yields Scale limitations Producer gas Slagging potential
Downdraft	Small scale applications Low particulates Low tar	Feed size limits Scale limitations Producer gas Moisture sensitive
Fluid Bed	Large scale applications Feed characteristics Direct/indirect heating Can produce syngas	Medium tar yield Higher particle loading
Circulating Fluid Bed	Large scale applications Feed characteristics Can produce syngas	Medium tar yield Higher particle loading
Entrained Flow	Can be scaled Potential for low tar Can produce syngas	Large amount of carrier gas Higher particle loading Potentially high S/C Particle size limits

Table 2: Gas composition for fluid bed and circulating fluid bed gasifiers

Gasifier	FERCO	Carbona	Princeton Model	IGT
Type	Indirect CFB	Air FB	Indirect FB	PFB
Agent	steam	air	steam	O2/steam
Bed Material	olivine	sand	none	alumina
Feed	wood chips	wood pellets	black liquor	wood chips
Gas Composition				
H2	26.2	21.70	29.4	19.1
CO	38.2	23.8	39.2	11.1
CO2	15.1	9.4	13.1	28.9
N2	2	41.6	0.2	27.8
CH4	14.9	0.08	13.0	11.2
C2+	4	0.6	4.4	2.0
GCV, MJ/Nm^3	16.3	5.4	17.2	9.2

Typical Gas Heating Values

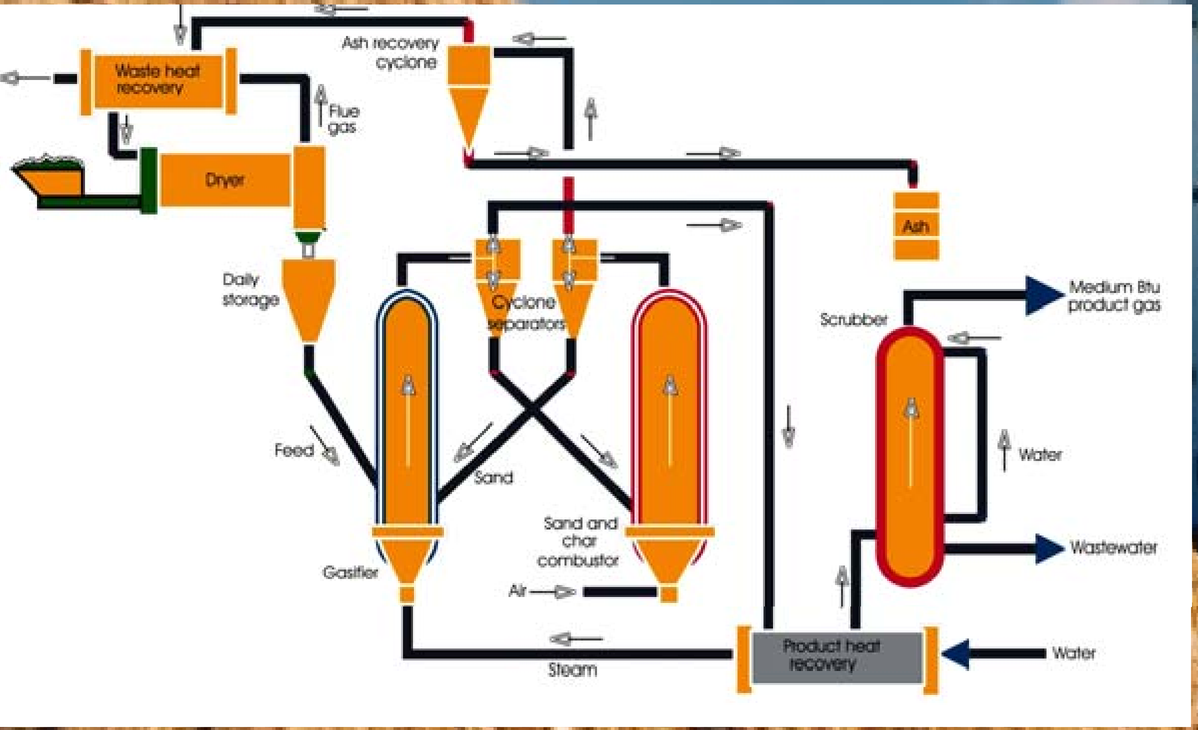
Gasifier	Inlet Gas	Product Gas Type	Product Gas HHV MJ/Nm^3
Partial Oxidation	Air	Producer Gas	7
Partial Oxidation	Oxygen	Synthesis Gas	10
Indirect	Steam	Synthesis Gas	15
		Natural Gas	38
		Methane	41

Biomass		Coal
↑	Oxygen	↓
↓	Sulfur	↑
↓	Ash	↑
↑	Alkali	↓
↑	H/C Ratio	↓
↓	Heating Value	↑
↑	Tar Reactivity	↓

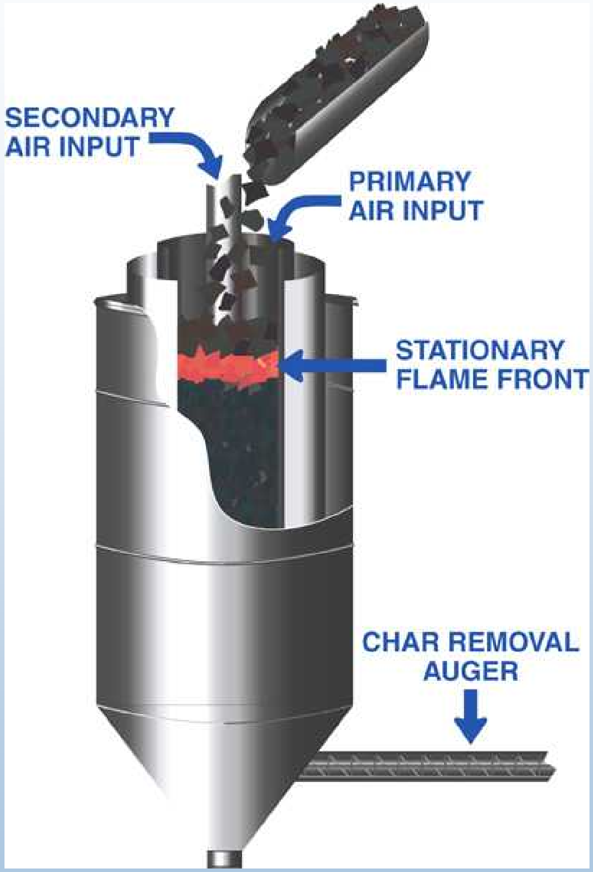
- Use coal gasifier cleanup technology for biomass
  - Issues
    - Coal cleanup designed for large, integrated plants
    - Extensive sulfur removal not needed for biomass
    - Biomass tars very reactive
    - Wet/cold cleanup systems produce significant waste streams that require cleanup/recovery – large plant needed for economy of scale for cleanup/recovery
    - Biomass particulates high in alkali
- Feed biomass to coal gasifiers
  - Issues
    - Feeding biomass (not just wood) – many commercial coal gasifiers are entrained flow requiring small particles
    - Gasifier refractory life/ash properties – biomass high in alkali
    - Character/reactivity of biomass tars may have unknown impact on chemistry/cleanup
    - Volumetric energy density a potential issue
    - Biomass reactivity – may react in feeder

FERCO GASIFIER- BURLINGTON, VT

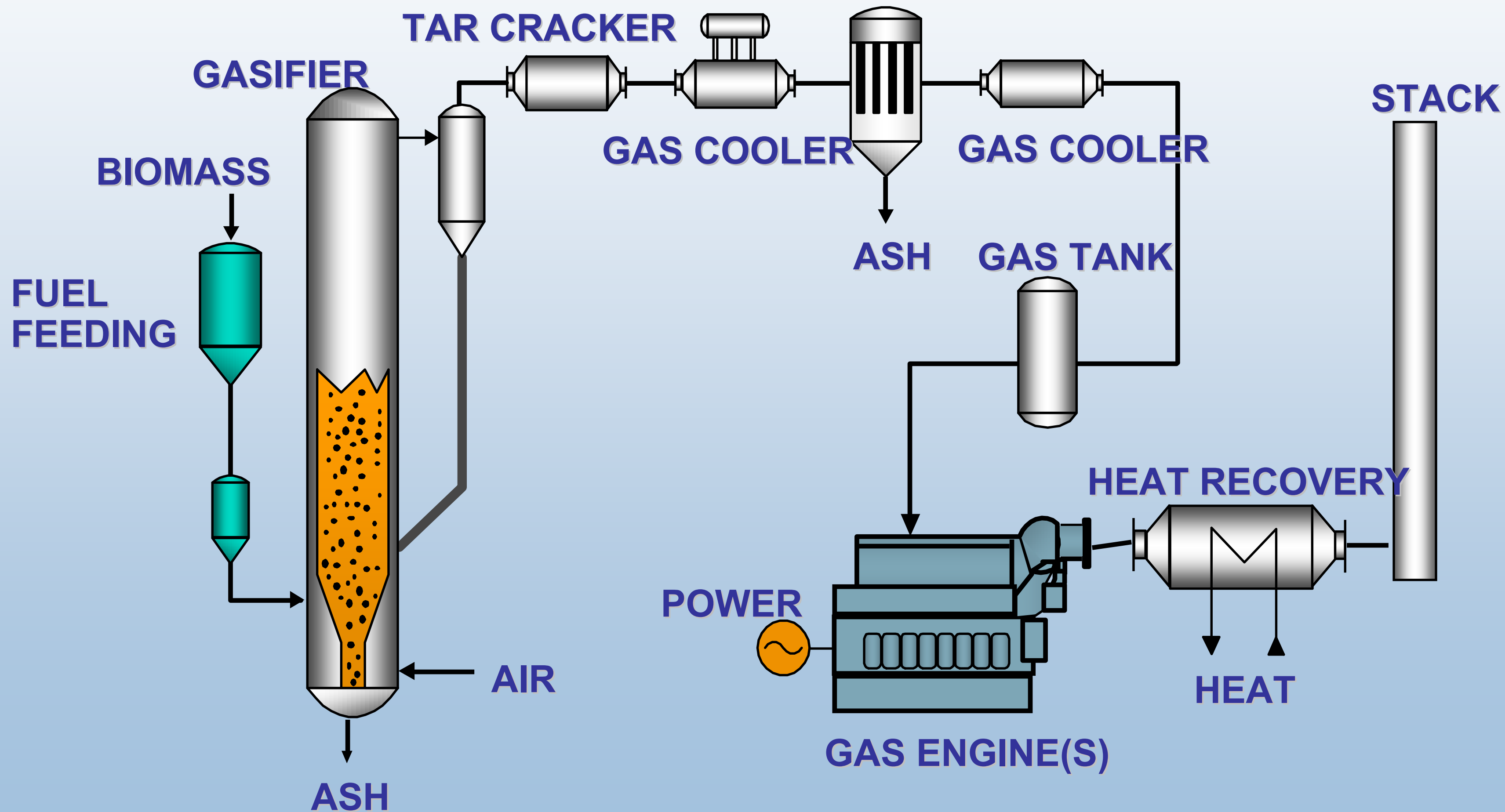
350 TPD

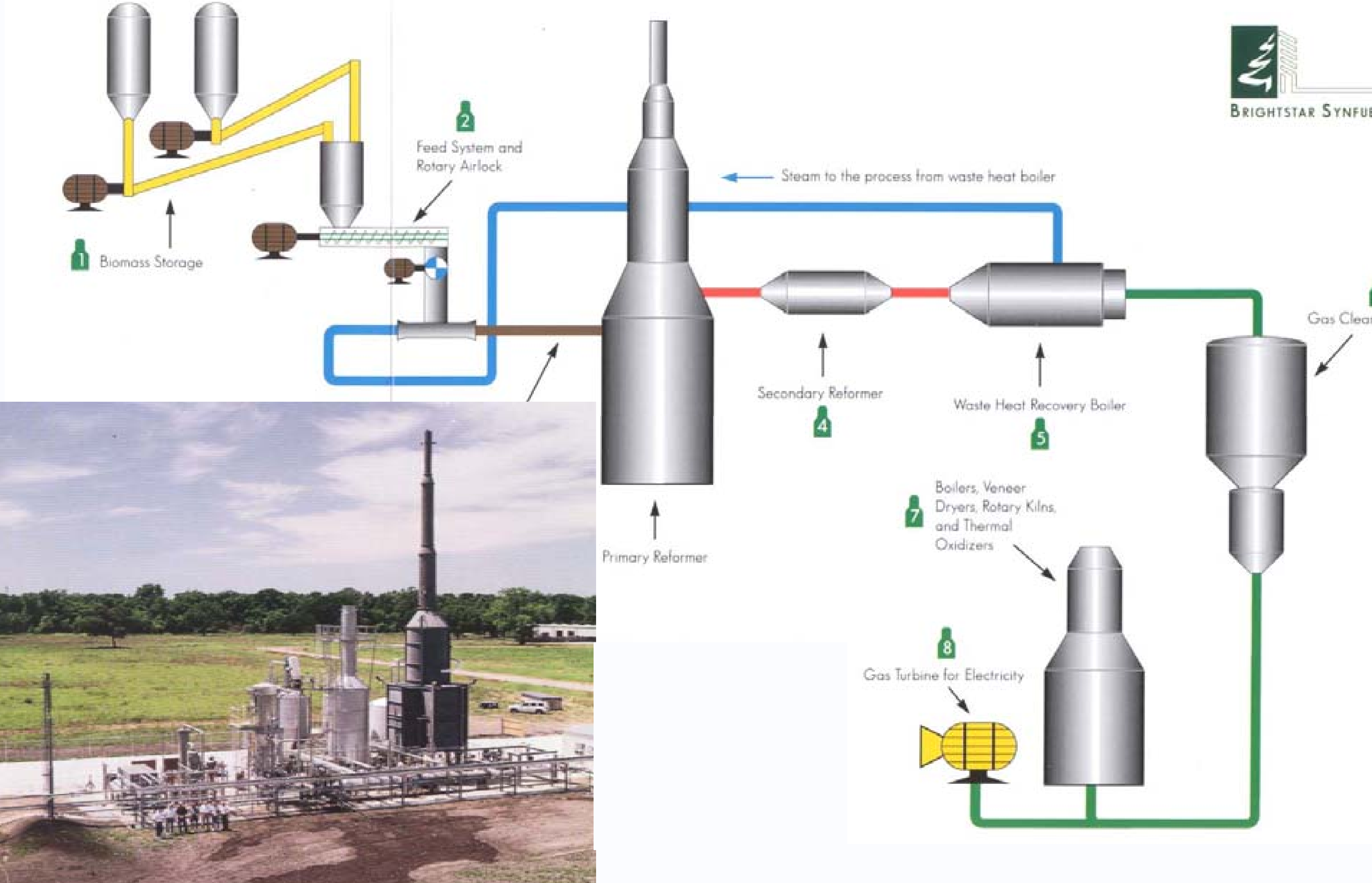


Community Power Corporation's BioMax 15 Modular Biopower System

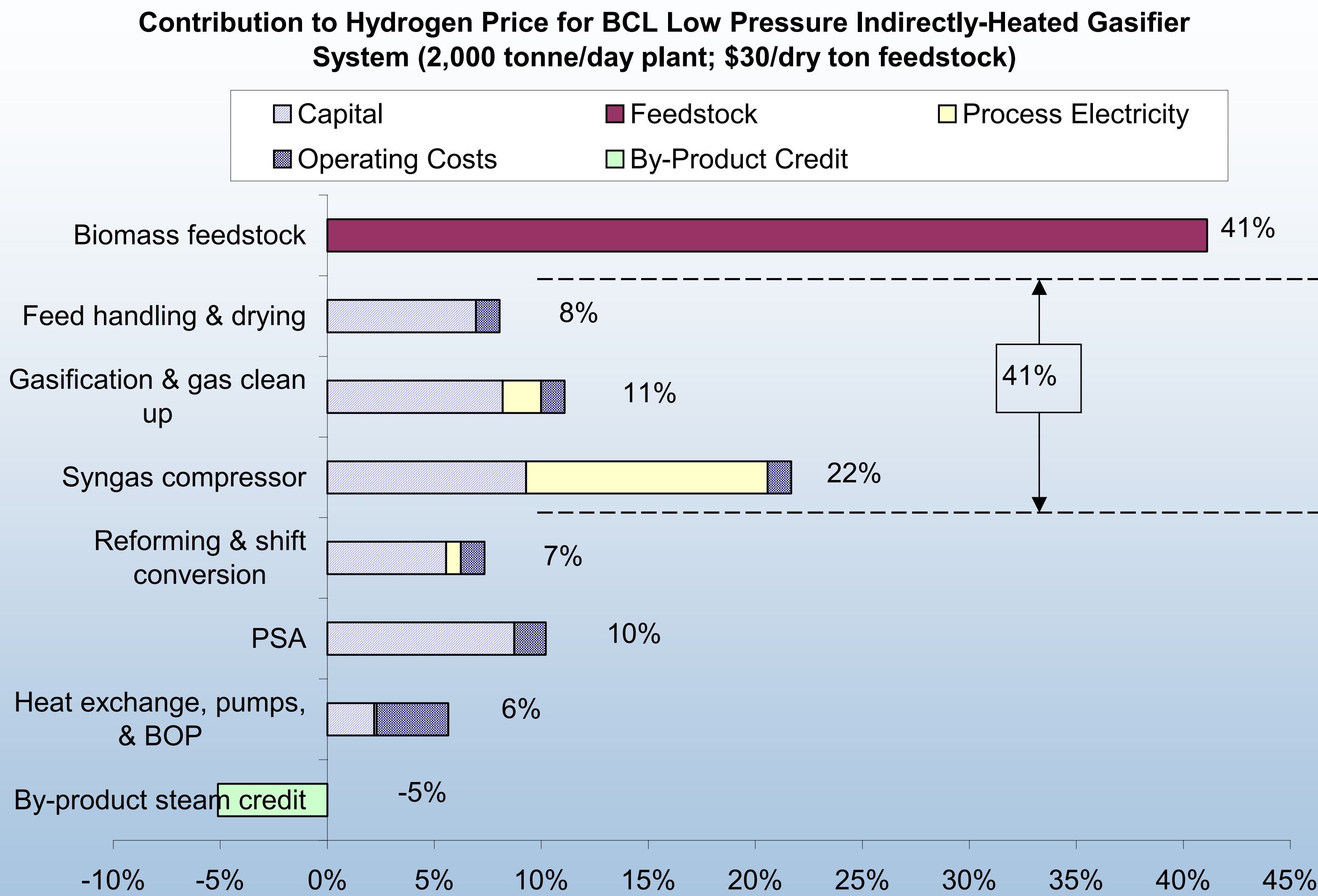


Carbona Project: Skive, Denmark

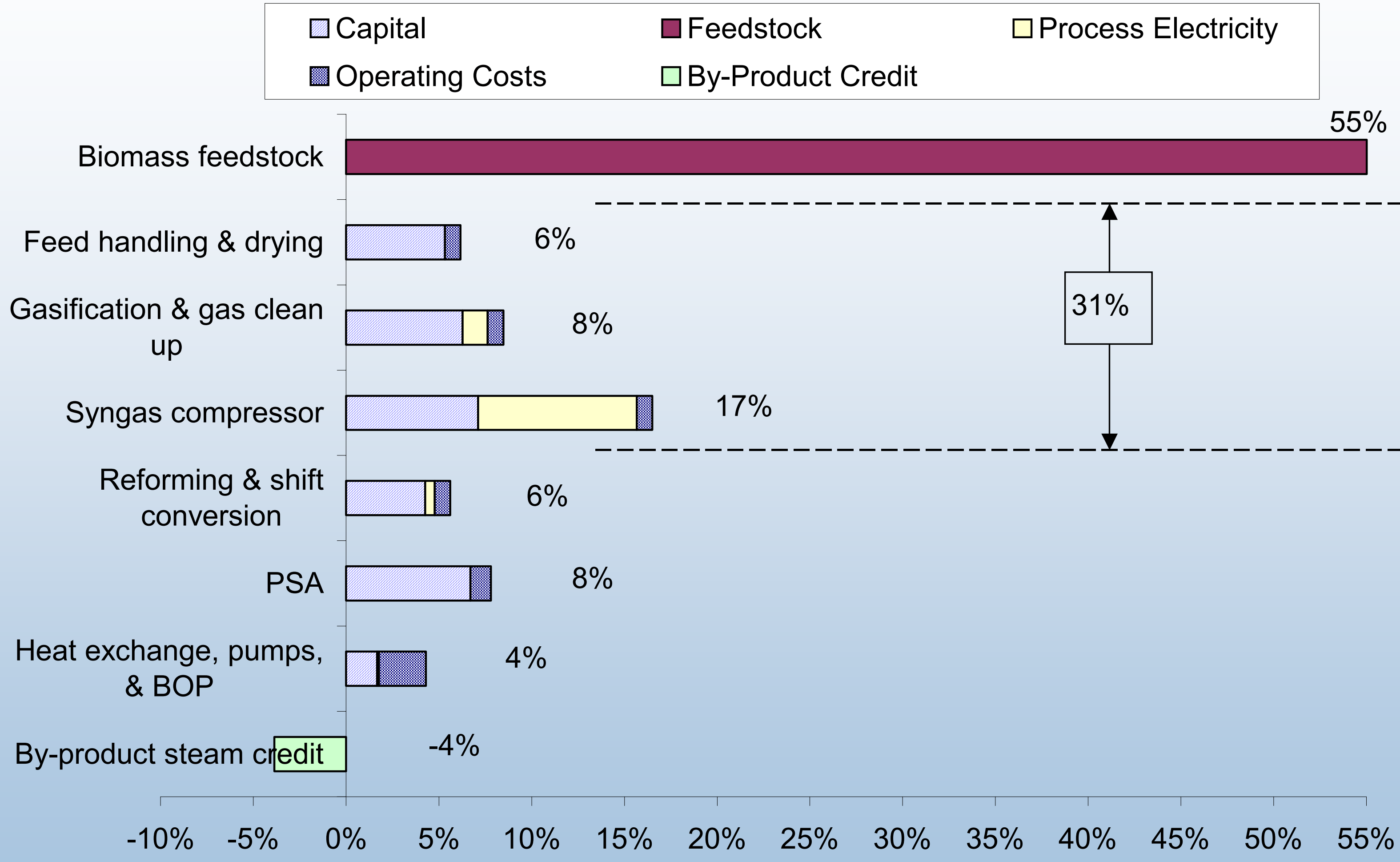




BSC Commercial Demonstration and Training Facility - St. Gabriel, LA

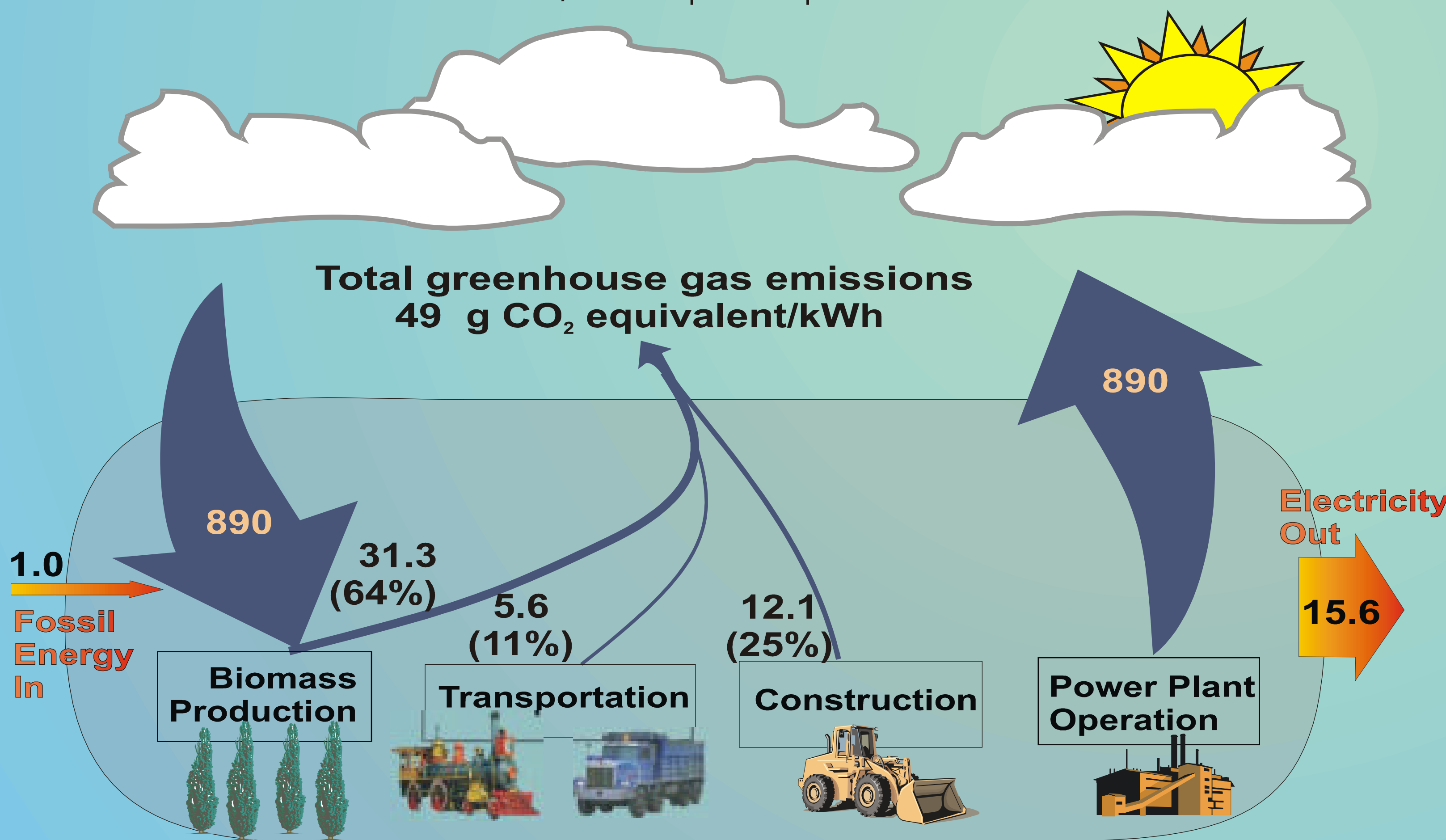

Contribution to Hydrogen Price for BCL Low Pressure Indirectly-Heated Gasifier System (2,000 tonne/day plant; $30/dry ton feedstock)
Capital
Feedstock
Process Electricity
Operating Costs
By-Product Credit
Biomass feedstock
41%
Feed handling & drying
8%
Gasification & gas clean up
11%
Syngas compressor
22%
Reforming & shift conversion
7%
PSA
10%
Heat exchange, pumps, & BOP
6%
By-product steam credit
-5%
41%
-10%
-5%
0%
5%
10%
15%
20%
25%
30%
35%
40%
45%

Contribution to Hydrogen Price for BCL Low Pressure Indirectly-Heated Gasifier System (2,000 tonne/day plant; $53/dry ton feedstock)



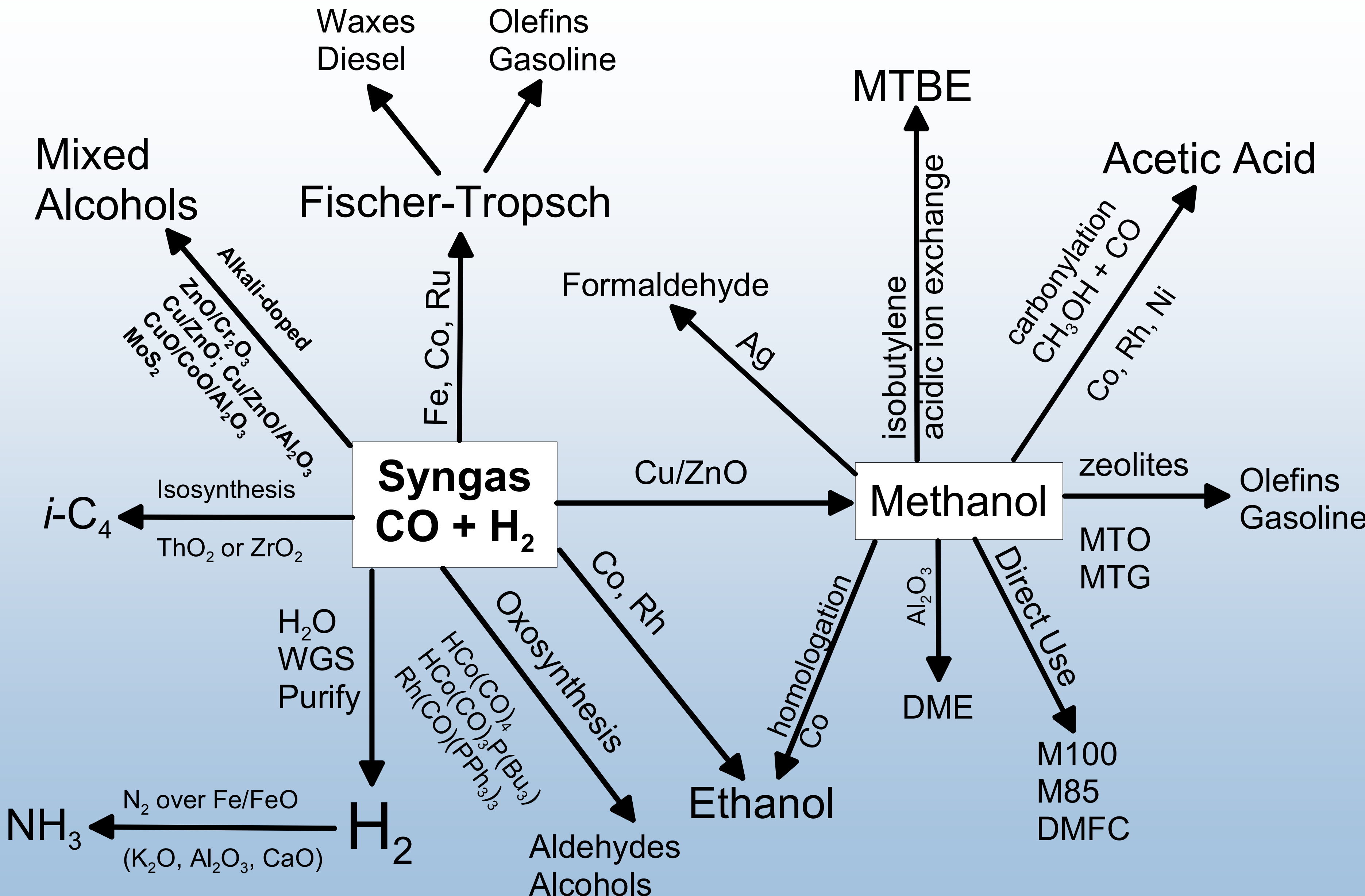
Life Cycle GWP and Energy Balance for Advanced IGCC Technology using Energy Crop Biomass

Future, wide-spread potential

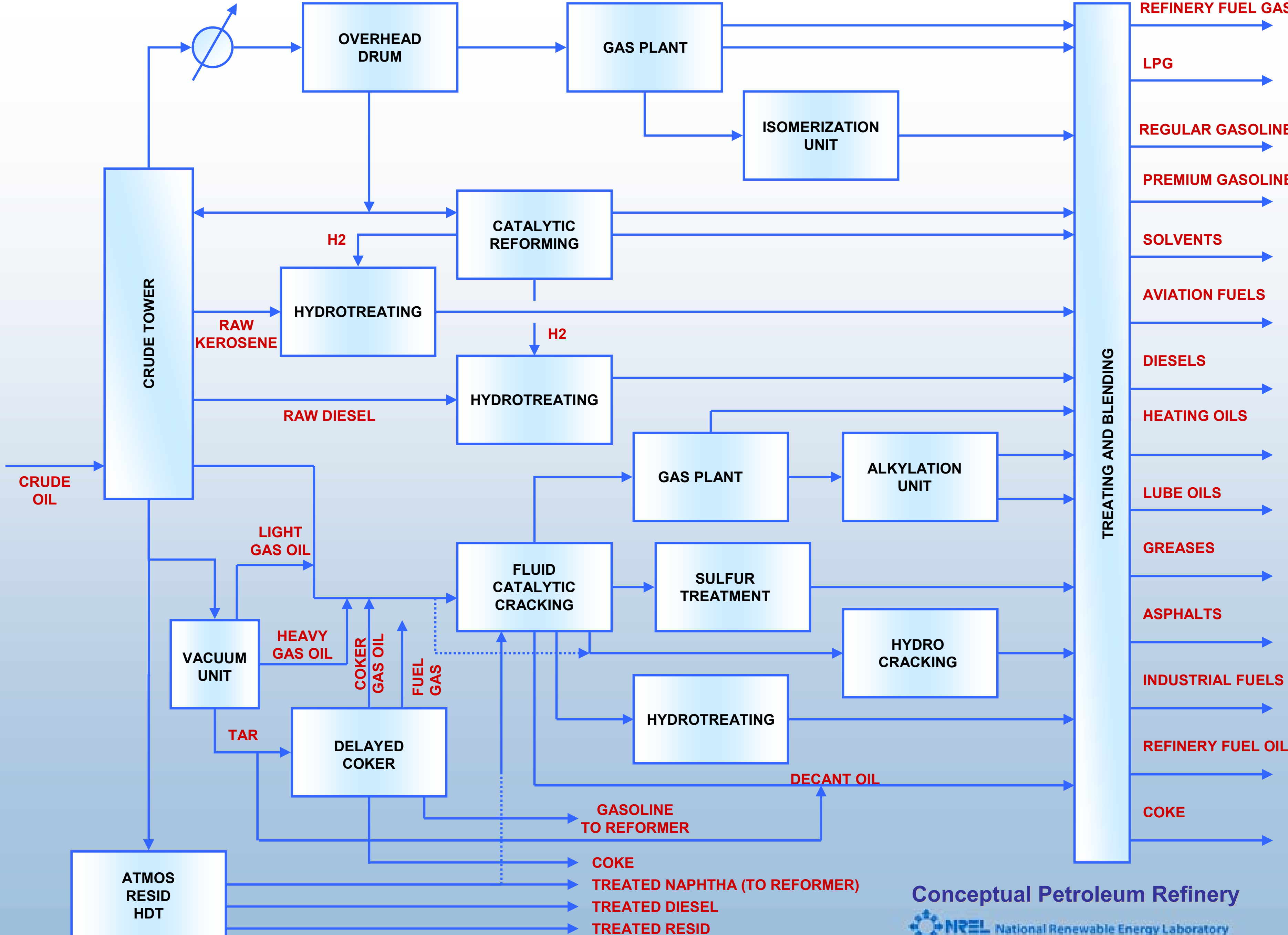


Biomass Power System

95% carbon closure

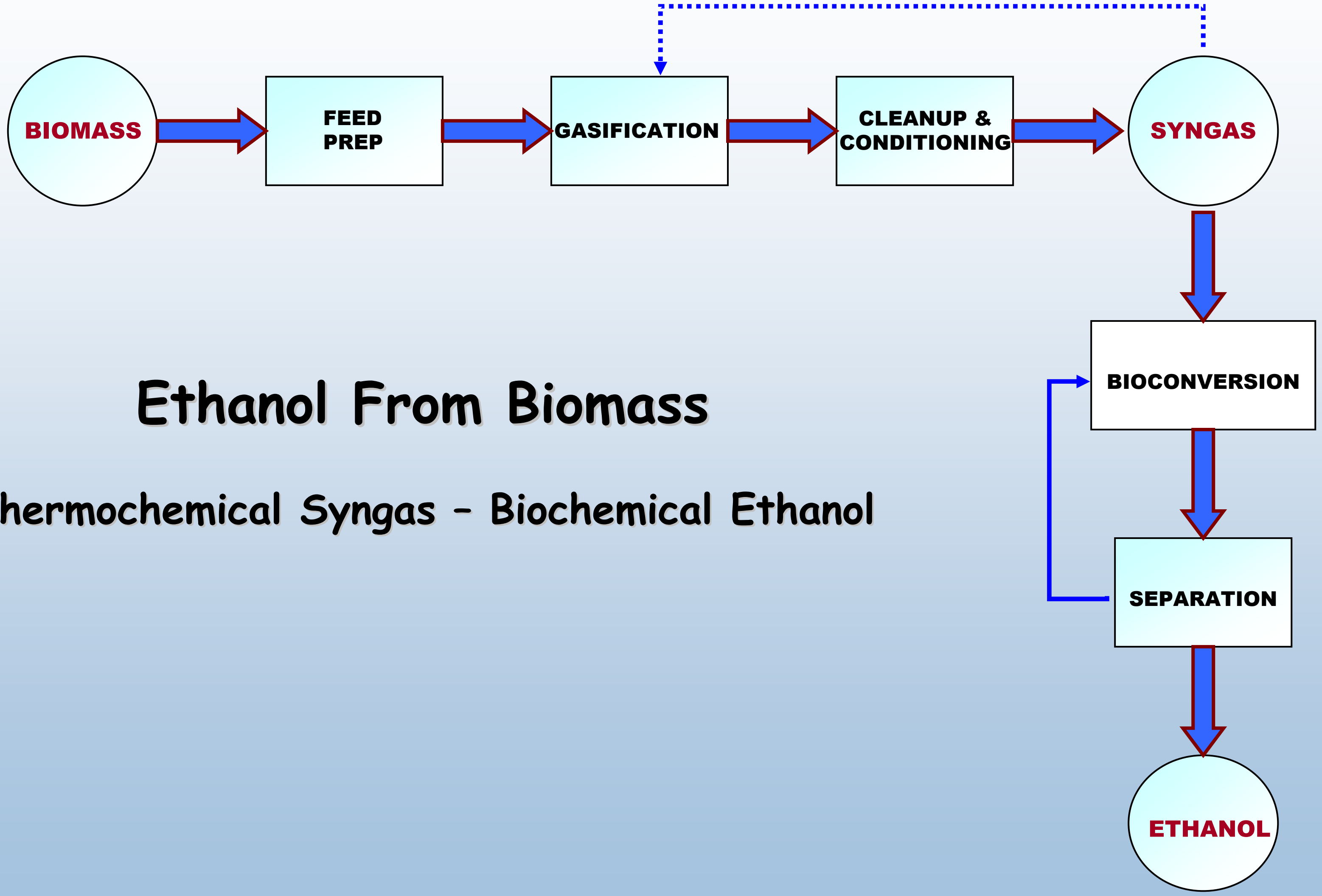


Waxes
Diesel
Olefins
Gasoline
MTBE
Mixed Alcohols
Fischer-Tropsch
Acetic Acid
Alkali-doped
ZnO/Cr2O3
Cu/ZnO; Cu/ZnO/Al2O3
CuO/CoO/Al2O3
MoS2
Fe, Co, Ru
Formaldehyde
Ag
isobutylene
acidic ion exchange
carbonylation
CH3OH + CO
Co, Rh, Ni
Syngas
CO + H2
Cu/ZnO
Methanol
zeolites
Olefins
Gasoline
MTO
MTG
Isosynthesis
i-C4
ThO2 or ZrO2
H2O
WGS
Purify
HCo(CO)4
HCo(CO)3P(Bu3)
Rh(CO)(PPh3)3
Oxosynthesis
Co, Rh
homologation
Co
Al2O3
DME
Direct Use
M100
M85
DMFC
N2 over Fe/FeO
NH3
(K2O, Al2O3, CaO)
H2
Aldehydes
Alcohols
Ethanol



Conceptual Petroleum Refinery

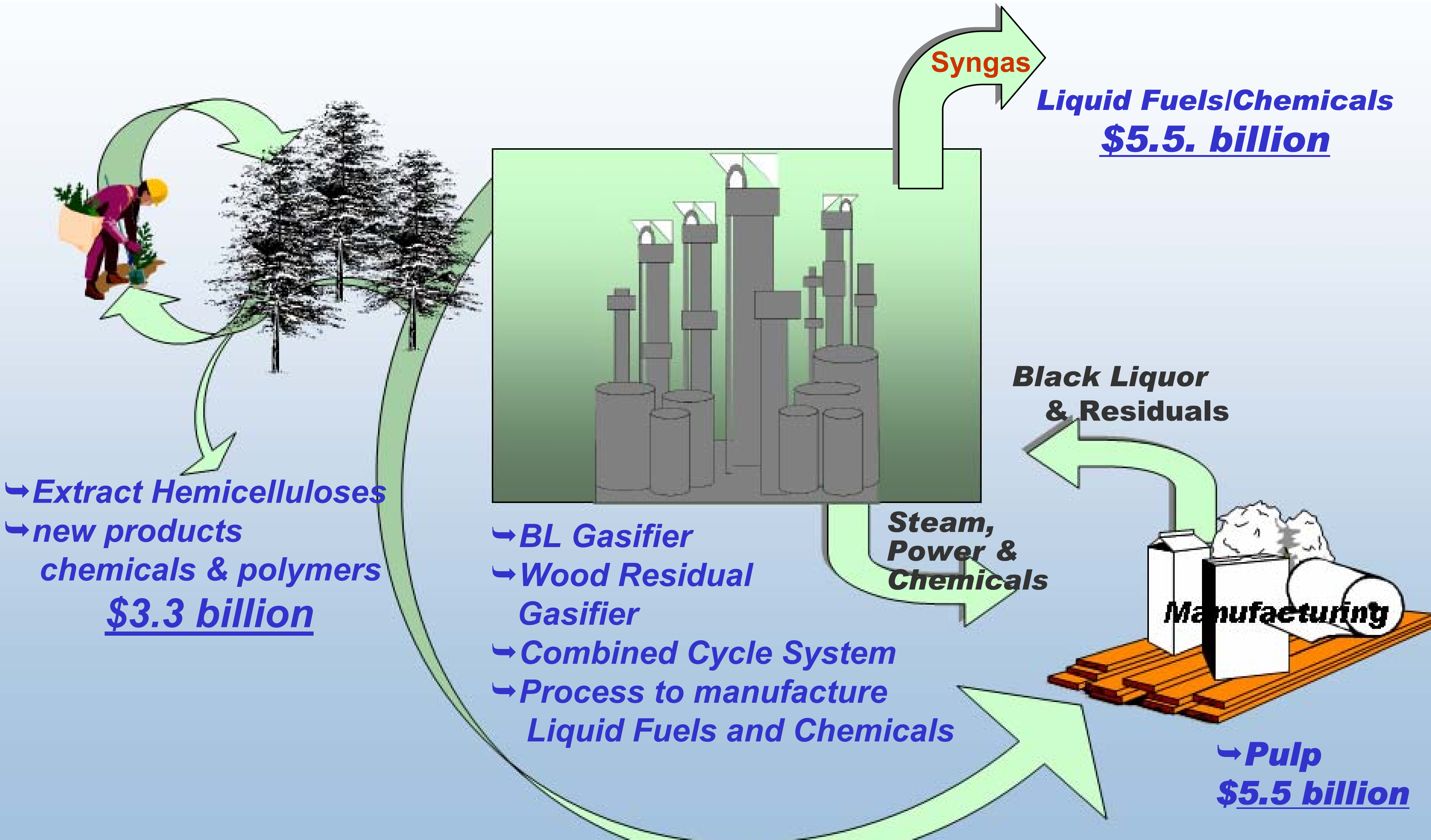
NREL National Renewable Energy Laboratory

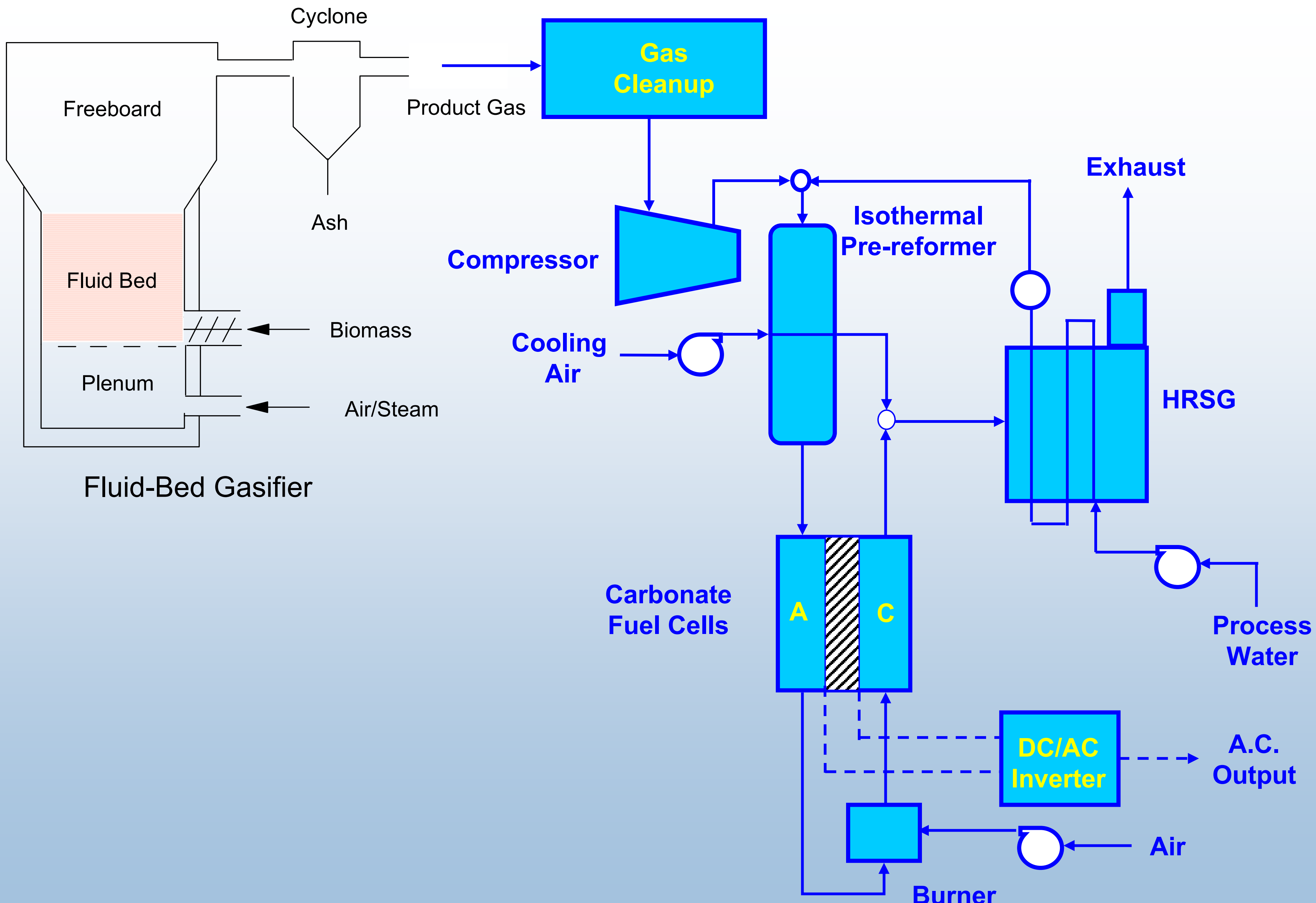


Ethanol From Biomass

Thermochemical Syngas – Biochemical Ethanol

Net Revenue Potential of Biorefinery on the U.S. Pulp Industry




Cyclone
Gas Cleanup
Freeboard
Product Gas
Ash
Exhaust
Isothermal Pre-reformer
Compressor
Fluid Bed
Biomass
Cooling Air
HRSG
Plenum
Air/Steam
Fluid-Bed Gasifier
Carbonate Fuel Cells
A
C
Process Water
DC/AC Inverter
A.C. Output
Air
Burner

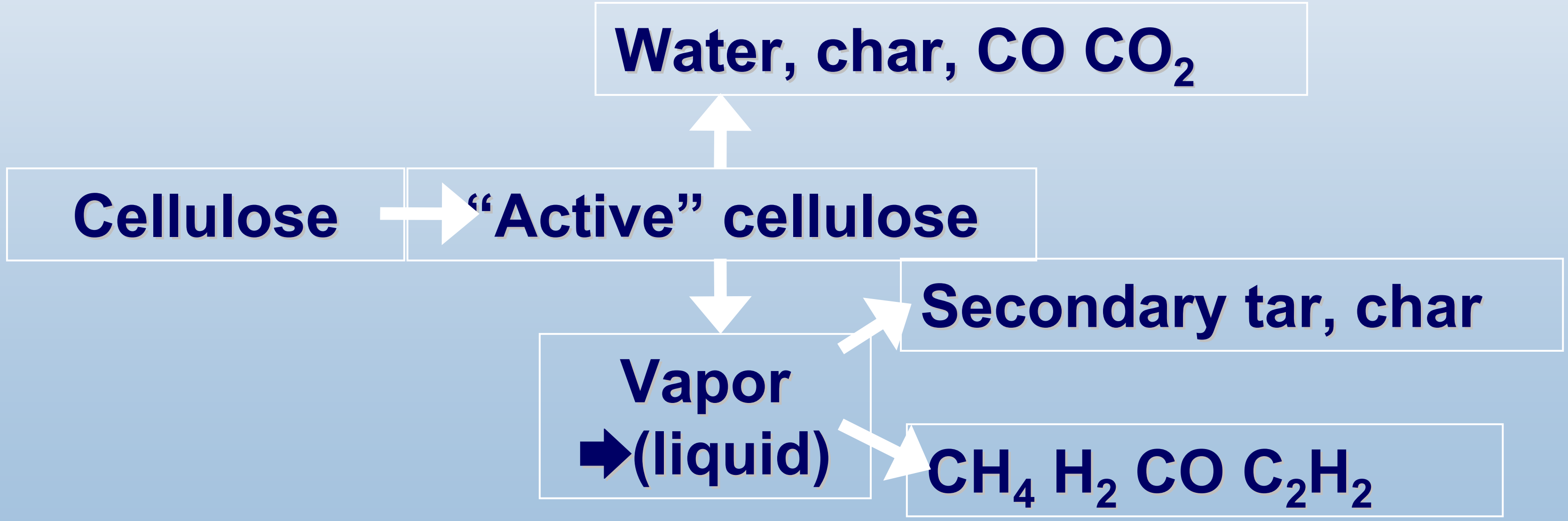
Pyrolysis

Pyrolysis

- Thermal decomposition occurring in the absence of oxygen
- Is always the first step in combustion and gasification processes
- Known as a technology for producing charcoal and chemicals for thousands years

Mechanisms of Pyrolysis

- Many pathways and mechanisms proposed
- Broido-Shafizadeh model for cellulose shows typical complexity of pathways and possibilities for product maximization



Biomass Pyrolysis Products

	Liquid	Char	Gas
•FAST PYROLYSIS	75%	12%	13%
•CARBONIZATION	30%	35%	35%
•GASIFICATION	5%	10%	85%

FAST PYROLYSIS:
- *moderate temperature*
- *short residence time*

CARBONIZATION:
- *low temperature*
- *long residence time*

GASIFICATION:
- *high temperature*
- *long residence time*

Fast Pyrolysis of Biomass

- Fast pyrolysis is a thermal process that rapidly heats biomass to a carefully controlled temperature (~500°C), then very quickly cools the volatile products (<2 sec) formed in the reactor

- Offers the unique advantage of producing a liquid that can be stored and transported
- Has been developed in many configurations
- At present is at relatively early stage of development

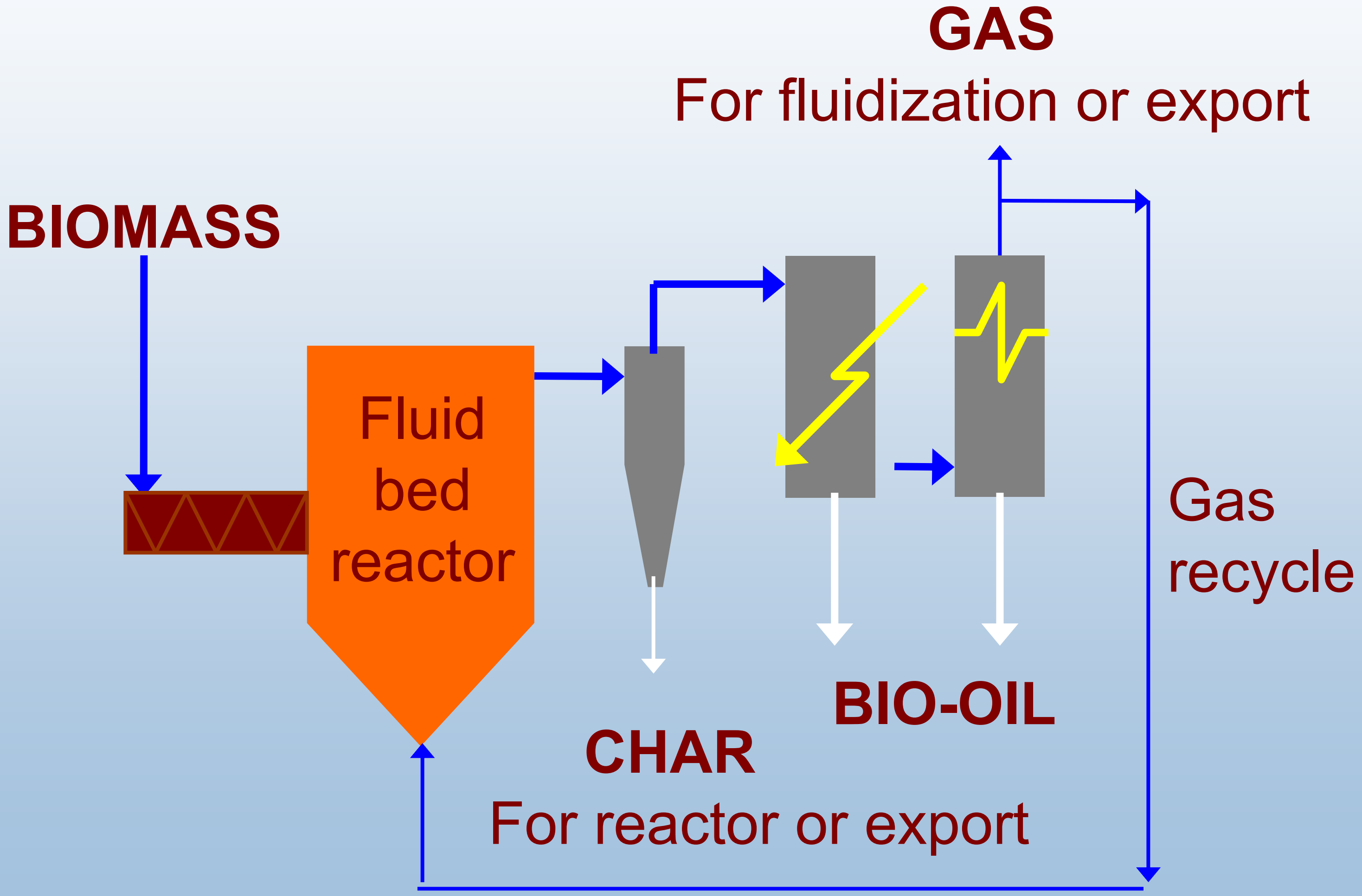
Process Requirements

- **Drying** — <10% moisture; feed and reaction water end up in bio-oil
- **Comminution** — 2mm (bubbling bed), 6 mm (CFB)
- **Fast pyrolysis** — High heat rate, controlled T, short residence time
- **Char separation** — Efficient char separation needed
- **Liquid recovery** — By condensation and coalescence.

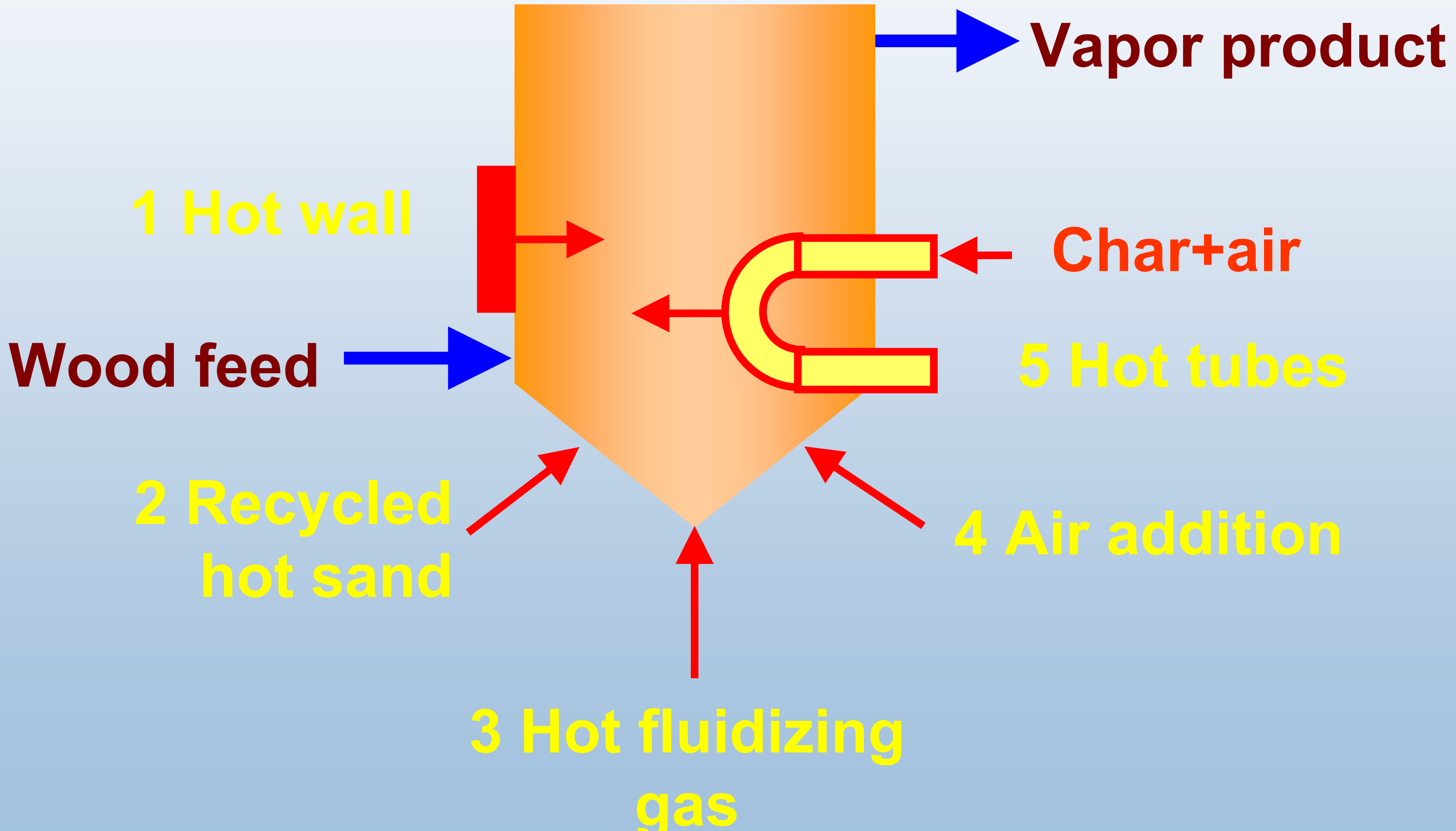
Operational Pyrolysis Units

Fluid beds	400 kg/h at DynaMotive 20 kg/h at RTI Many research units
CFBs	1000 kg/h at Red Arrow (Ensyn) 20 kg/h at VTT (Ensyn) 350 kg/h (Fortum, Finland)
Rotating cone	200 kg/h at BTG (Netherlands)
Vacuum	3500 kg/h at Pyrovac
Auger	200 kg/h at ROI

Bubbling Fluid Bed Pyrolysis



Fluid Bed Heating Options



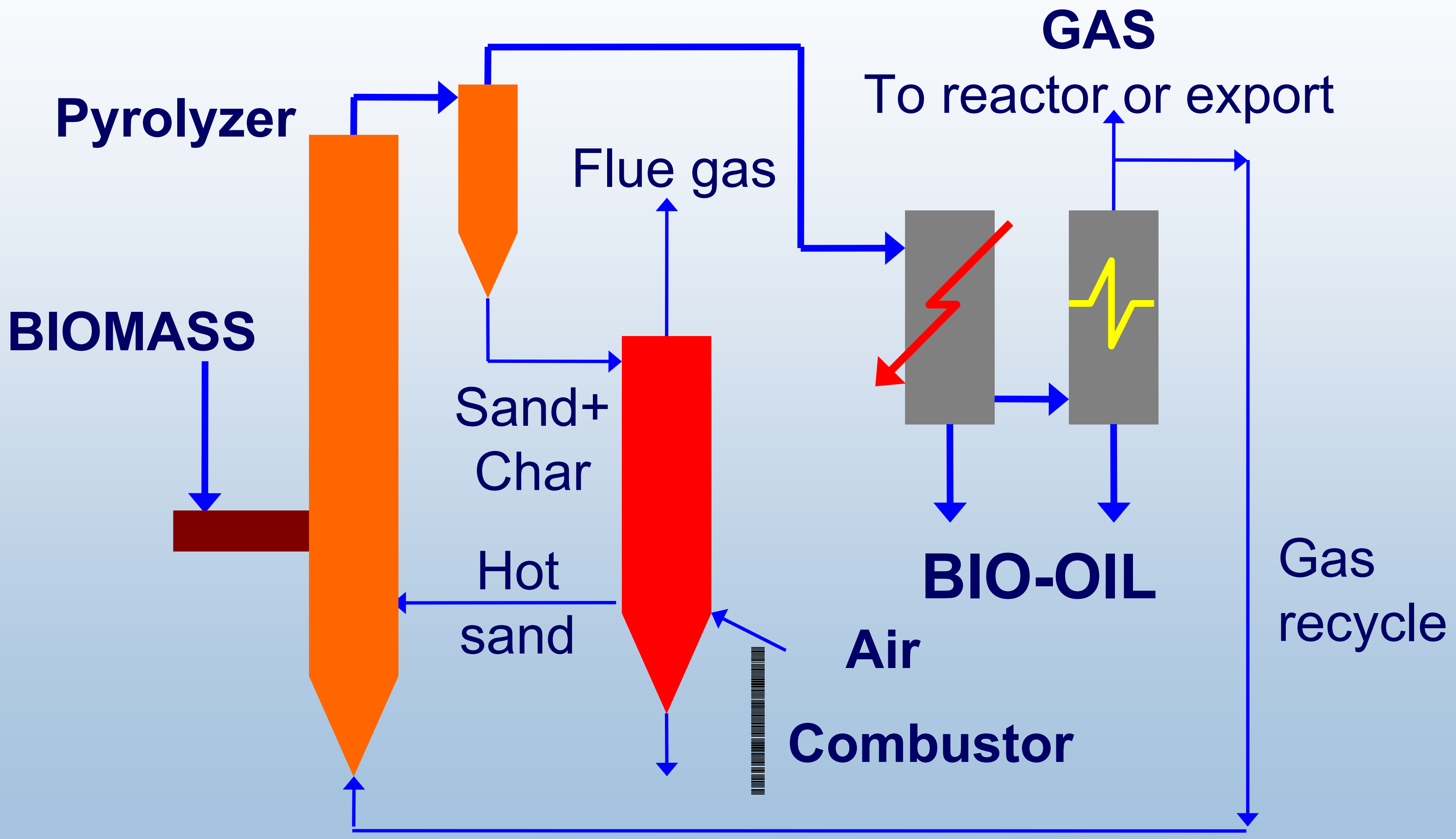
Bubbling Fluid Bed

250 kg/h pilot plant at Wellman, UK

Fluid Bed Reactors

- Good temperature control,
- Char removal is usually by ejection and entrainment; separation by cyclone,
- Easy scaling,
- Well understood technology since first experiments at University of Waterloo in 1980s
- Small particle sizes needed,
- Heat transfer to bed at large scale has to be proven.

Circulating Fluid Beds



CFB and Transported Beds

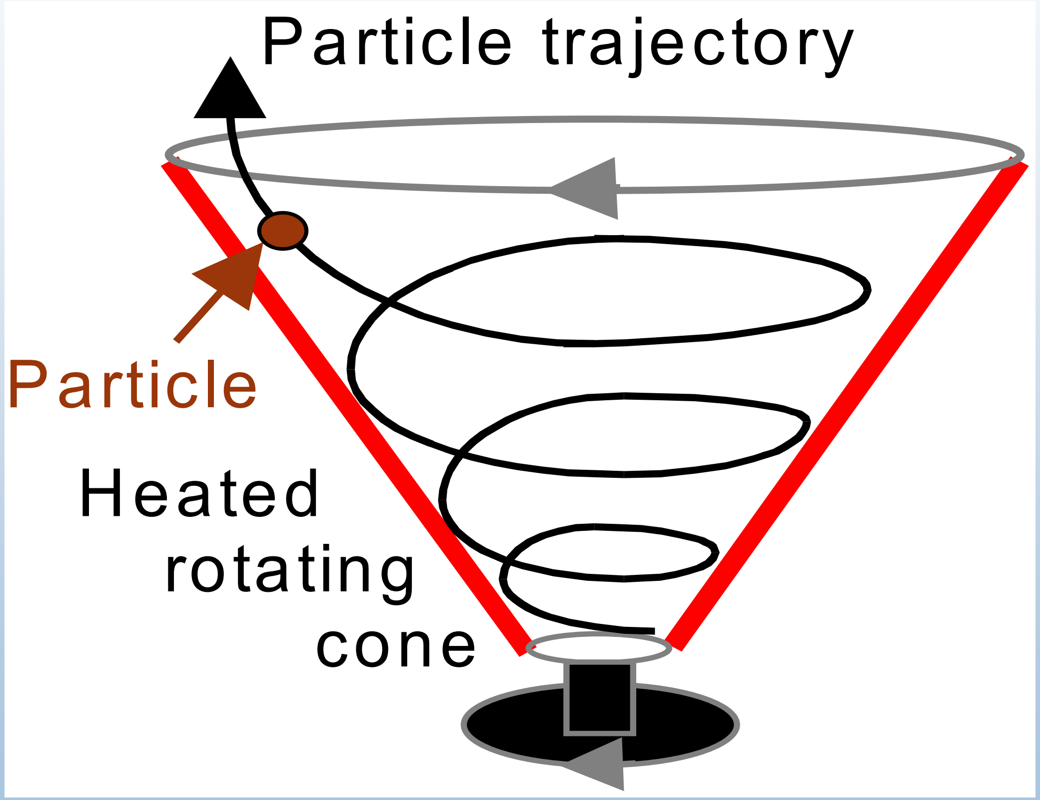
- Good temperature control in reactor,
- Larger particle sizes possible,
- CFBs suitable for very large throughputs,
- Well understood technology,
- Hydrodynamics more complex, larger gas flows in the system,
- Char is finer due to more attrition at higher velocities; separation is by cyclone,
- Closely integrated char combustion requires careful control,
- Heat transfer to bed at large scale has to be proven.

Rotating Cone (BTG)

Centrifugation drives hot sand and biomass up rotating heated cone;

Vapors are condensed;

Char is burned and hot sand is recirculated.



Vacuum Moving Bed

- Developed at Université Laval, Canada, scaled up by Pyrovac
- Pilot plant operating at 50 kg/h
- Demonstration unit at 3.5 t/h
- Analogous to fast pyrolysis as vapor residence time is similar.

- Lower bio-oil yield 35-50%
- Complicated mechanically (stirring wood bed to improve heat transfer)

Auger Reactor

- Developed for biomass pyrolysis by Sea Sweep, Inc (oil adsorbent) then ROI (bio-oil);
- 5 t/d (200 kg/h) mobile plant designed for pyrolysis of chicken litter;
- Compact, does not require carrier gas;
- Lower process temperature (400ºC);
- Lower bio-oil yields
- Moving parts in the hot zone
- Heat transfer at larger scale may be a problem

Char Removal

- Char acts as a vapor cracking catalyst so rapid and effective removal is essential.
- Cyclones are usual method of char removal. Fines pass through and collect in liquid product.
- Hot vapor filtration gives high quality char free product. Char accumulation cracks vapors and reduces liquid yield (~20%). Limited experience is available.
- Liquid filtration is very difficult due to nature of char and pyrolytic lignin.

Liquid Collection

- Primary pyrolysis products are vapors and aerosols from decomposition of cellulose, hemicellulose and lignin.
- Liquid collection requires cooling and agglomeration or coalescence of aerosols.
- Simple heat exchange can cause preferential deposition of heavier fractions leading to blockage.
- Quenching in product liquid or immiscible hydrocarbon followed by electrostatic precipitation is preferred method.

Fast Pyrolysis Bio-oil

Bio-oil is water miscible and is comprised of many oxygenated organic chemicals.

- **Dark brown mobile liquid,**
- **Combustible,**
- **Not miscible with hydrocarbons,**
- **Heating value ~ 17 MJ/kg,**
- **Density ~ 1.2 kg/l,**
- **Acid, pH ~ 2.5,**
- **Pungent odour,**
- **"Ages" - viscosity increases with time**

Bio-oil Properties

The complexity and nature of the liquid results in some unusual properties.

Due to physical-chemical processes such as:

- Polymerization/condensation
- Esterification and etherification
- Agglomeration of oligomeric molecules

Properties of bio-oil change with time:

- Viscosity increases
- Volatility decreases
- Phase separation, deposits, gums

Upgrading of Bio-oils

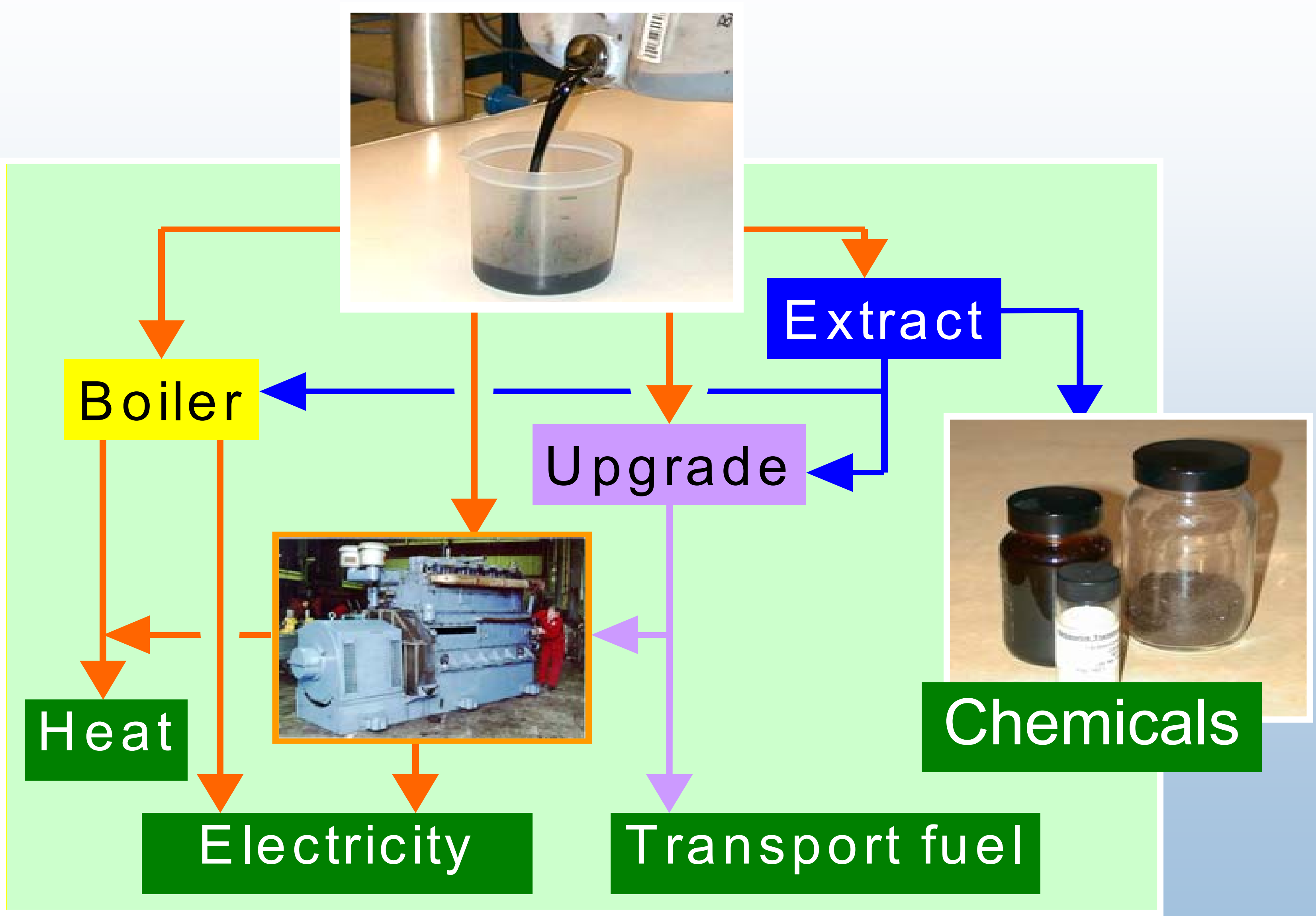
Physical Methods

- Filtration for char removal,
- Emulsification with hydrocarbons,
- Solvent addition,

Chemical Methods

- Reaction with alcohols,
- Catalytic deoxygenation:
  - Hydrotreating,
  - Catalytic (zeolite) vapor cracking.

Applications of Bio-oils



Bio-oil Cost

Different claims of the cost of production:

- Ensyn $4-5/GJ ($68-75/ton)
- BTG $6/GJ ($100/ton)

$$\text{Cost} = \text{Wood cost}/10 + 8.87 * (\text{Wood throughput})^{-0.347}$$

$/GJ $/dry ton dry t/h

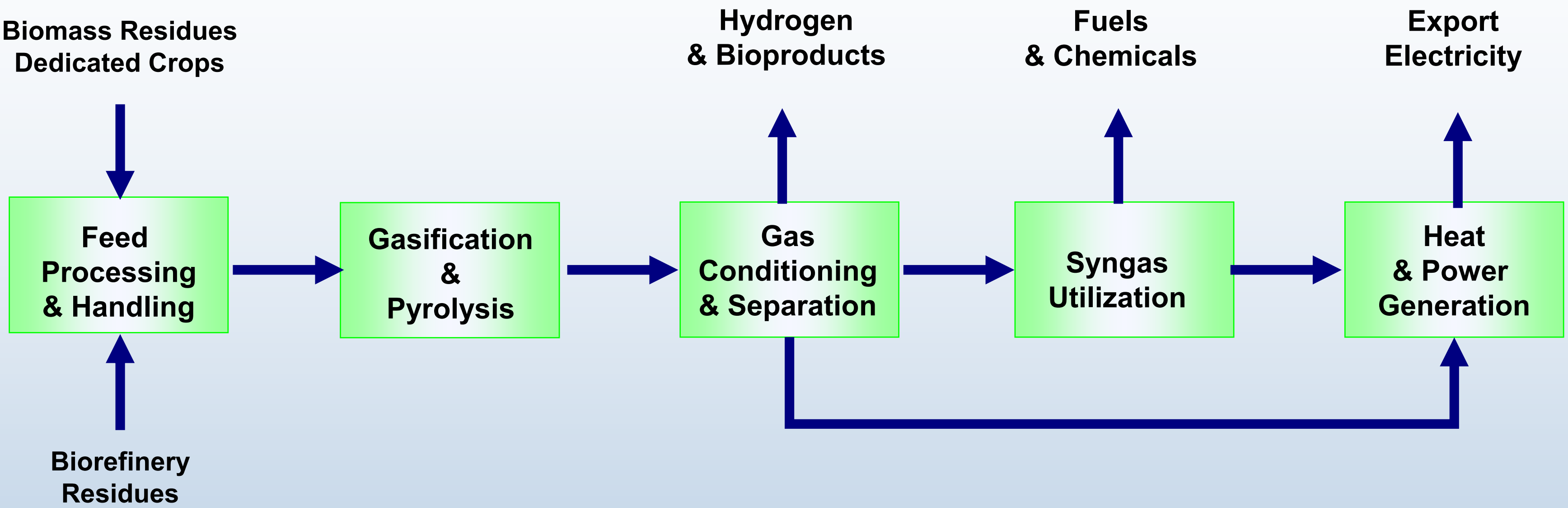
A.V. Bridgwater, A Guide to Fast Pyrolysis of Biomass for Fuels and Chemicals, PyNe Guide 1, www.pyne.co.uk

Why Is Bio-oil Not Used More?

- ✓ Cost : 10% – 100% more than fossil fuel,
- ✓ Availability: limited supplies for testing
- ✓ Standards; lack of standards and inconsistent quality inhibits wider usage,
- ✓ Incompatibility with conventional fuels,
- ✓ Unfamiliarity of users
- ✓ Dedicated fuel handling needed,
- ✓ Poor image.

Research Opportunities

Technical Barrier Areas



- Feed Processing and Handling
- Gasification / Conversion
- Gas Cleanup and Catalytic Conditioning
- Syngas Utilization
- Process Integration
- Process Control, Sensors, and Optimization

Biomass Thermochemical Conversion Primary Technical Barriers

Gasification

- Feed Pretreatment
  - Feeder reliability
  - Feed modification
- Gasification
  - Tar & Heteroatom chemistry
  - Gasifier Design
  - Catalysis
- Gas Cleanup & Conditioning
  - Catalytic Conversion
  - Condensing Cleanup
  - Non-condensing Cleanup
- Syngas Utilization
  - Cleanliness requirements
  - Gas composition
- Process Integration
- Sensors and Controls

Pyrolysis

- Catalytic Pyrolysis
- Oil Handling
  - Toxicity
  - Stability
  - Storage
  - Transportation
- Oil Properties
  - Ash
  - Acidity
- Oil Commercial Properties
  - Commercial Specifications
  - Use in Petroleum Refineries

Black Liquor Gasification

- Containment
  - Metals
  - Refractories
  - Vessel design
  - Bed behavior/agglomeration
- Mill Integration
  - Steam
  - Power
  - Causticizing
- Fuels Chemistry
  - Carbon management
  - Tars
  - Sulfur management
  - Alkali management
  - Halogen management
- Sensors and Controls

Possible Reading

1. Bain, R. L.; Amos, W. P.; Downing, M.; Perlack, R. L. (2003). Biopower Technical Assessment: State of the Industry and the Technology. 277 pp.; NREL Report No. TP-510-33123.
2. Bridgewater, A.V. (2003). A Guide to Fast Pyrolysis of Biomass for Fuels and Chemicals, PyNe Guide 1, www.pyne.co.uk
3. Brown, R. C. (2003). Biorenewable Resources: Engineering New Products From Agriculture, Iowa State Press, ISBN:0-8138-2263-7.
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5. Probstein, R. F. and R. E. Hicks (1982). Synthetic Fuels, McGraw-Hill, Inc., ISBN 0-07-050908-5.
6. Van Loo, S. and J. Koppejan (eds.) (2002). Handbook of Biomass Combustion and Co-firing, Twente University Press, ISBN 9036517737.