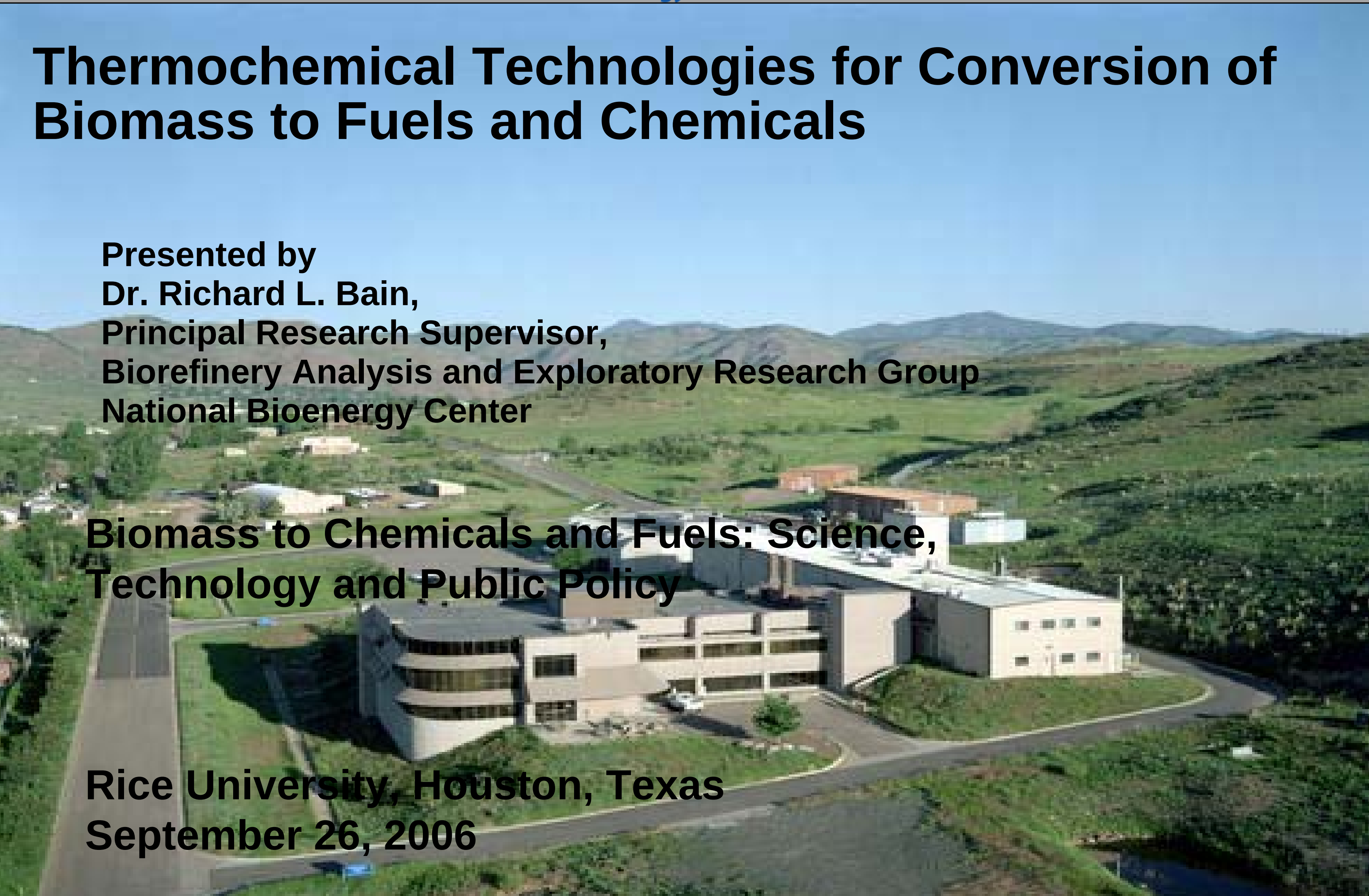


Thermochemical Technologies for Conversion of Biomass to Fuels and Chemicals

Presented by
Dr. Richard L. Bain,
Principal Research Supervisor,
Biorefinery Analysis and Exploratory Research Group
National Bioenergy Center

Biomass to Chemicals and Fuels: Science, Technology and Public Policy

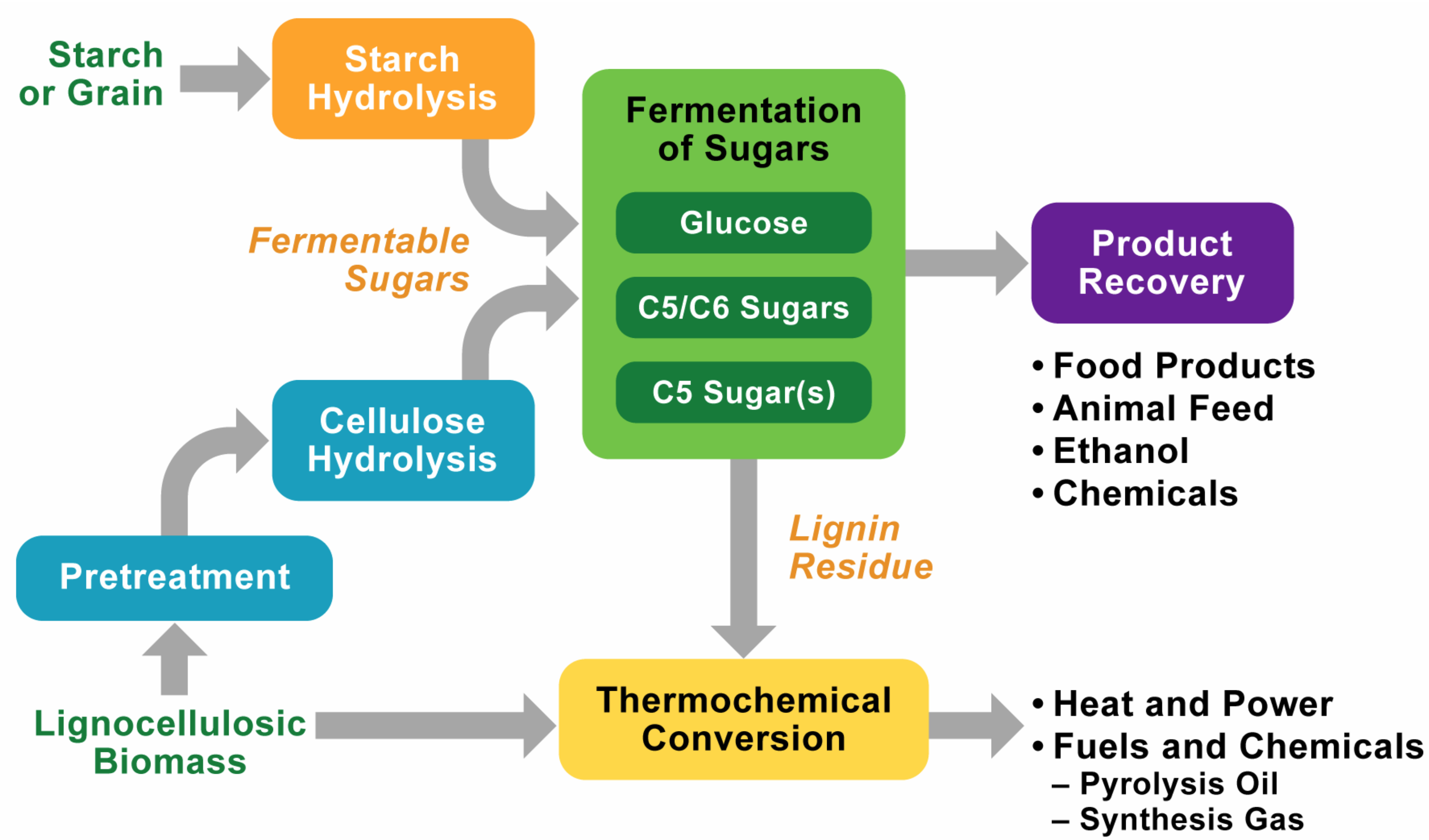
Rice University, Houston, Texas
September 26, 2006

Disclaimer and Government License

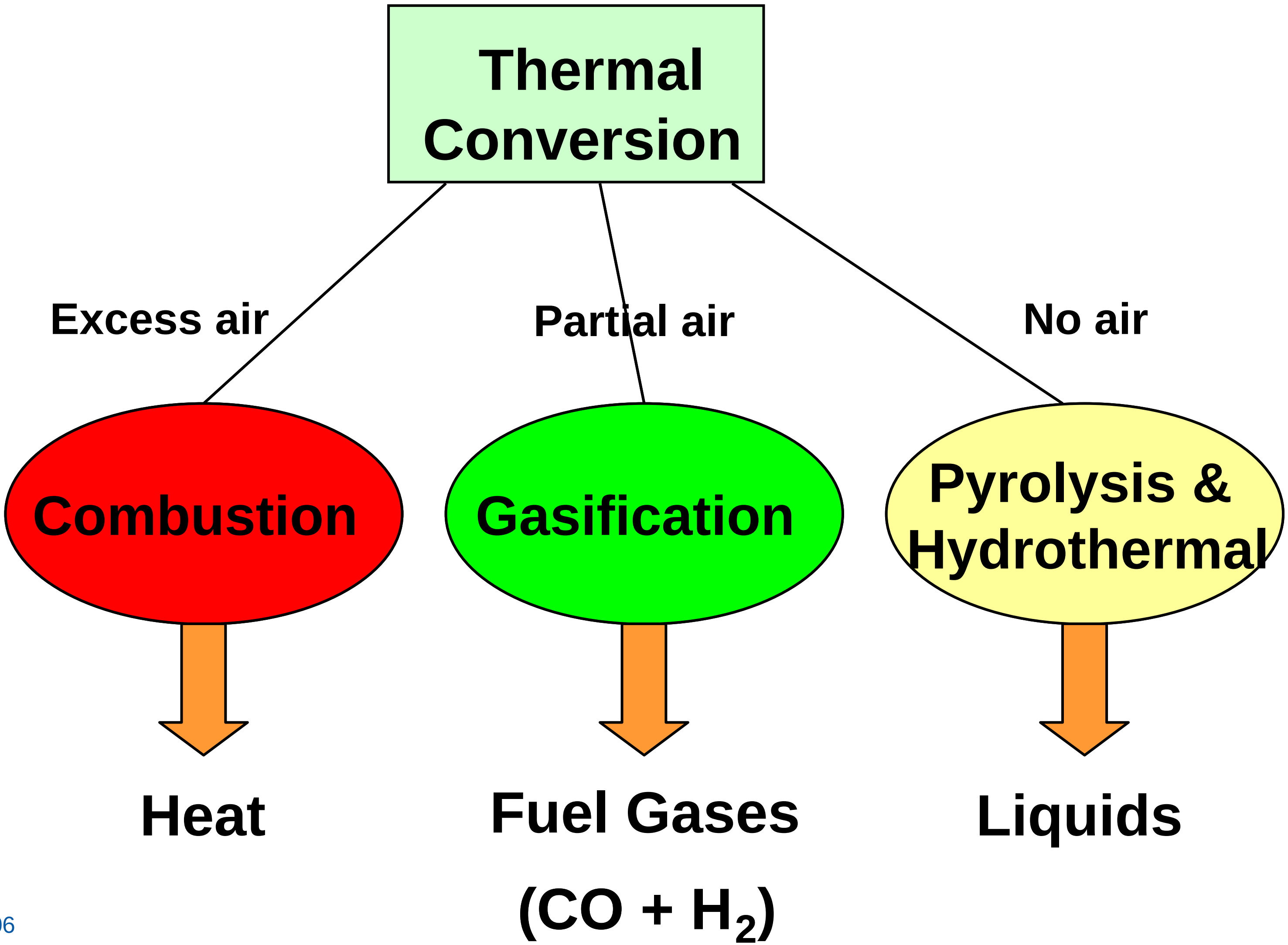
Presentation Outline

- Overview
- Biomass Properties
- Gasification Based Technologies
- Pyrolysis Based Technologies
- Other Technologies

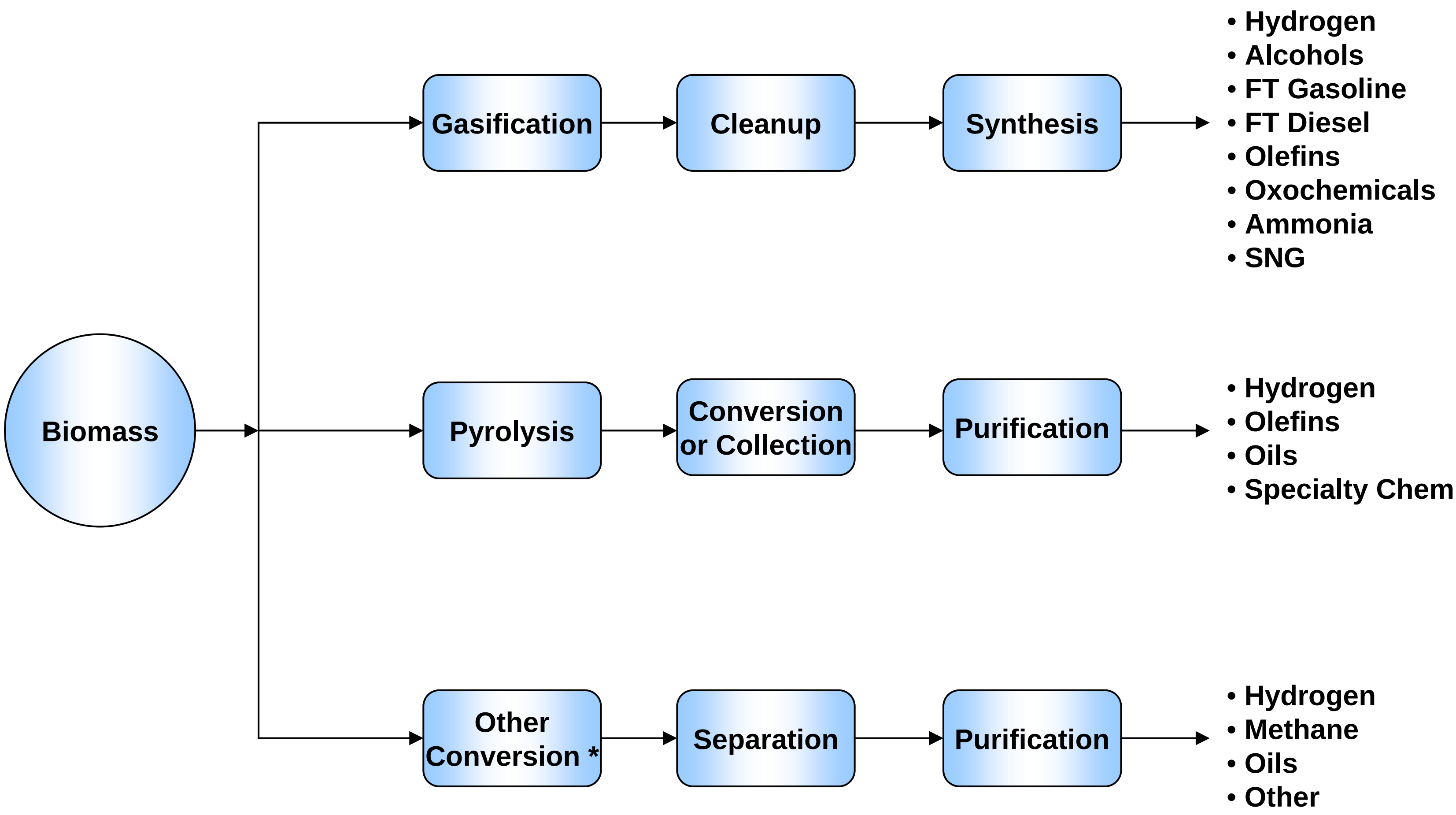
Integrated biorefineries will involve both biochemical and thermochemical processes



The primary conversion routes give different types of products

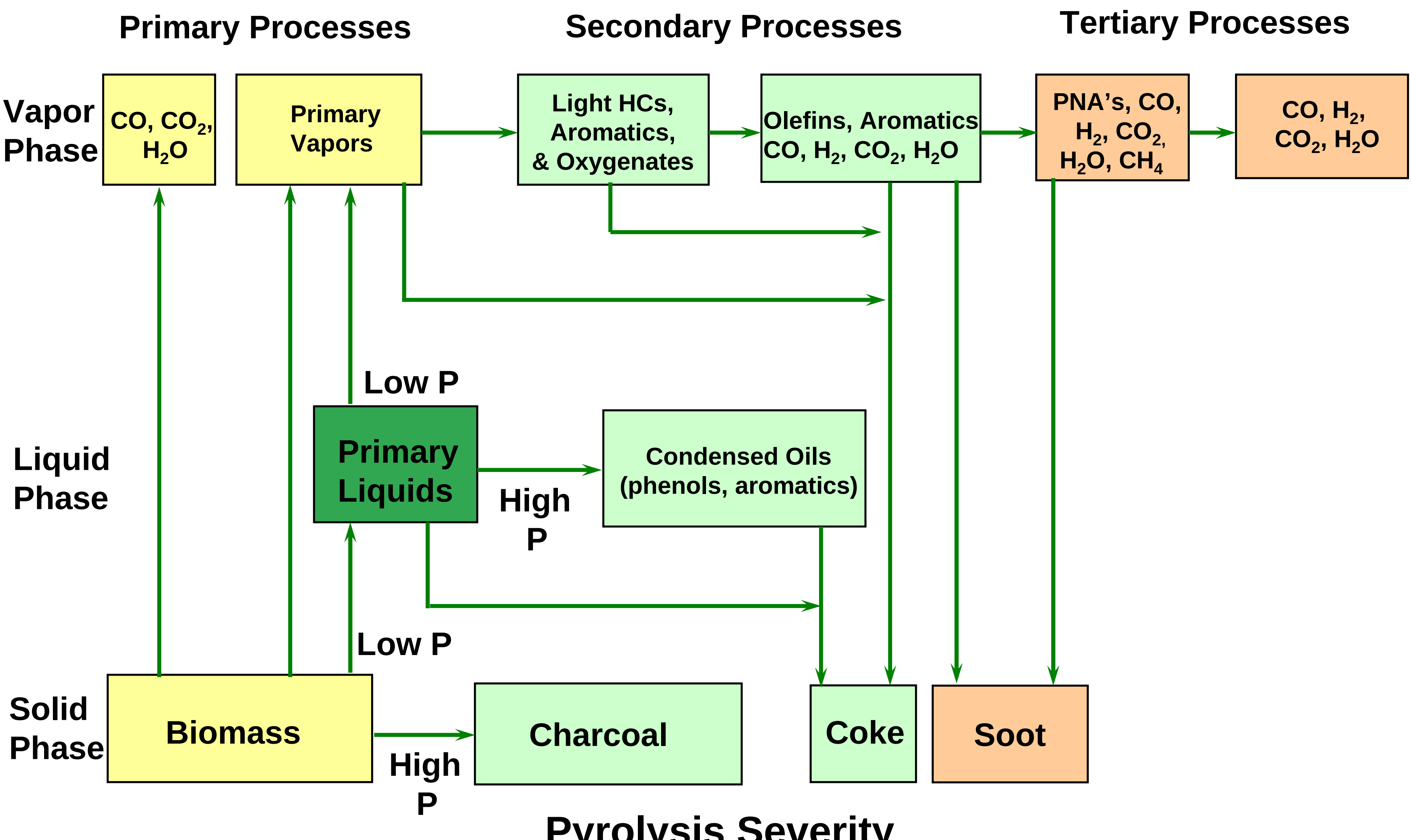


Fungible fuels & chemicals are major products. New classes of products (e.g., oxygenated oils) require market development



* Examples: Hydrothermal Processing, Liquefaction, Wet Gasification

Thermal Conversion involves primary, secondary, and tertiary reactions



To understand thermochemical conversion we need to know the physical and thermal properties that influence thermal behavior

National Renewable Energy Laboratory

The basic properties for the comparison of thermal behavior are proximate and ultimate analyses

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	

Gasification has a long history of development and use

Murdoch (1792) coal distillation

London gas lights 1802

Blau gas – Fontana 1780

1900s Colonial power

MeOH 1913 BASF

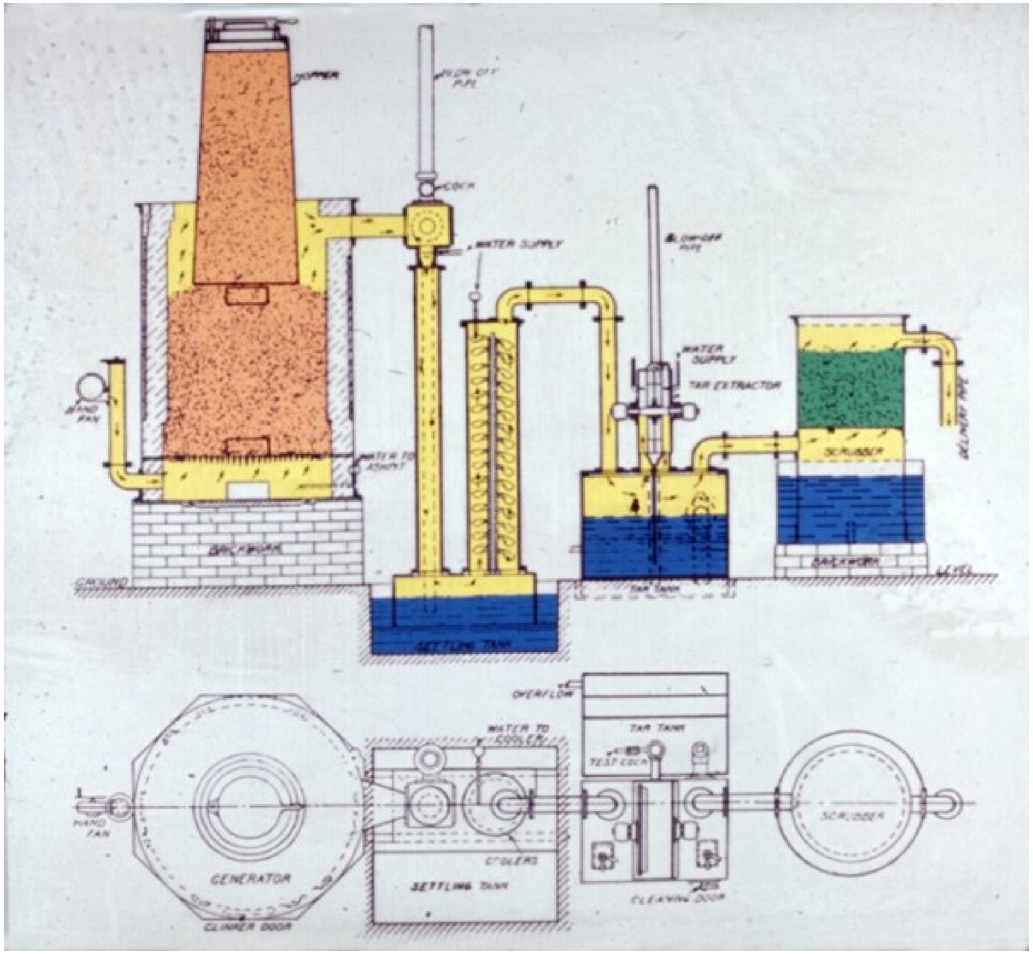
Fischer Tropsch 1920s

Vehicle Gazogens WWII

SASOL 1955 - Present

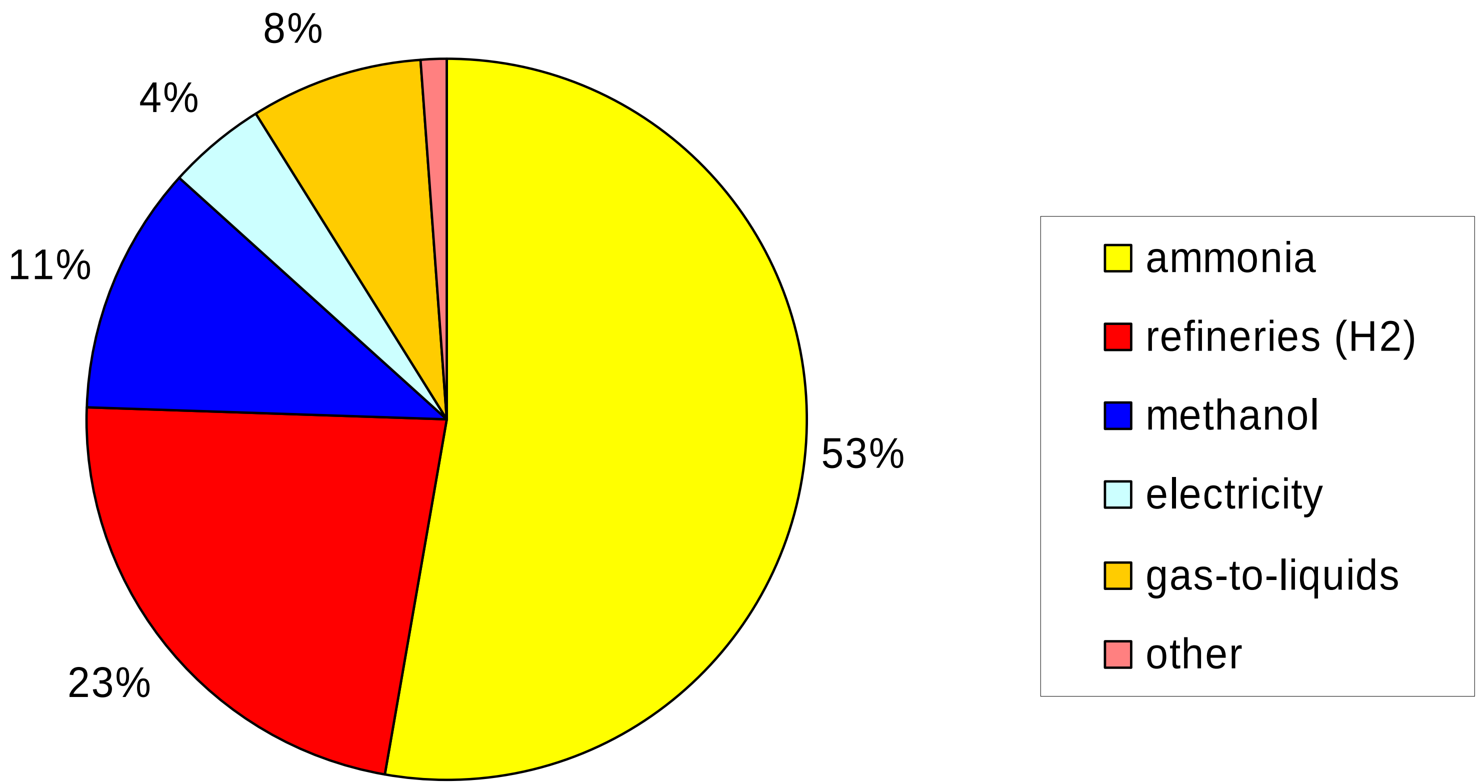
GTL 1995 – Present

Hydrogen – Future?



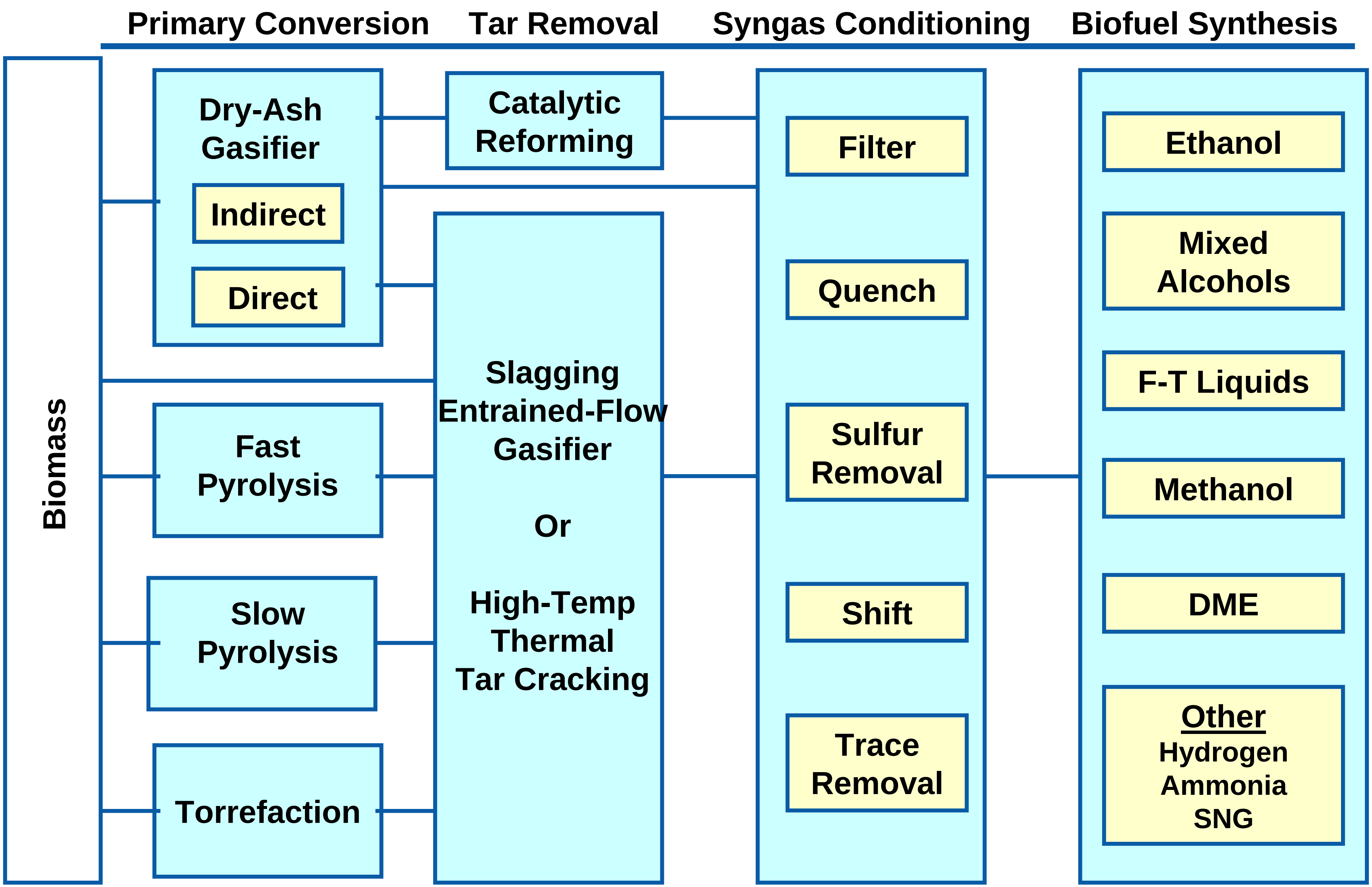
Circa 1898

The world syngas market is approximately 6 EJ/yr



A. van der Drift, R. van Ree, H. Boerrigter and K. Hemmes: *Bio-syngas: key intermediate for large scale production of green fuels and chemicals*. In: The 2nd World Conference on Biomass for Energy, Industry, and Climate Protection, 10-14 May 2004, Rome, Italy, pp. 2155-2157 (2004).

There are a number of gasification pathways



Source: ECN (2006), ECN-C-06-001

A large number of companies are involved in biomass thermal conversion

Product → Bio-Oil | Syngas

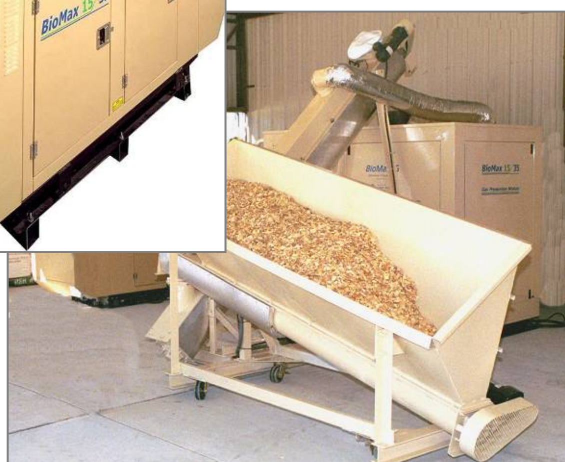
Dry Ash ↔ Slag

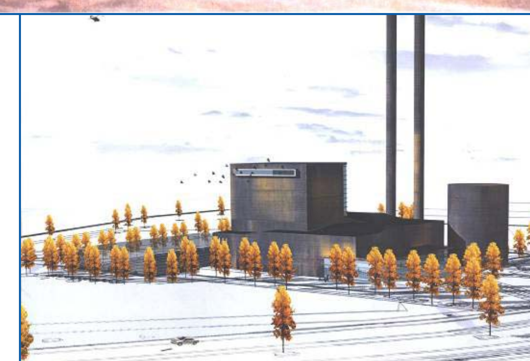
High Pressure ↕ Low Pressure 0.2 MPa

	Low (300-600°C)	Medium (700-850°C)	High (900-1200°C)
Product	Bio-Oil	Syngas	Syngas
High Pressure	Changing World Technologies Gas Product: PNNL Wet Gasification (CH4/H2)	GTI (O2) Carbona (O2) HTW O2) Foster Wheeler (O2)	Chemrec (O2) Future Energy (Siemens) Choren – 2 stage
Pressure	10-25 MPa	1- 3 MPa	2 – 3 MPa
Feed	Feed: Biomass	Feed: Biomass MTCI-also Black Liquor	Feed: Black Liquor
Low Pressure 0.2 MPa	ENSYN Dynamotive BTG Fortum	FERCO (Indirect) MTCI (Indirect) Pearson (Indirect) TUV (Indirect) For CHP:TPS (Air) Carbona (Air) Lurgi (Air) Foster Wheeler (Air) EPI (Air) Primenergy (Air) Community Power Frontline	Chemrec (Air)

Small and medium size combined heat and power is a good opportunity for biomass

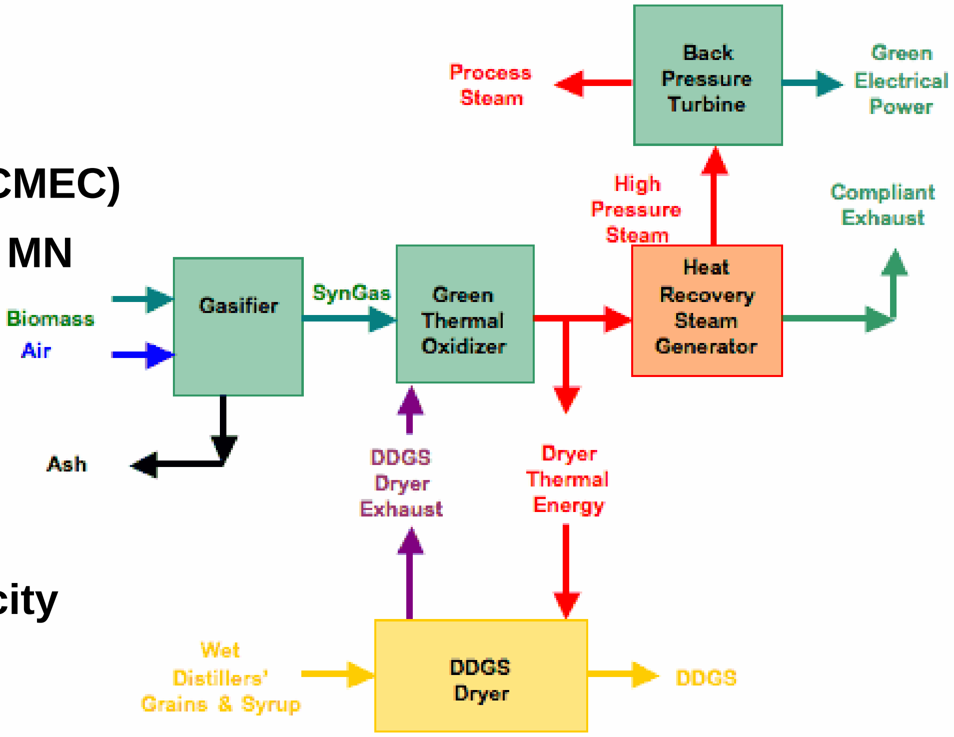
Credit: Carbona Corp





Credit: Community Power Corp

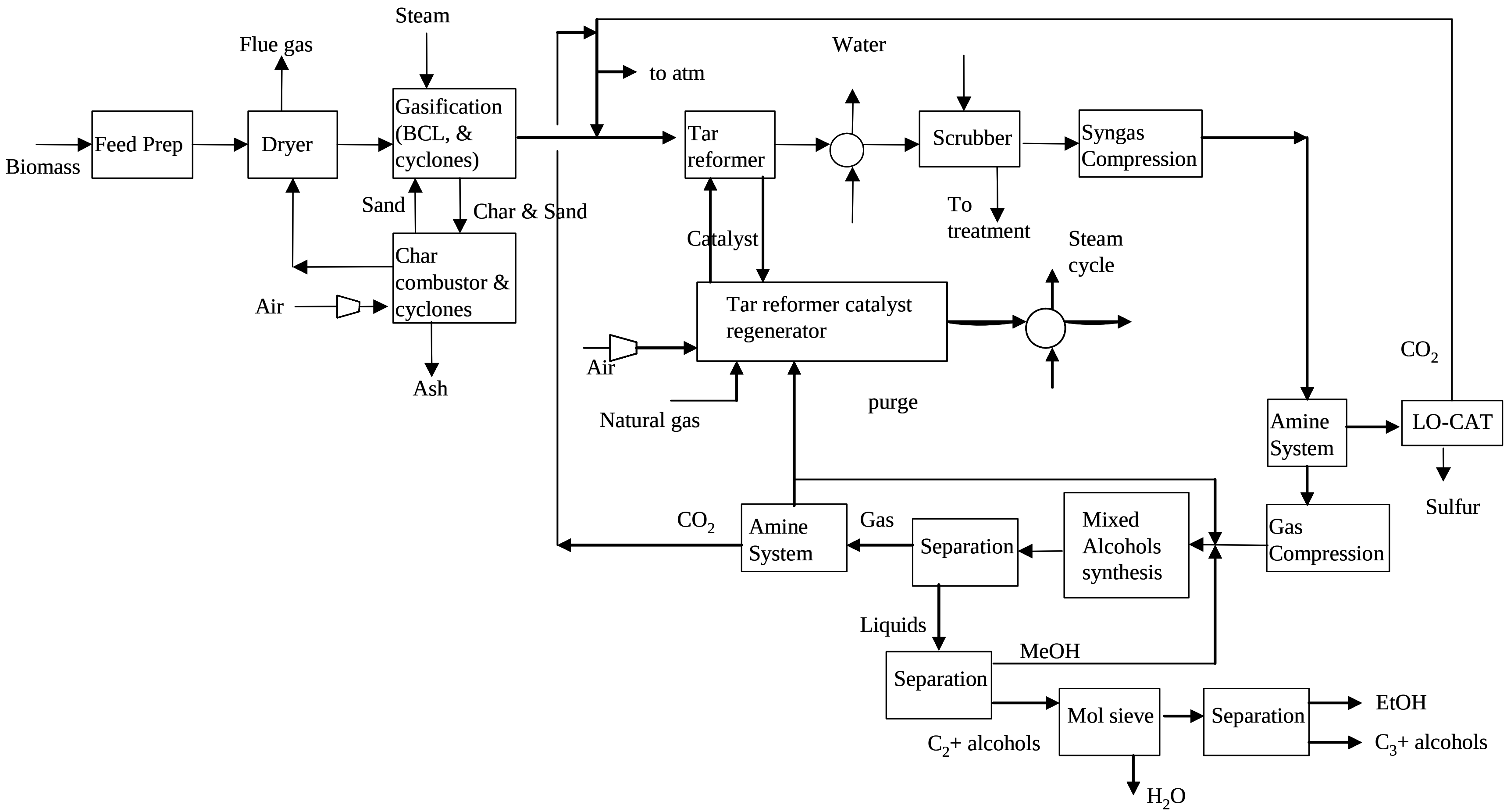
Producers are starting to use biomass gasifiers for CHP in corn ethanol facilities



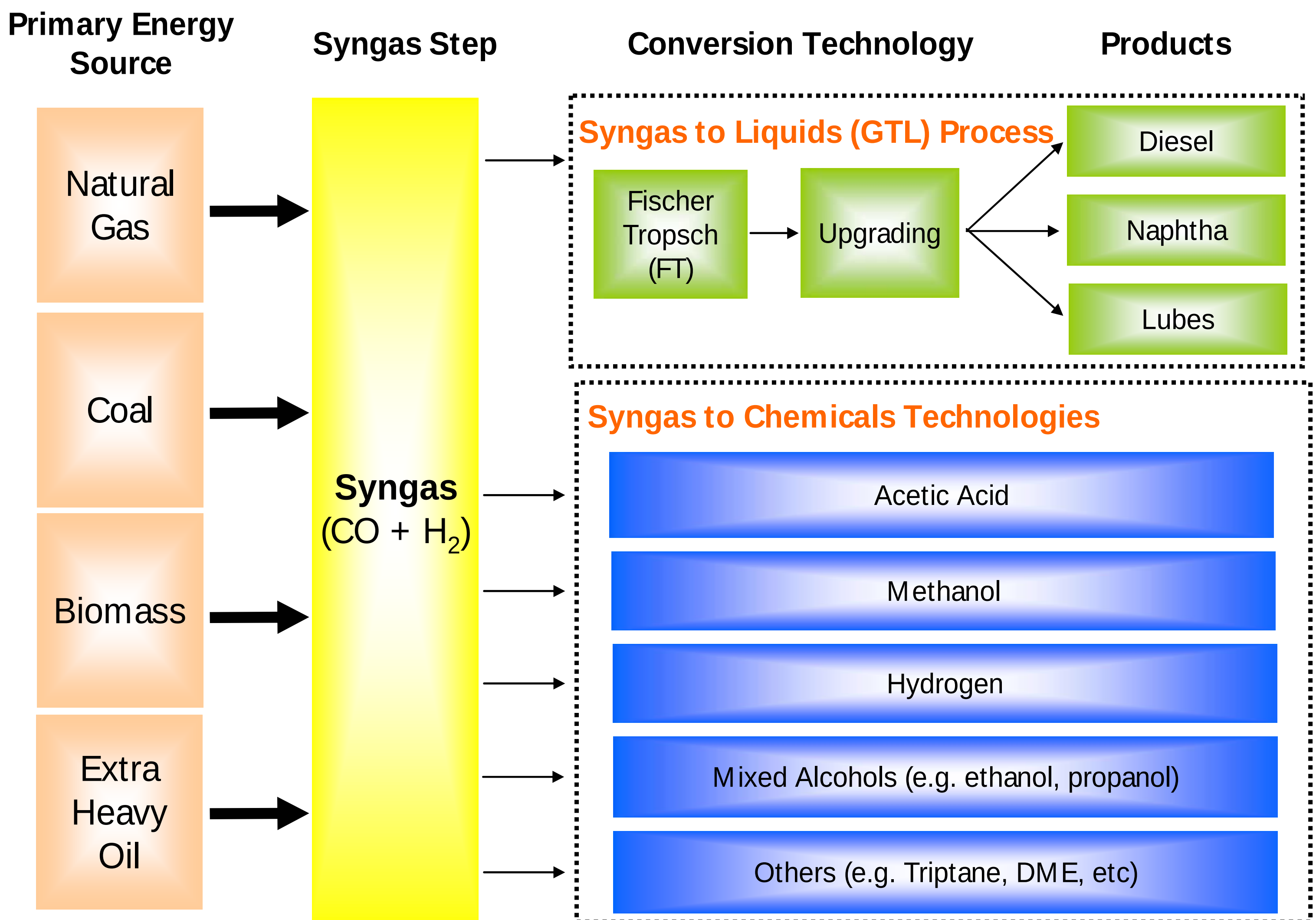
- Central Minnesota Ethanol Cooperative (CMEC)
- 15million gpy ethanol plant in Little Falls, MN
- Funding – USDA, XCEL Energy, Private
- E&C – Sebesta Blomberg
- Gasifier – Primenergy
- 280 tpd wood
- 50 k-lb/hr high pressure steam for electricity
- 35 MMBtu/hr thermal energy

http://www.primenergy.com/Projects_detail_LittleFalls.htm **8/28/06**

Transportation fuels production will probably be at larger scale because of process complexity and capital intensive nature. There may be opportunities for smaller modular "skid mount" systems.



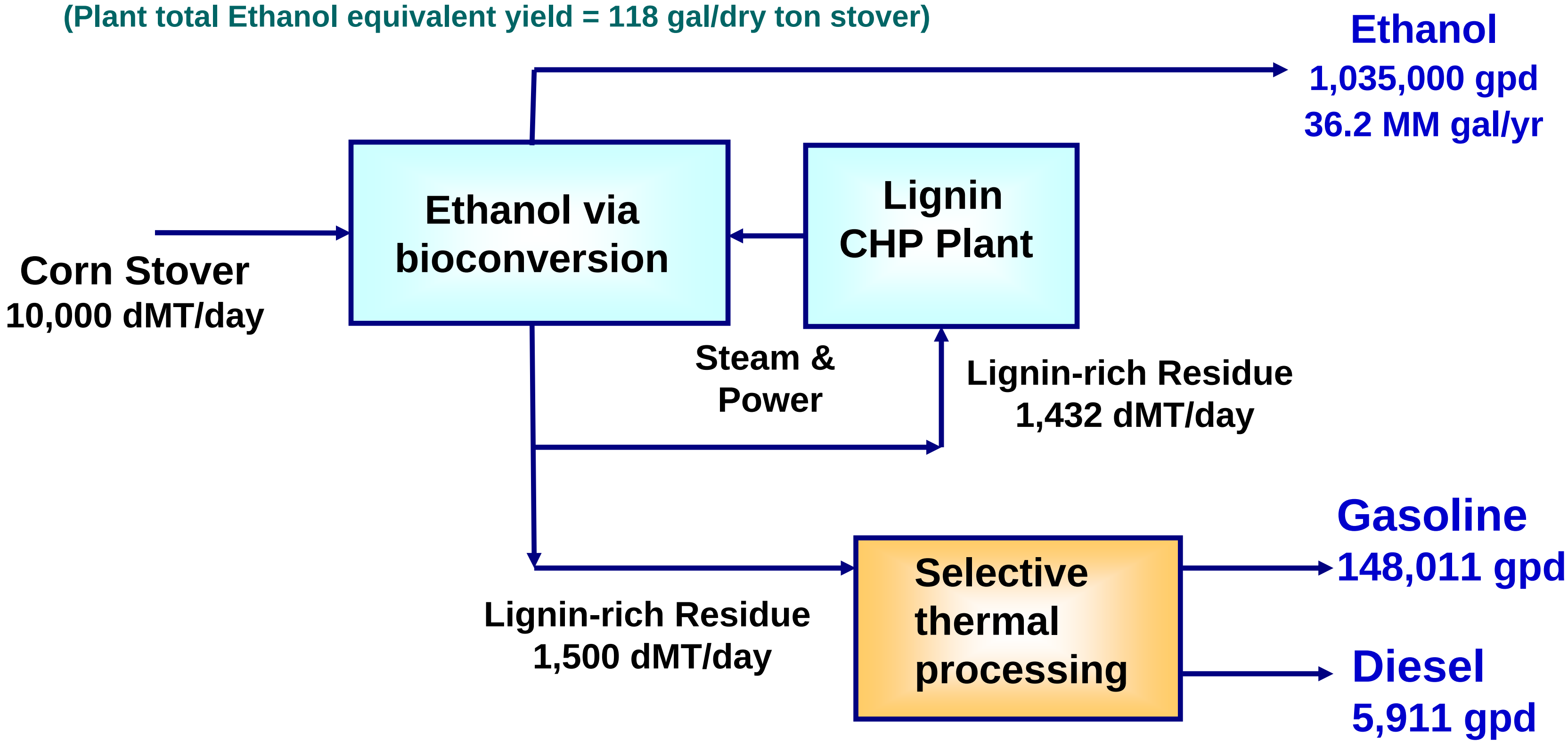
Hydrocarbon fungibility will be a key to success



Source: BP

A 30x30 advanced integrated biorefinery scenario, i.e., the E85 Refinery, includes both thermochemical and biochemical processing

Ethanol yield = 94 gal/dry ton stover
Gasoline yield = 90 gal/dry ton of lignin (13 gal/ton of stover)
(Plant total Ethanol equivalent yield = 118 gal/dry ton stover)

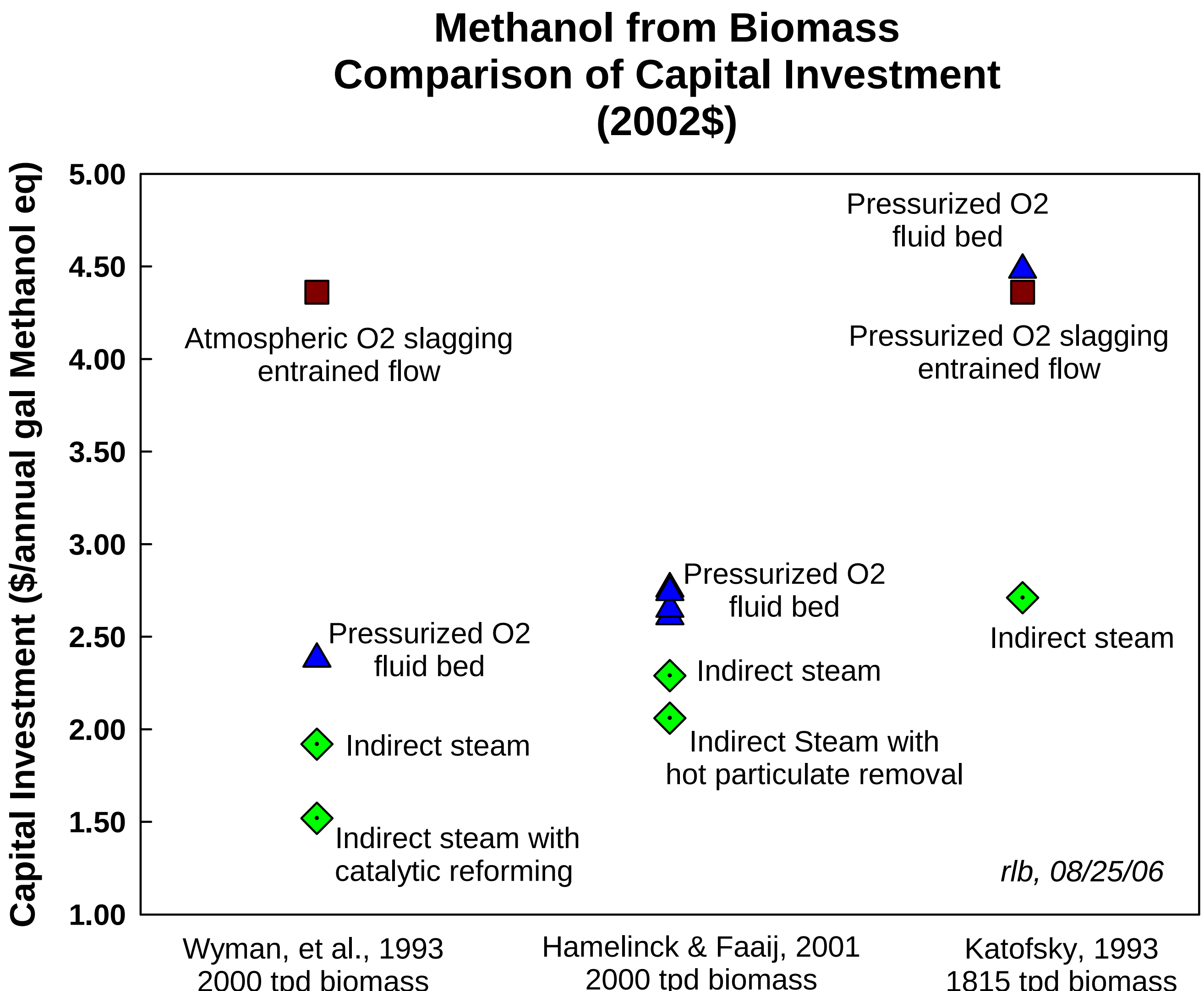


Minimum gasoline selling price = $0.51/gal gasoline
(Minimum Ethanol equivalent selling price = $0.35/galEtOH)

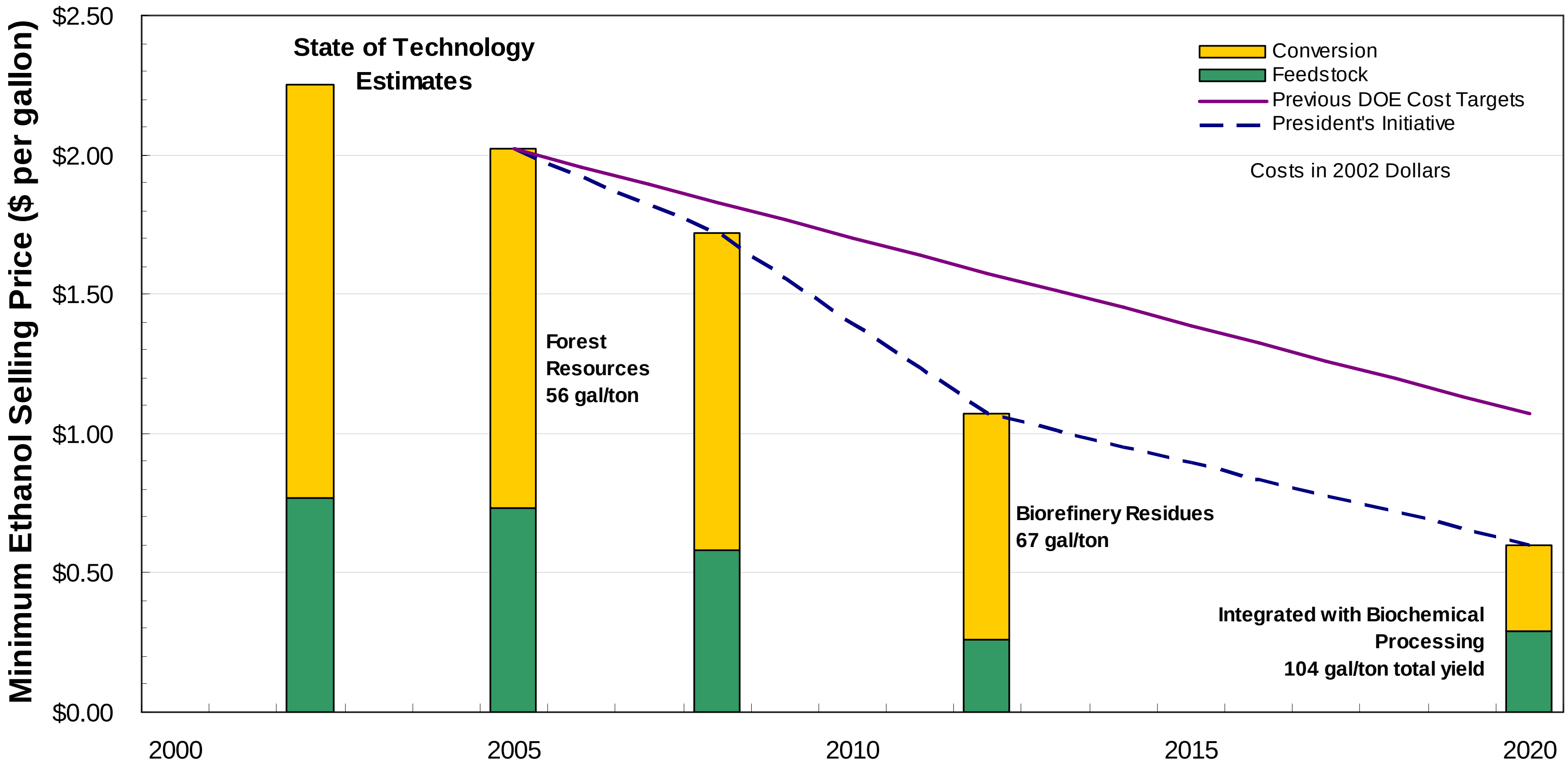
(Diesel is recycled to produce a lignin slurry feed)

Plant Minimum Ethanol equivalent selling price = $0.57/gal EtOH

Although ethanol and Fischer-Tropsch liquids are presently preferred products, previous work on methanol can help guide analysis



Analysis of ethanol from TC mixed alcohols shows the potential to reach the DOE goal of $1.07/gal in 2012



Pyrolysis is usually performed at lower temperature to produce a liquid biocrude.

- 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

The distribution of products depends on temperature and residence time

	Liquid	Char	Gas
FAST PYROLYSIS	75%	12%	13%
	moderate temperature		
	short residence time		
CARBONIZATION	30%	35%	35%
	low temperature		
	long residence time		
GASIFICATION	5%	10%	85%
	high temperature		
	long residence time		

Source: Bridgewater and Czernik

There are a number of operating systems in North America and Europe

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**

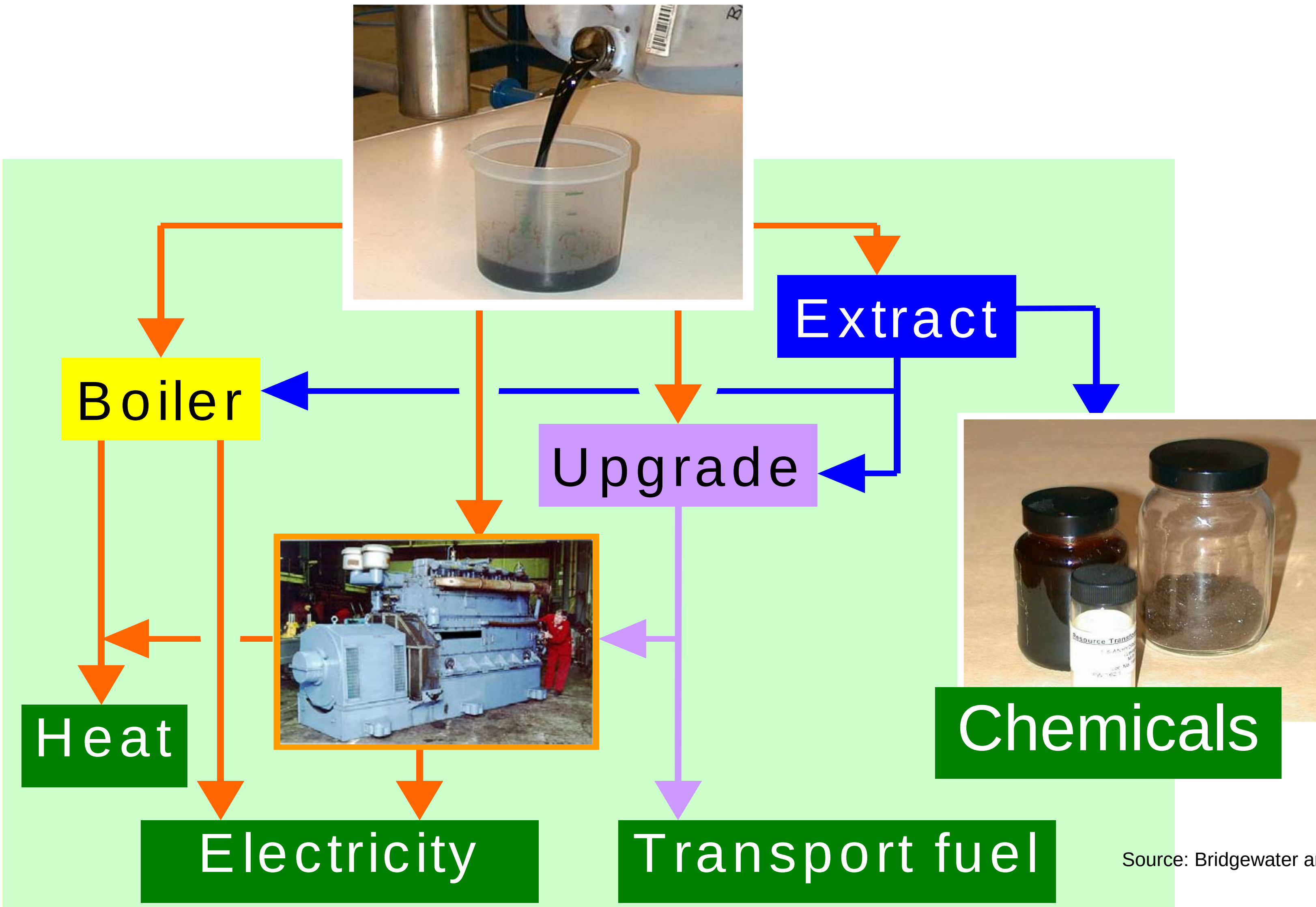
Source: Bridgewater and Czernik

Biocrude 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**

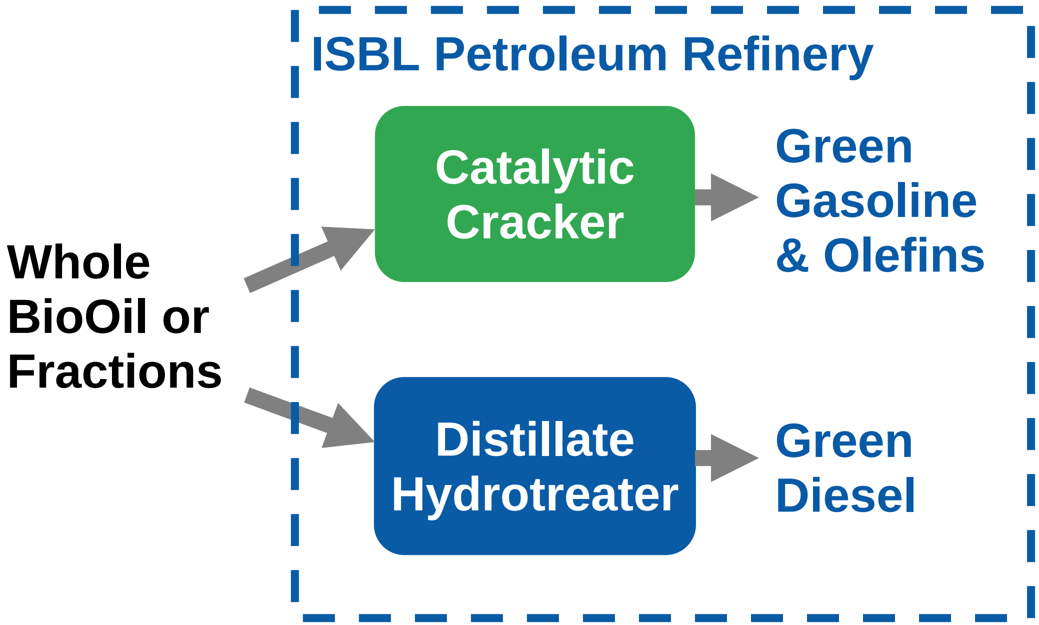
Source: Bridgewater and Czernik

There are a number of applications for biocrudes



Source: Bridgewater and Czernik

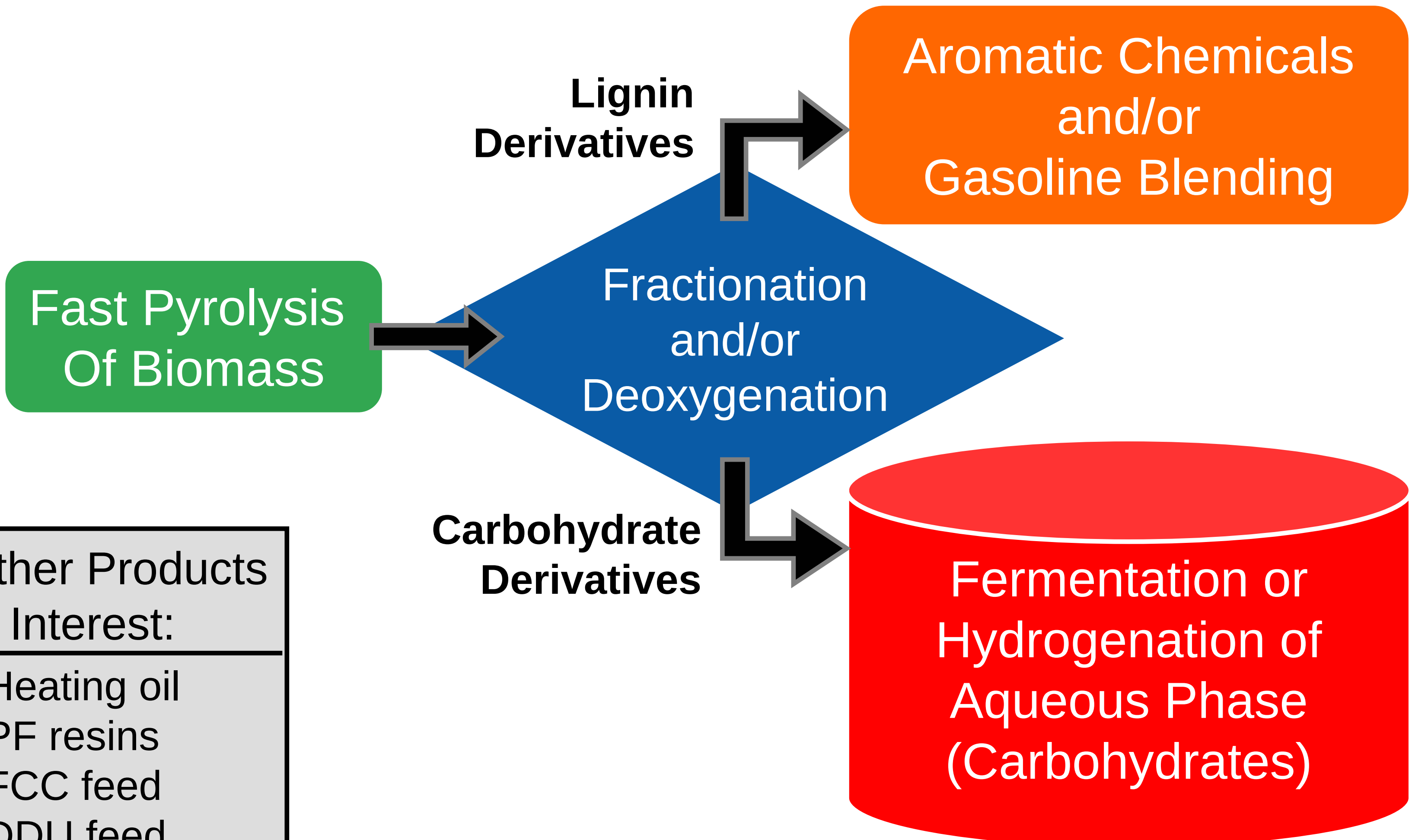
The biocrude can be upgraded in a petroleum refinery



- Must reduce acidity, improve stability and bio-oil miscibility with petroleum
- Deoxygenation may be required on either side of battery limits
- Fractionation could be beneficial, and may be performed outside the petroleum refinery
- Other processing options exist ISBL of the petroleum refinery

Based on UOP/NREL/PNNL R&D Project DOE-FG36-05GO15085 (2004 - 2005), and Colin Schaverien's (Shell) Biorefining presentation at 1st International Biorefinery Workshop, July 20-21, 2005, Washington D.C.

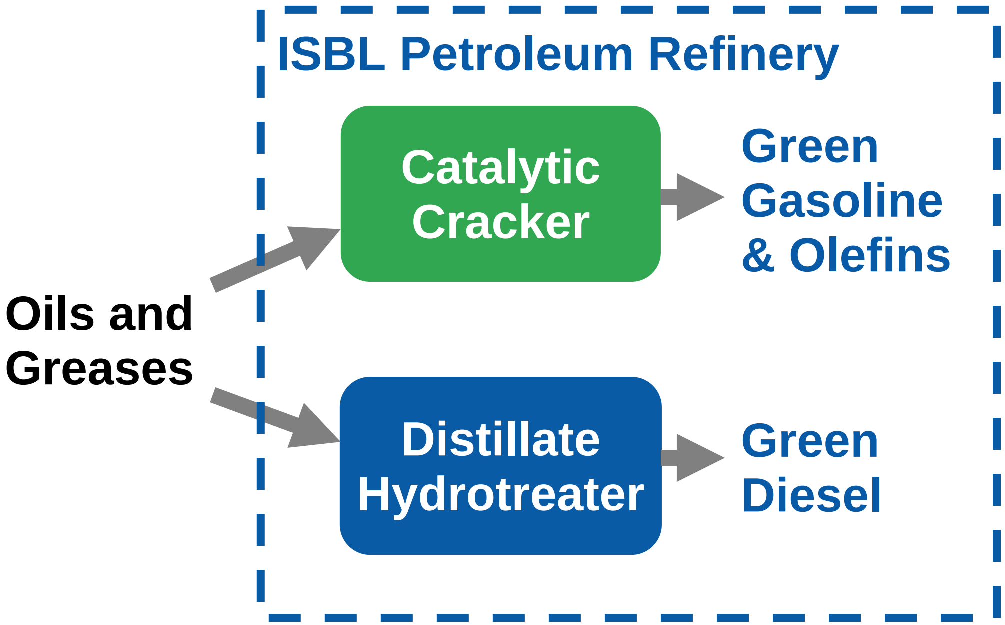
A pyrolysis-based biorefinery can produce multiple products



Other Products of Interest:

- Heating oil
- PF resins
- FCC feed
- DDU feed

Oils, fats & greases can be used as bio-renewable petroleum refinery feedstocks



- **Co-processing of oils and greases with petroleum fractions**
- **Utilize existing process capacity**
- **Potential for lower conversion costs (than FAME)**
- **Higher quality diesel blending component**
- **G/D flexibility**

Based on Presentations at 1st International Biorefinery Workshop, Washington DC, July 20-21, 2005

- ***Future Energy for Mobility***, James Simnick, **BP**
- ***From Bioblending to Biorefining***, Veronique Hervouet, **Total**
- ***Opportunities for Biorenewables in Petroleum Refineries***, Jennifer Holmgren, **UOP**

Green diesel has very attractive properties

	Biodiesel (FAME)	Green Diesel
% Oxygen	11	0
Density g/ml	.883	.78
Sulfur content	<10ppm	<10ppm
Heating Value (lower) MJ/kg	38	44
% change in NOx emission	0 to +10	0 to -10
Cloud Point °C	-5	-5 to -30
Distillation 10-90% pt	340-355	265-320
Cetane	50	80-90

Marinangeli, R., et.al. (2005). "Opportunities for Biorenewables in Oil Refineries: Final Technical Report," UOP, Des Plaines, IL; DOE Report No. DE-FG36-05GO15085

Hydrothermal treatment can be used to produce liquid products, and is being developed by companies such as Changing World Technologies and Biofuel BV

- **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**

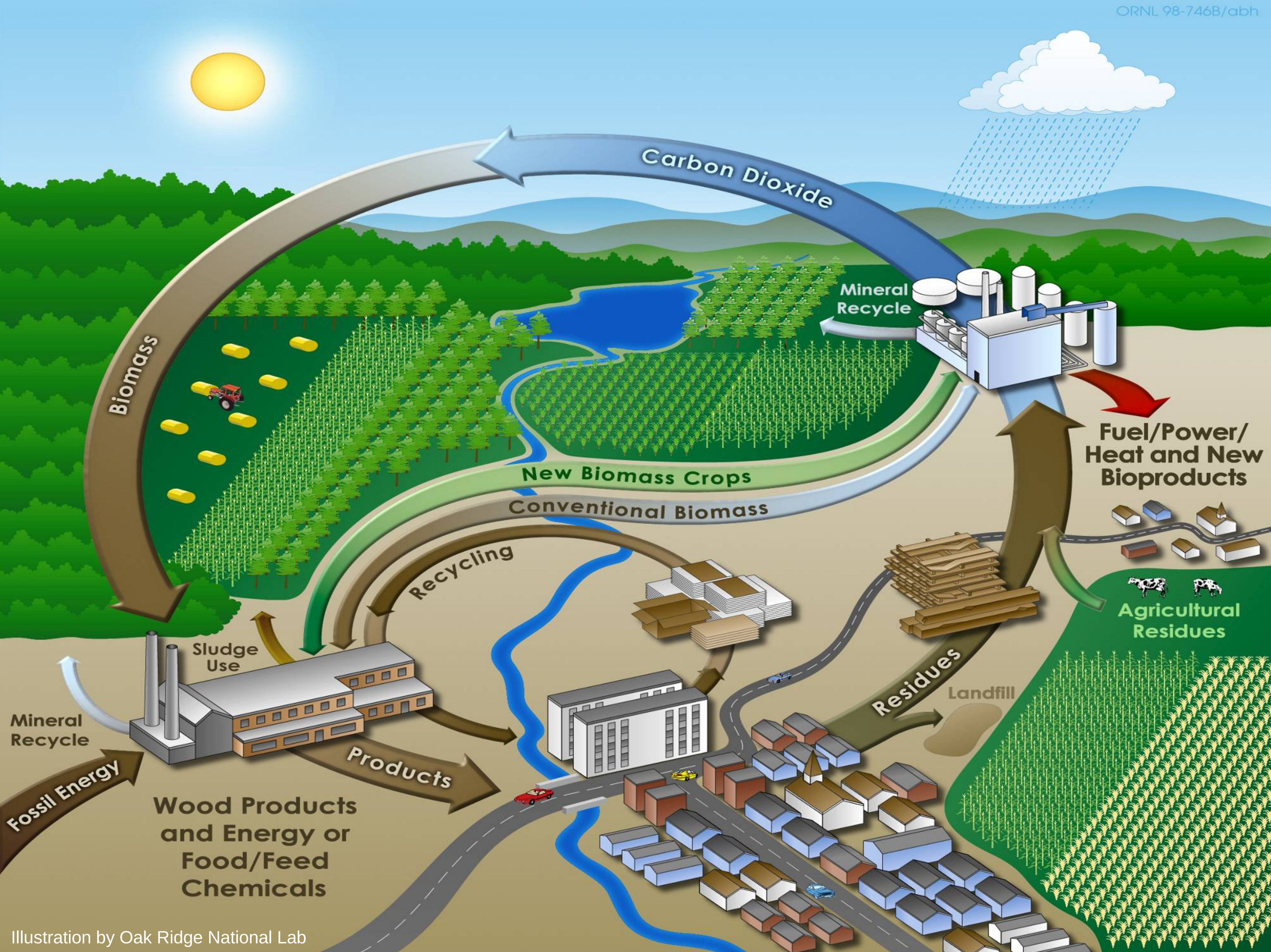


Illustration by Oak Ridge National Lab