Overview of Thermochemical Biorefining

Growing the Bioeconomy
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Bryan M. Jenkins
University of California, Davis

Principal Biomass Conversion Pathways

- Production
- Collection
- Processing
- Storage
- Transportation

- Thermochemical Conversion
  - Combustion
  - Gasification
  - Pyrolysis
  - Refining
- Biochemical Conversion
  - Anaerobic/Fermentation
  - Aerobic Processing
  - Biophotolysis
- Physicochemical
  - Esters
  - Alkanes

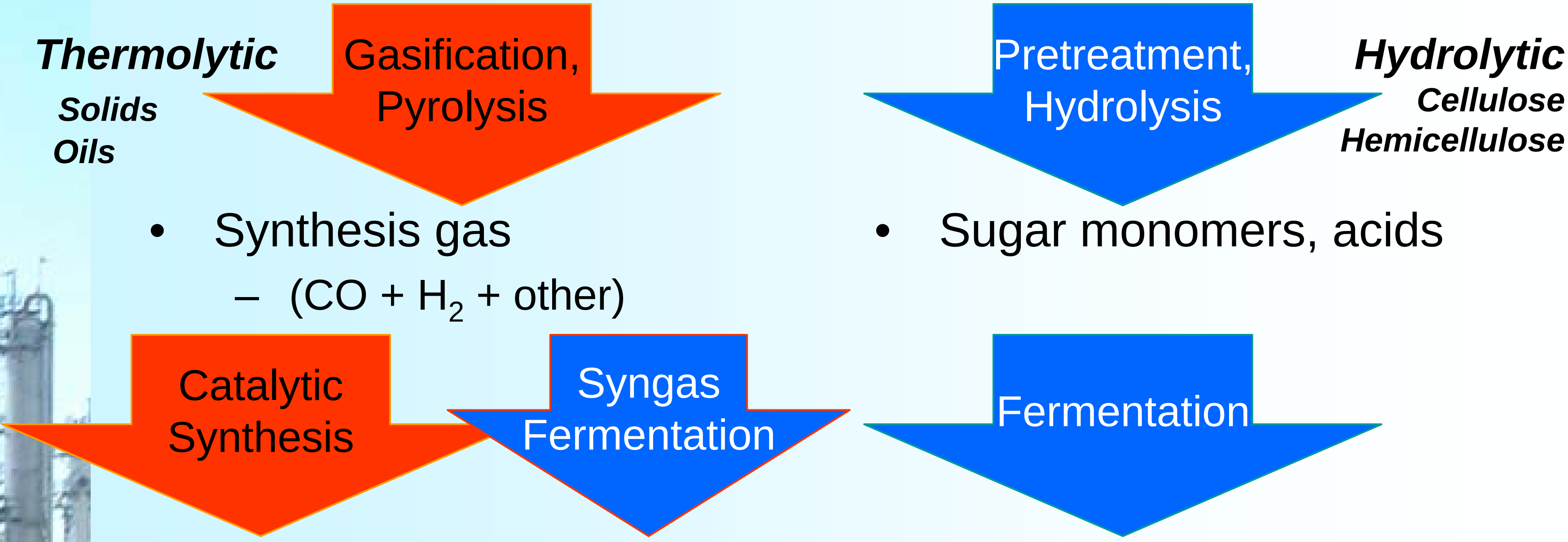
- Energy
  - Heat
  - Electricity
- Fuels
  - Solids
  - Liquids
  - Gases
- Products
  - Chemicals
  - Materials

Biomass Feedstock

Integrated Biorefinery

Value added products

Biorefining Approaches for Lignocellulose



- Thermochemical

Thermolytic

Solids
Oils

Gasification, Pyrolysis

- Synthesis gas
  - (CO + H_2 + other)

Catalytic Synthesis

Syngas Fermentation

- Hydrocarbons, mixed alcohols, hydrogen, ammonia, SNG, ethanol, higher alcohols…

- Biochemical

Pretreatment, Hydrolysis

Hydrolytic

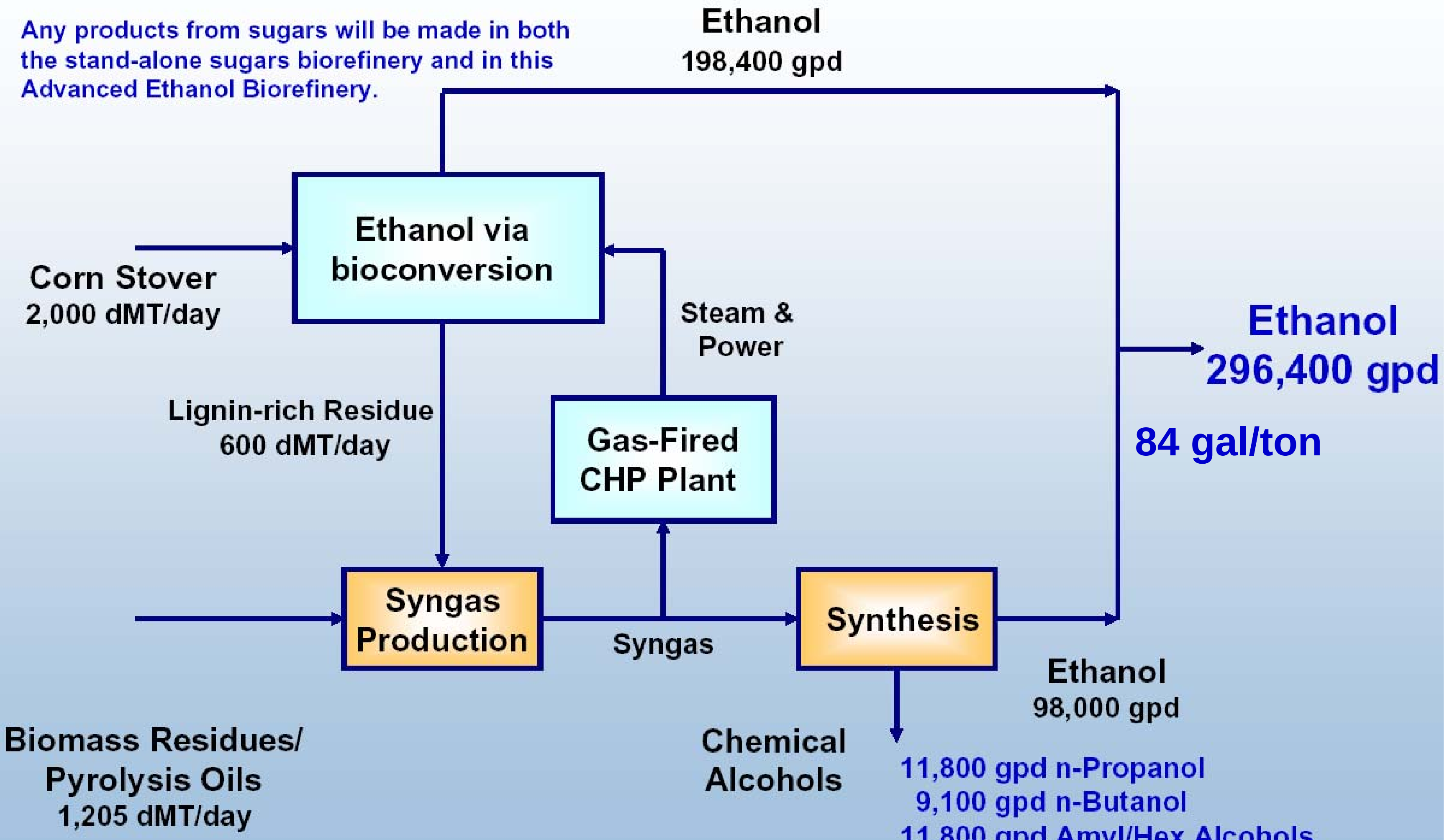
Cellulose
Hemicellulose

- Sugar monomers, acids

Fermentation

- Ethanol, higher alcohols, biomethane, acids…

Integrated Thermo-Biorefinery (Advanced Biorefinery)



Any products from sugars will be made in both the stand-alone sugars biorefinery and in this Advanced Ethanol Biorefinery.

Ethanol 296,400 gpd

84 gal/ton

11,800 gpd n-Propanol
9,100 gpd n-Butanol
11,800 gpd Amyl/Hex Alcohols

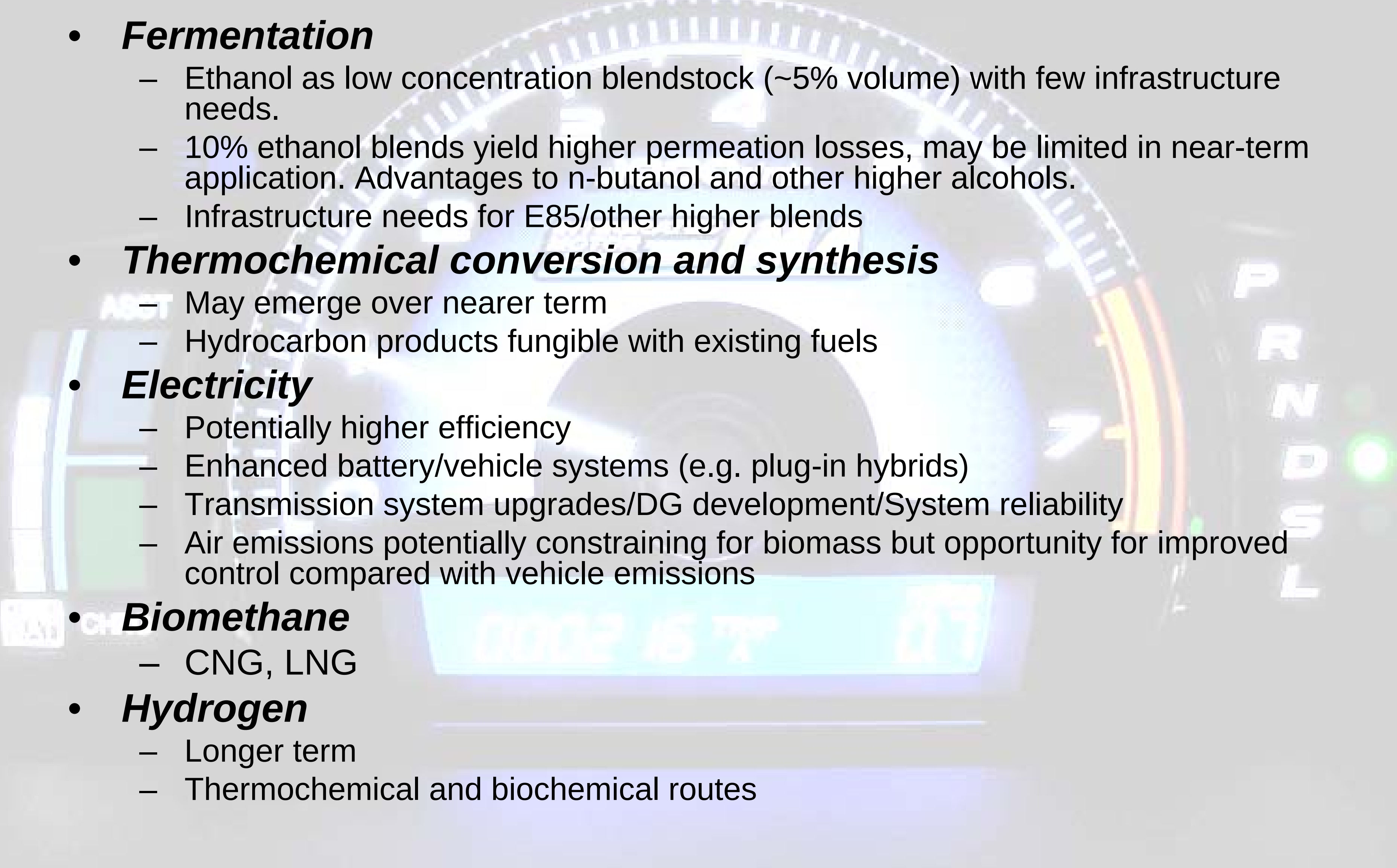
Source: Spath, 2005; Bain, 2005

Biofuels

Fuel	Conversion Process		
	Thermochemical	**Biochemical**	**Physicochemical**
Solids	**Chars/Charcoal**	**Biosolids**	**Biomass** **(incl. densified and other processed fuel)**
Liquids	**Methanol** **Biomass-to-Liquids (BTL/Fischer-Tropsch)** **Ethanol** **Dimethyl ether (pressurized)** **Bio-oils (pyrolysis oils)** **Bioparaffins**	**Ethanol** **Other Alcohols** **Liquified-BioMethane (LNG)**	**Plant Oils** **Yeast Oils** **Algal Oils** **Biodiesel (esters)** **Alkanes (catalytic)**
Gases	**Producer gas** **Synthesis gas (Syngas)** **Hydrogen**	**Biogas (incl. landfill gas, digester gas)** **Biomethane** **Hydrogen**	

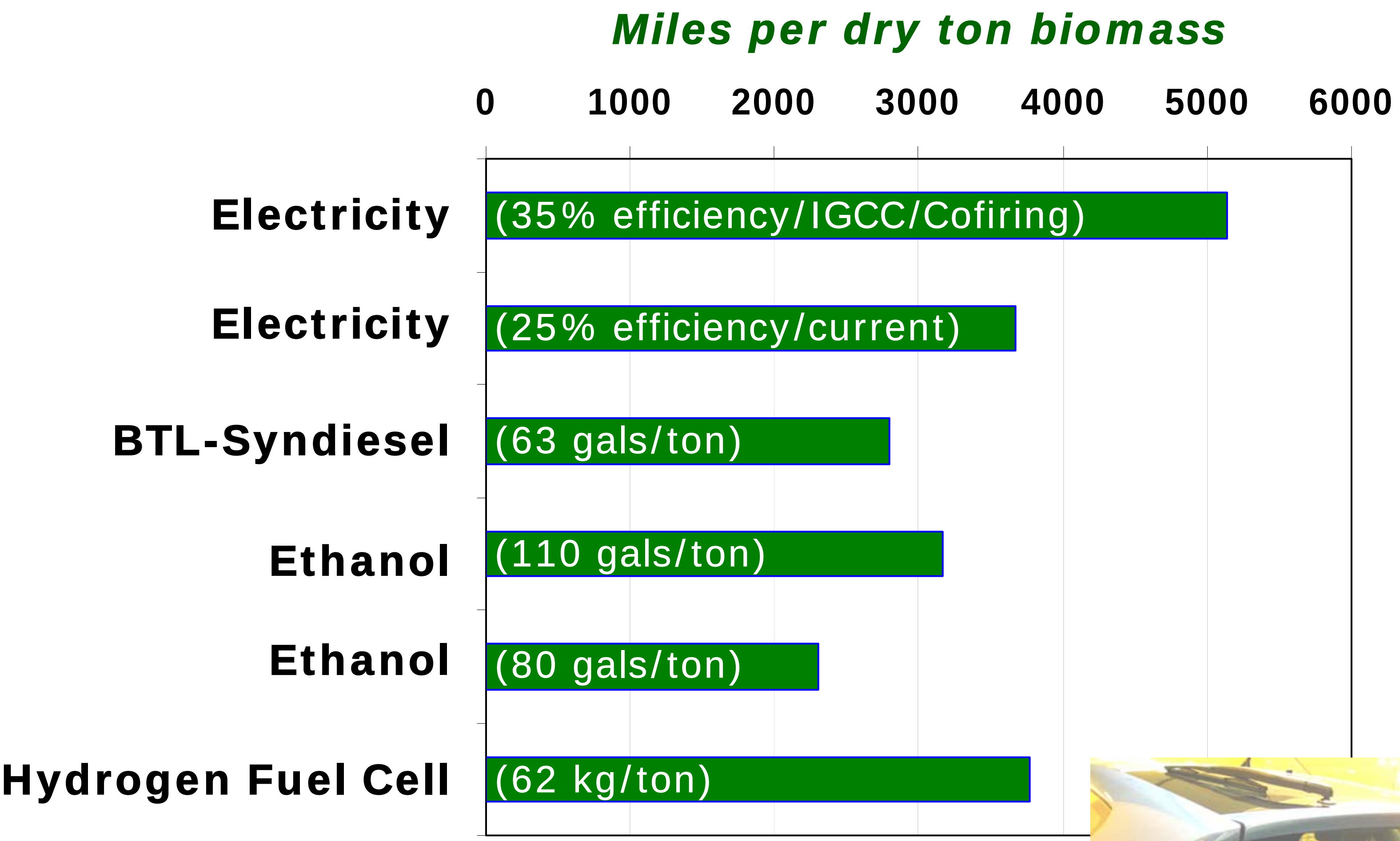
Biofuels can be blended with other fuels, e.g. E-85, B20

Competitive Biofuel Transportation Energy Paths



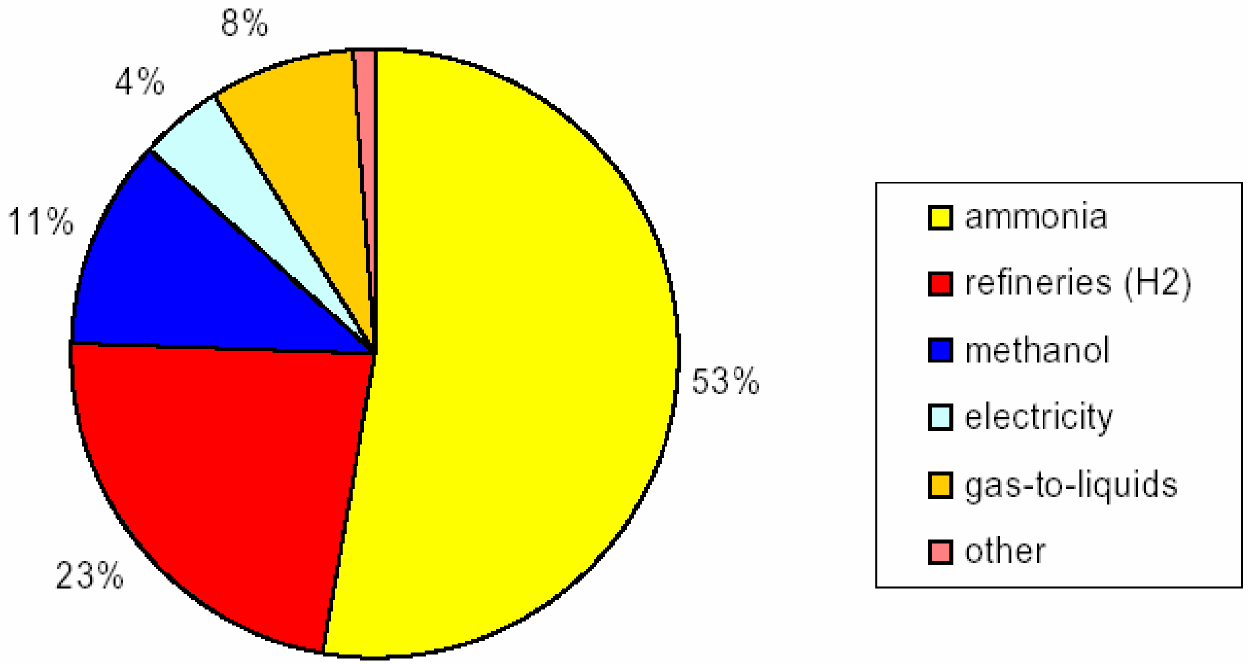
- ***Fermentation***
  - Ethanol as low concentration blendstock (~5% volume) with few infrastructure needs.
  - 10% ethanol blends yield higher permeation losses, may be limited in near-term application. Advantages to n-butanol and other higher alcohols.
  - Infrastructure needs for E85/other higher blends
- ***Thermochemical conversion and synthesis***
  - May emerge over nearer term
  - Hydrocarbon products fungible with existing fuels
- ***Electricity***
  - Potentially higher efficiency
  - Enhanced battery/vehicle systems (e.g. plug-in hybrids)
  - Transmission system upgrades/DG development/System reliability
  - Air emissions potentially constraining for biomass but opportunity for improved control compared with vehicle emissions
- ***Biomethane***
  - CNG, LNG
- ***Hydrogen***
  - Longer term
  - Thermochemical and biochemical routes

Transport Range for Bioenergy



Based on hybrid vehicle with 44 miles per gallon fuel economy on gasoline, 260 Wh/mile battery (source: B. Epstein, E2). Electricity includes generating efficiency, transmission, distribution, and battery charging losses. Ethanol, BTL-Syndiesel, and H_2 include fuel distribution transport energy.

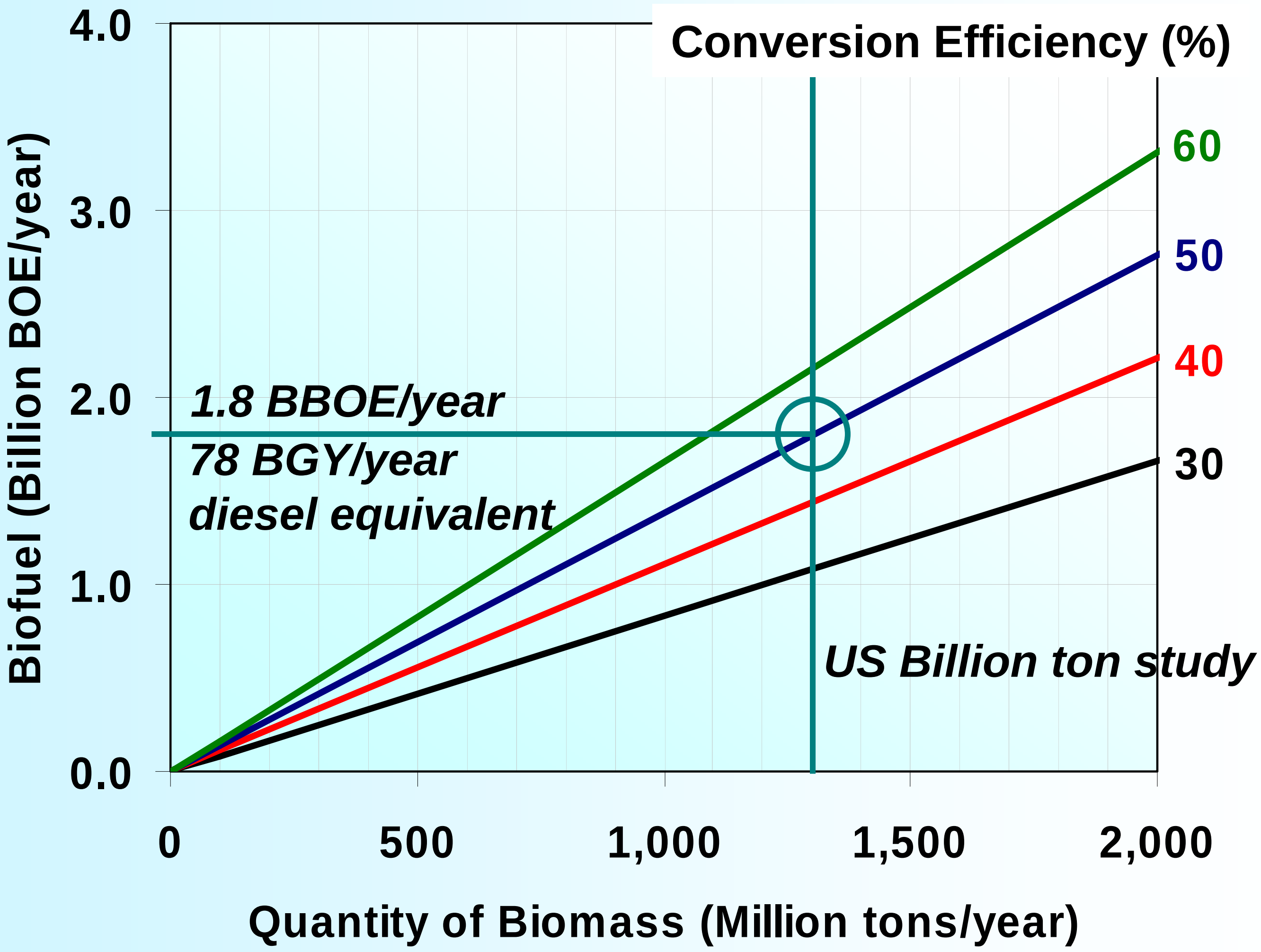
World Syngas Market— 6 Exajoules/year (5.7 Quads/year)



Equivalent of 980 million bbl/year or 2.7 million bbl/day (bbld).

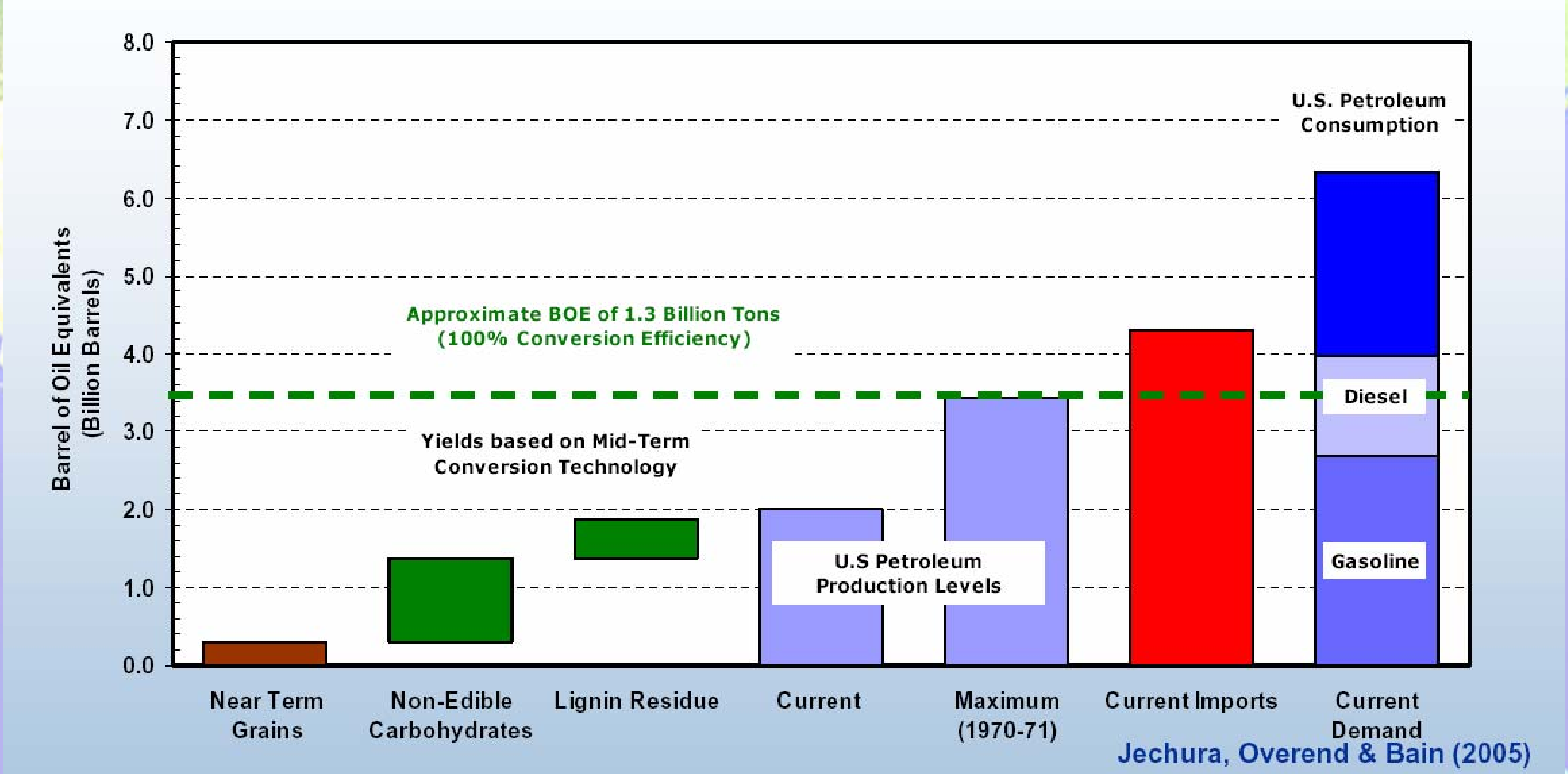
Source: IEA

Biofuel Potential



1.8 BBOE/year
78 BGY/year
diesel equivalent

Biofuel Potential in US Transportation

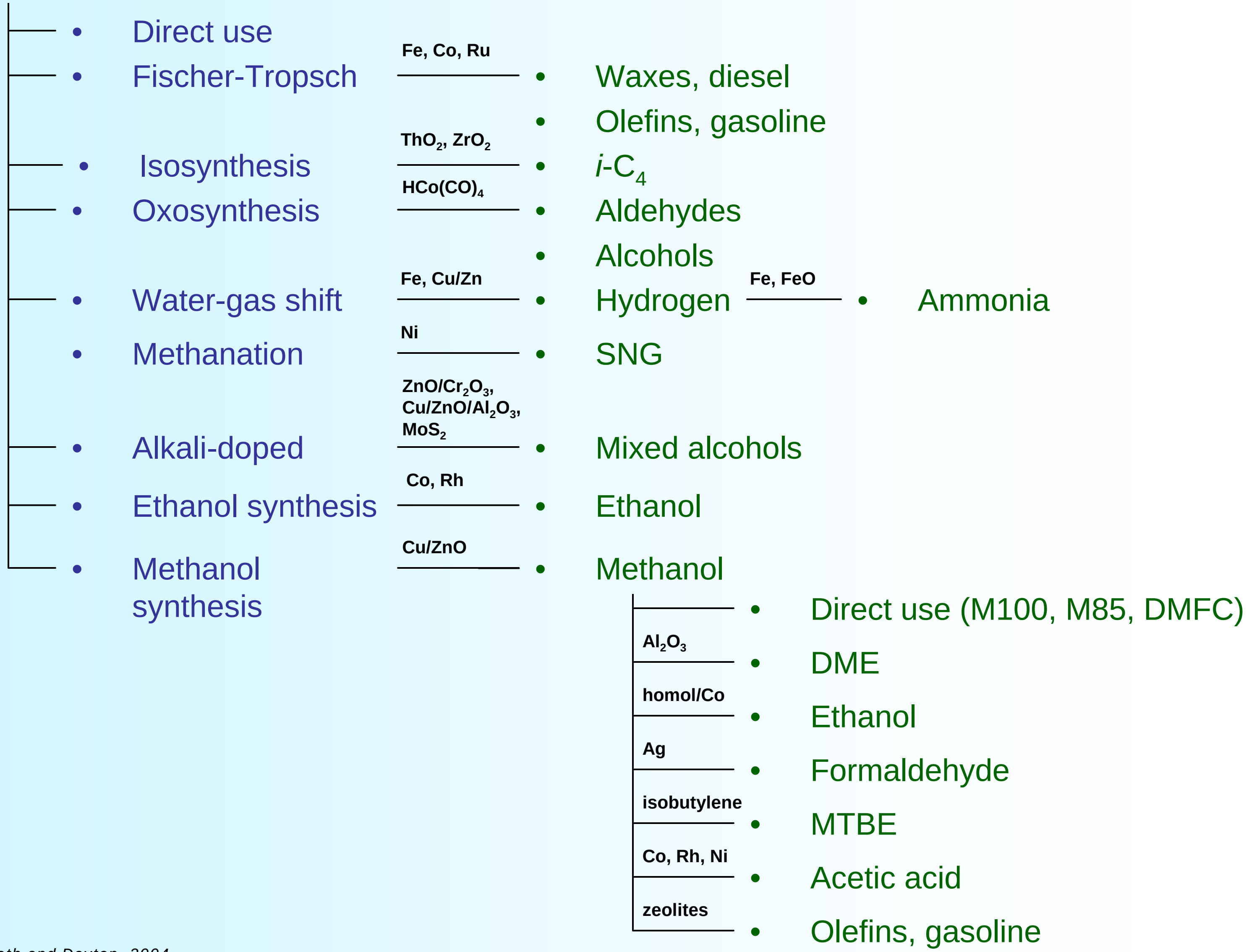


Jechura, Overend & Bain (2005)

source: Bain, 2005

Thermo-biorefining

Syngas



Direct use				
Fischer-Tropsch	Fe, Co, Ru	Waxes, diesel		
		Olefins, gasoline		
Isosynthesis	ThO_2, ZrO_2	*i*-C_4		
Oxosynthesis	$HCo(CO)_4$	Aldehydes		
		Alcohols		
Water-gas shift	Fe, Cu/Zn	Hydrogen	Fe, FeO	Ammonia
Methanation	Ni	SNG		
Alkali-doped	ZnO/Cr_2O_3, $Cu/ZnO/Al_2O_3$, MoS_2	Mixed alcohols		
Ethanol synthesis	Co, Rh	Ethanol		
Methanol synthesis	Cu/ZnO	Methanol		

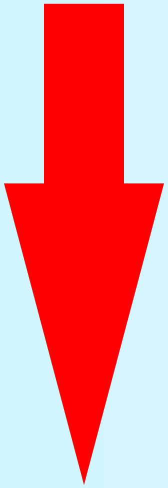
Methanol:

	Direct use (M100, M85, DMFC)
Al_2O_3	DME
homol/Co	Ethanol
Ag	Formaldehyde
isobutylene	MTBE
Co, Rh, Ni	Acetic acid
zeolites	Olefins, gasoline

adapted from Spath and Dayton, 2004

Thermal Gasification

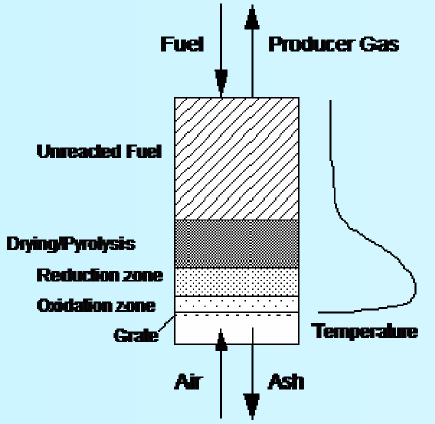
Fuel + Oxidant/Heat



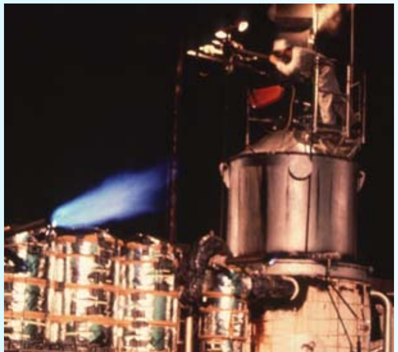
Partial Oxidation/Air or Oxygen
Steam/Carbon Dioxide/Hydrogen
Indirect Heating

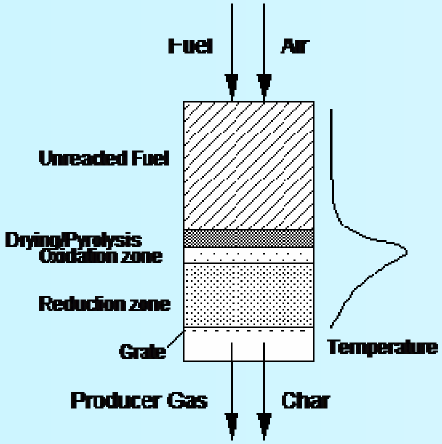
$CO + H_2 + HC + CO_2 + N_2 + H_2O +$
Char + Tar + PM + $H_2S + NH_3 +$
Other + Heat

Classification by Reactor Type: Fixed/Moving Beds

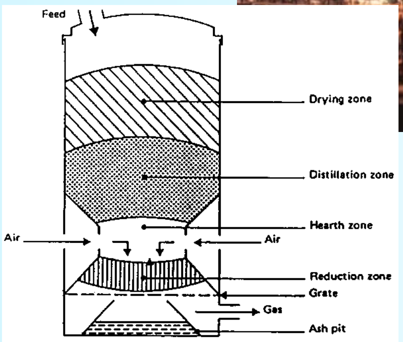


Updraft gasifier



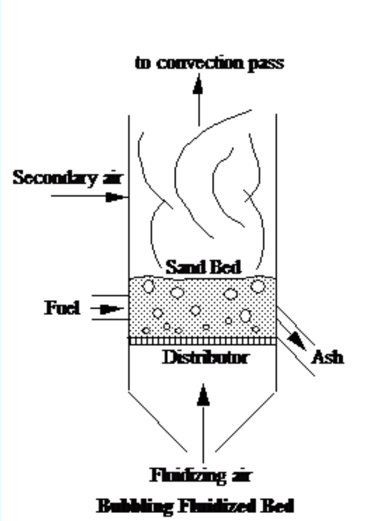


Downdraft gasifier

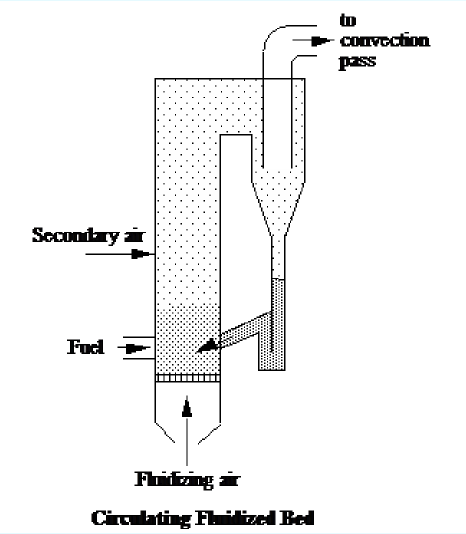


- Updraft
  - Countercurrent
  - High moisture fuel (<60% wet basis)
  - High tar production except with post-reactor catalytic cracking or dual stage air injection
  - Low carbon ash
- Downdraft
  - Cocurrent
  - Moisture < 30%
  - Lower tar than uncontrolled updraft
  - Carbonaceous char
- Crossdraft
  - Adaptation for high temperature charcoal gasification

Classification by Reactor Type: Fluidized Beds



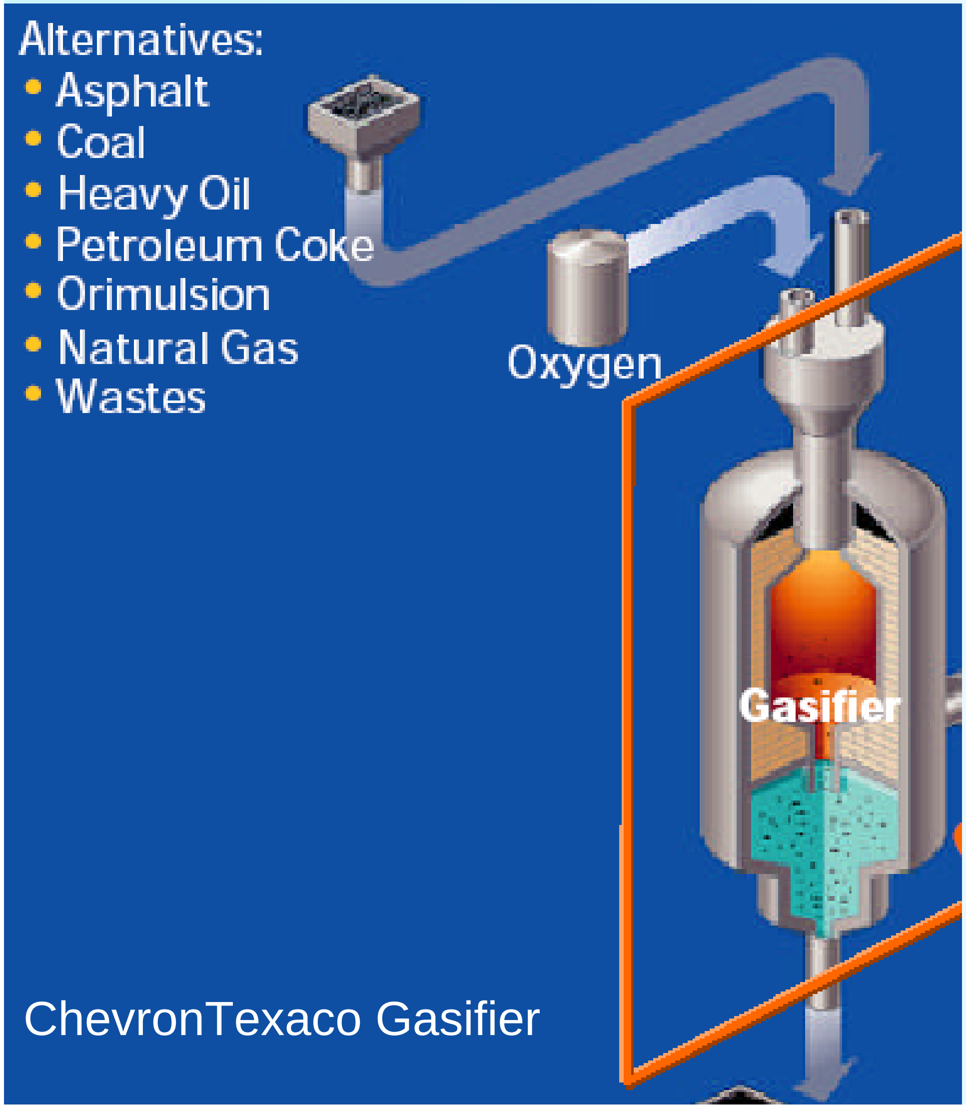
Bubbling Fluidized Bed



Circulating Fluidized Bed

- Bubbling beds
  - Lower velocity
  - Low entrainment/elutriation
  - Simple design
  - Lower capacity and potentially less uniform reactor temperature distribution than circulating beds
- Circulating beds
  - Higher velocity
  - Solids separation/recirculation
  - More complex design
  - Higher conversion rates and efficiencies

Classification by Reactor Type: Entrained Beds



ChevronTexaco Gasifier

- Solids or slurry entrained on gas flow
  - Small particle size
  - Entrained flow used as component in some developmental pyrolytic biomass reactor systems

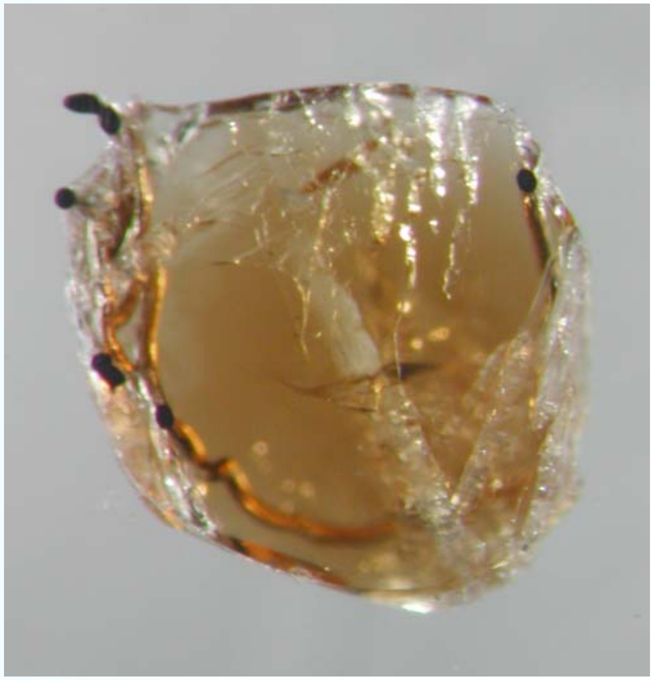
Reactions and Products

- Oxidation $C + O_2 = CO_2$
- Boudard reaction $C + CO_2 = 2CO$
- Hydrogasification $C + 2H_2 = CH_4$
- Water-gas reactions $C + H_2O = CO + H_2$
  $C + 2H_2O = CO_2 + 2H_2$
- Water-gas shift $CO + H_2O = CO_2 + H_2$
- Methanation $CO + 3H_2 = CH_4 + H_2O$

Composition of Raw Gas from Steam Gasification

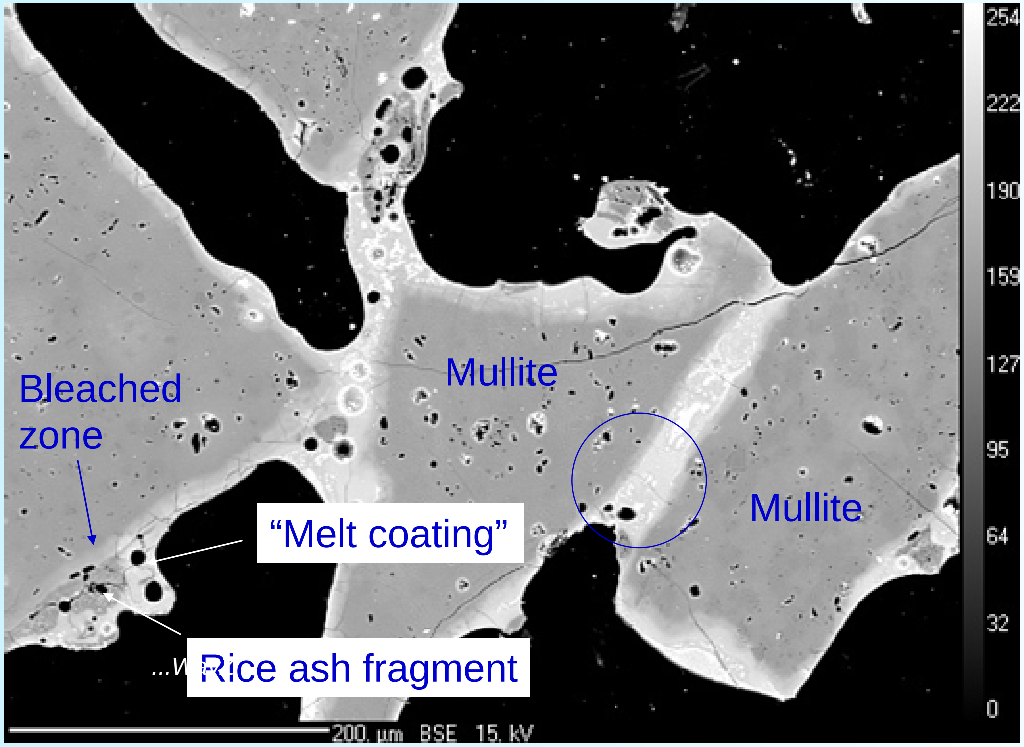
	% by volume dry (except as noted)
H_2O	30 – 45 (wet)
CH_4	10 - 11
C_2H_4	2.0 - 2.5
C3 fraction	0.5 – 0.7
CO	24 – 26
CO_2	20 – 22
H_2	38 – 40
N_2	1.2- 2.0
H_2S	130 – 170 ppmv
NH_3	1100 – 1700 ppmv
Tar	2 – 5 g Nm^{-3}
Particulate Matter	20 – 30 g Nm^{-3}
Lower Heating Value	~350 Btu ft^{-3}

Inorganic Material Behavior



- Potential for slagging, fouling, and agglomeration of fluid bed medium
- Higher risk with high-alkali herbaceous biomass
- Feedstock modification to reduce risk or use slagging reactors

Back-scattered electron image

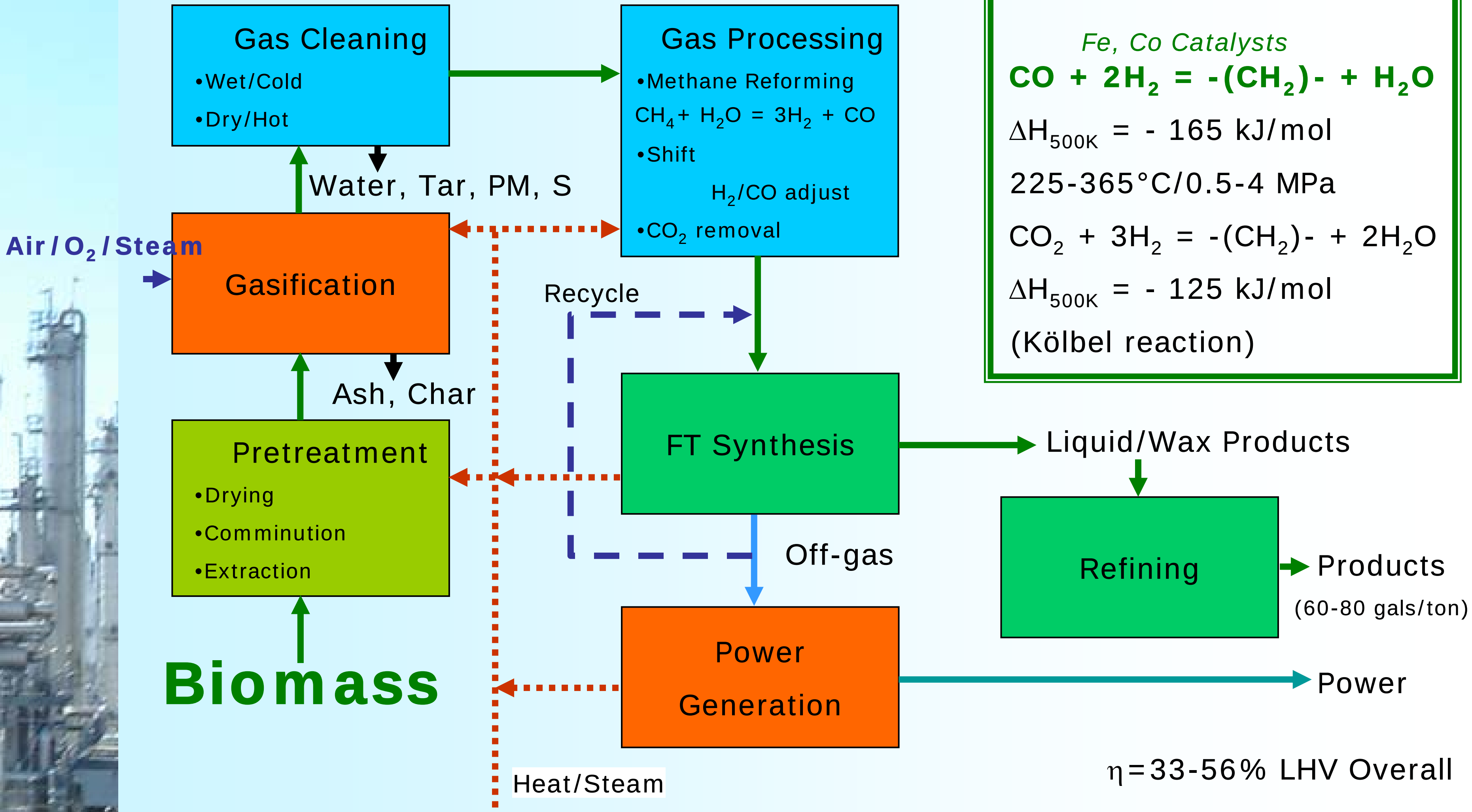


Liquid Synthesis
GTL—Gas to Liquids (commercial)

- Natural gas (or biomethane) reforming
  - Steam reforming: $CH_4 + H_2O = CO + 3H_2$
  - Partial oxidation: $CH_4 + 1.5O_2 = CO + 2H_2O$
  - Water-gas shift: $CO + H_2O = CO_2 + H_2$
  - Example: Methane/Oxygen-fired autothermal reforming (Haldor Topsøe)
- Fischer-Tropsch Synthesis
  - $CO + 2H_2 = \text{-}(CH_2)\text{-} + H_2O$
  - Example: Sasol slurry phase reactor
    - (gas fed liquid hydrocarbon-catalyst slurry)
- Product Upgrading
  - Hydrotreating for olefin and oxygenate conversion
  - Hydrocracking to naphtha and diesel
  - Fractionation
- Yield: 3.5 bbl/1000 m^3

  (4 bbld/1000 cows through biomethane)

BTL: Biomass To Liquids



Fischer-Tropsch Synthesis

Fe, Co Catalysts

$CO + 2H_2 = -(CH_2)- + H_2O$

$\Delta H_{500K} = - 165$ kJ/mol

225-365°C/0.5-4 MPa

$CO_2 + 3H_2 = -(CH_2)- + 2H_2O$

$\Delta H_{500K} = - 125$ kJ/mol

(Kölbel reaction)

Gas Cleaning

- Wet/Cold
- Dry/Hot

Gas Processing

- Methane Reforming

$CH_4 + H_2O = 3H_2 + CO$

- Shift

H_2/CO adjust

- CO_2 removal

Water, Tar, PM, S

Air/O_2/Steam

Gasification

Ash, Char

Pretreatment

- Drying
- Comminution
- Extraction

Biomass

Recycle

FT Synthesis

Liquid/Wax Products

Off-gas

Refining

Products

(60-80 gals/ton)

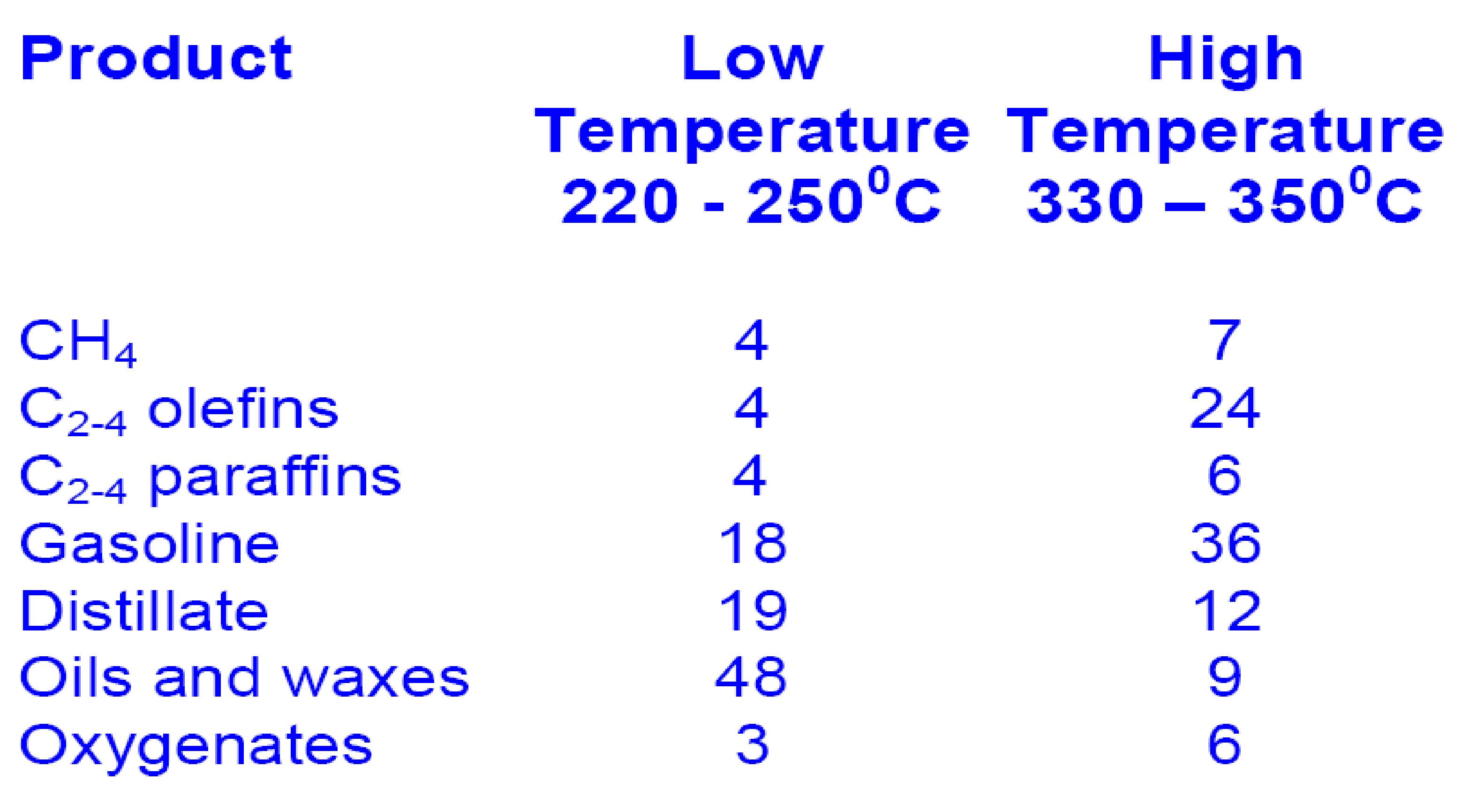
Power Generation

Power

Heat/Steam

η=33-56% LHV Overall

FT Product Distribution



Product	Low Temperature 220 - 250^{0}C	High Temperature 330 – 350^{0}C
CH_4	4	7
$C_{2\text{-}4}$ olefins	4	24
$C_{2\text{-}4}$ paraffins	4	6
Gasoline	18	36
Distillate	19	12
Oils and waxes	48	9
Oxygenates	3	6

Fe catalyst

source: Jager, 2003

Gas Cleaning

- **Syngas contaminant concentration limits**

Particulate matter	**~0 (> 2 µm)**
Tar	**~0 ppm**
Sulfur	**60 ppb - 1 ppm**
Halides	**10 ppb**
Nitrogen	**10 ppmv NH_3** **~0 ppmv NO_x** **10 ppb HCN** **(except for ammonia synthesis)**

Adapted from Dayton, 2005

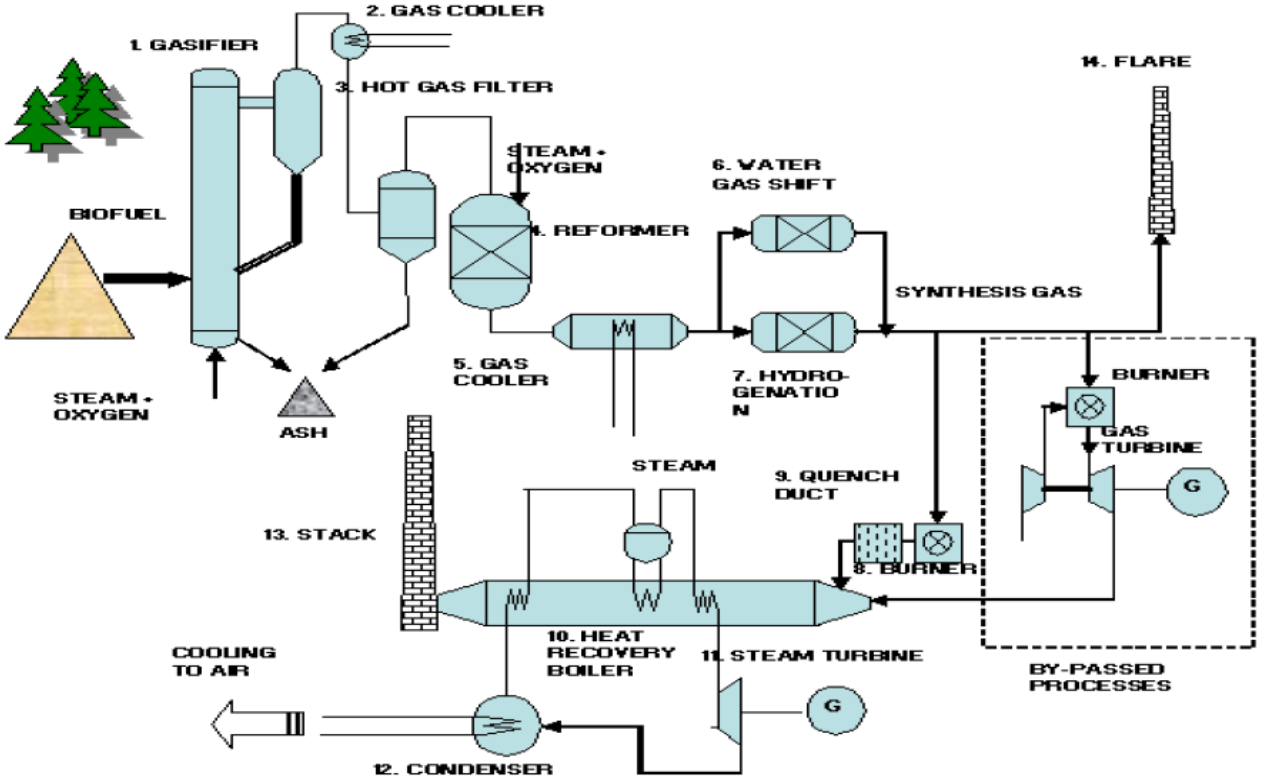
Biomass FT Development

- Värnamo, Sweden
  - pressurized fluidized bed gasifier
  - steam/oxygen blown
  - conversion of IGCC
- Choren, Germany
  - 2-stage gasification
  - VW and Daimler-Chrysler
- Güssing, Austria
  - FT slurry reactor

CHRISGAS (Värnamo) Demonstration

Pressurized fluidized bed

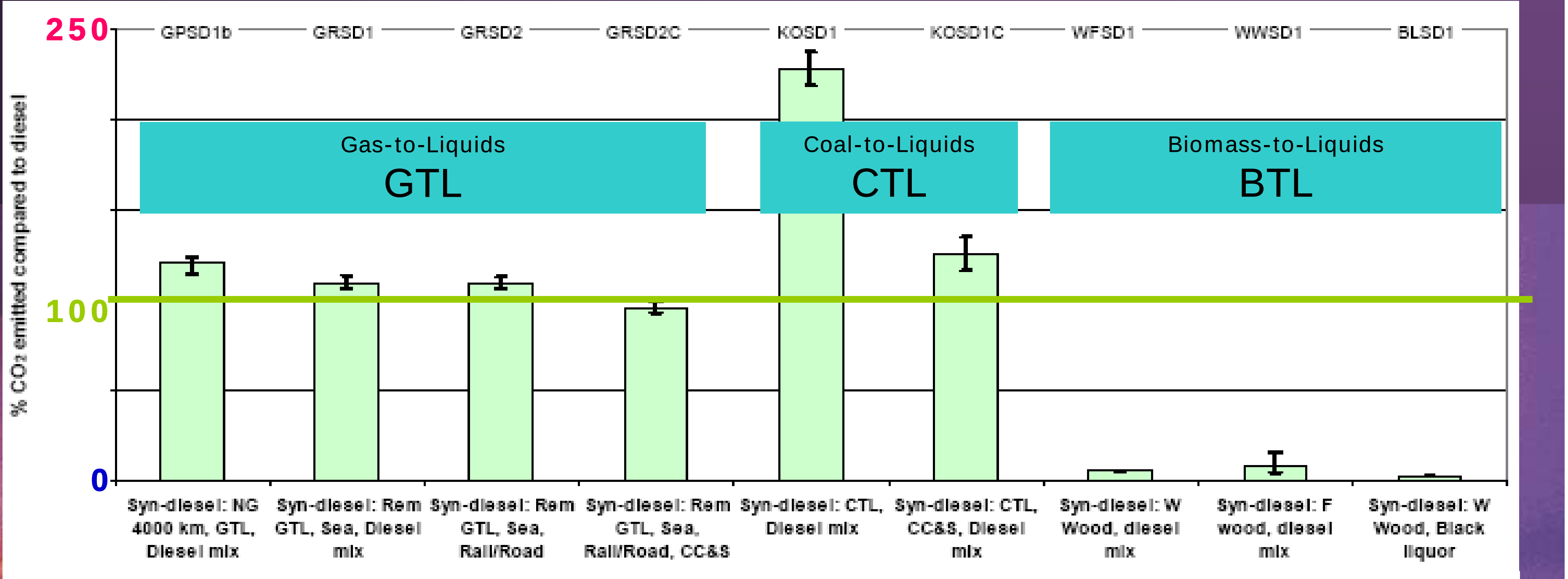
- FT, H_2, DME, Methanol



CHRISGAS
fuels from biomass

Source: Bengtsson, 2005

Net CO_2 Emissions for Syndiesels



% CO_2 emitted compared to diesel

Image: http://www.fischer-tropsch.org/

WELL-TO-WHEELS ANALYSIS OF FUTURE AUTOMOTIVE FUELS AND POWERTRAINS IN THE EUROPEAN CONTEXT (May, 2006)

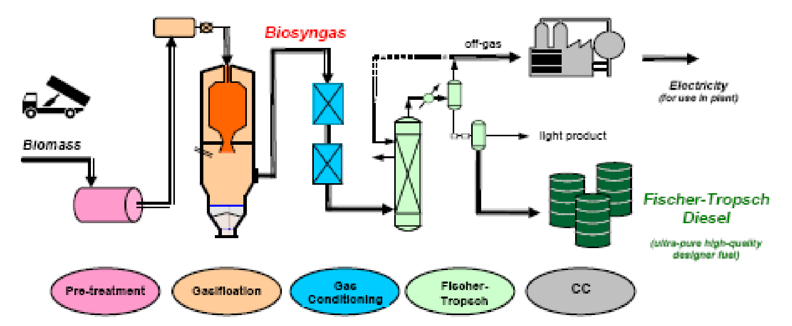
http://ies.jrc.cec.eu.int/media/scripts/getfile.php?file=fileadmin/H04/Well_to_Wheels/WTT/WTT_Report_030506.pdf

Thermochemical Biofuel Lifecycle Energy Ratios

Biomass to:	**Fossil Energy Ratio**	**Primary Energy Ratio**
FT liquid	6 -17	0.16 – 0.42
Ethanol	16	0.35
Mixed Alcohols	8 -13	0.18 – 0.29
Methanol	12 - 26	0.29 – 0.64
Olefins via methanol	8 – 19	0.20 – 0.45

Source: Spath and Dayton, 2003

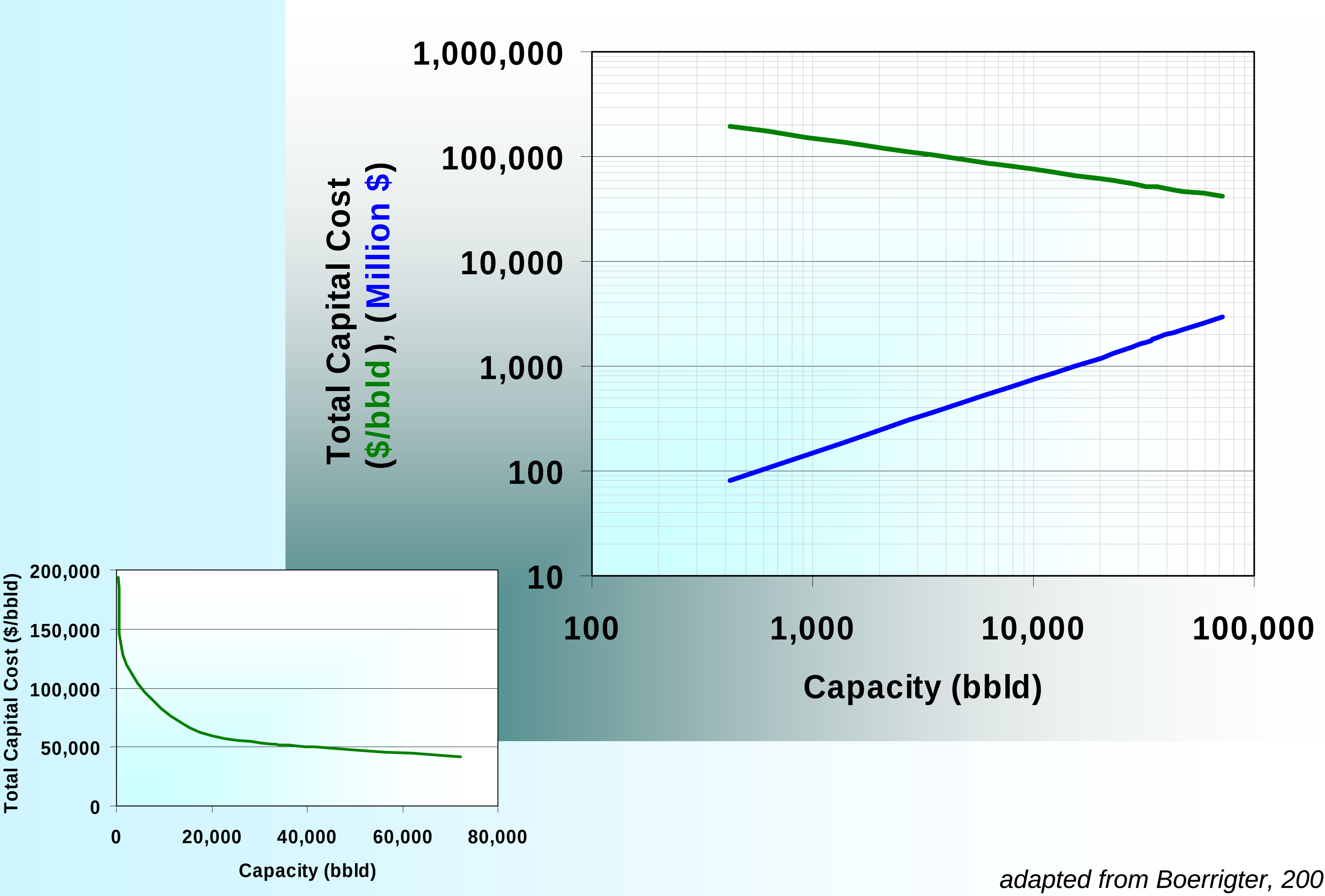
Capital Cost Basis for a 34,000 bbl/day Biofuel FT Refinery



	Cost (Million $)
Air separation unit	**207**
Gasifier	**138**
H_2 manufacturing and syngas conditioning	**46**
Gas cleaning	**161**
Fischer-Tropsch synthesis	**115**
Product upgrading	**69**
Site and auxiliaries	**735**
Indirect costs and working capital	**298**
Total capital investment	**1,768**

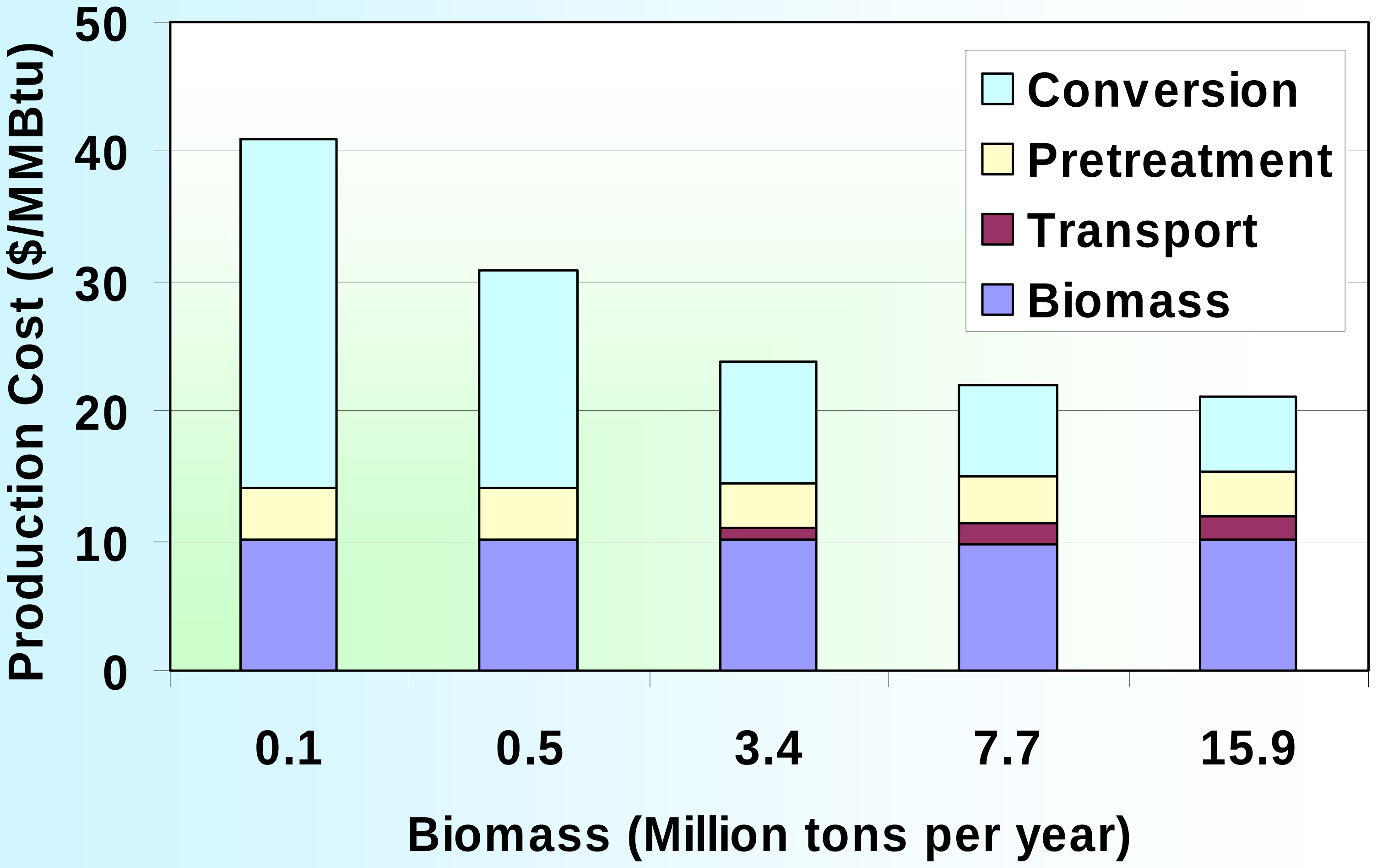
adapted from Boerrigter, 2006

Capital Cost Economy of Scale for FT Biorefinery



adapted from Boerrigter, 2006

FT Biofuel Production Cost

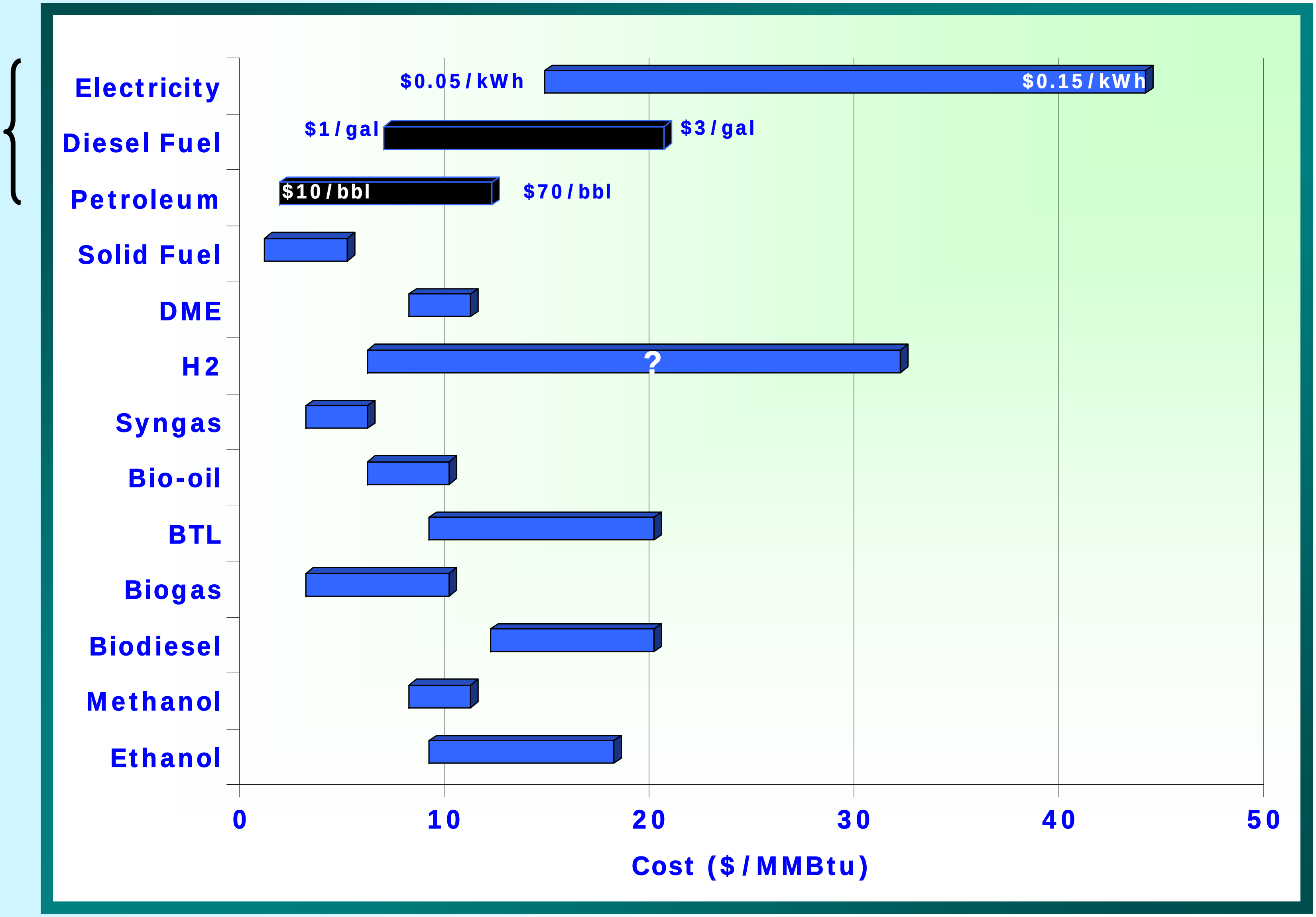


MWth	**50**	**250**	**1,800**	**4,100**	**8,500**
bbl/d	**425**	**2,125**	**15,300**	**34,849**	**72,248**

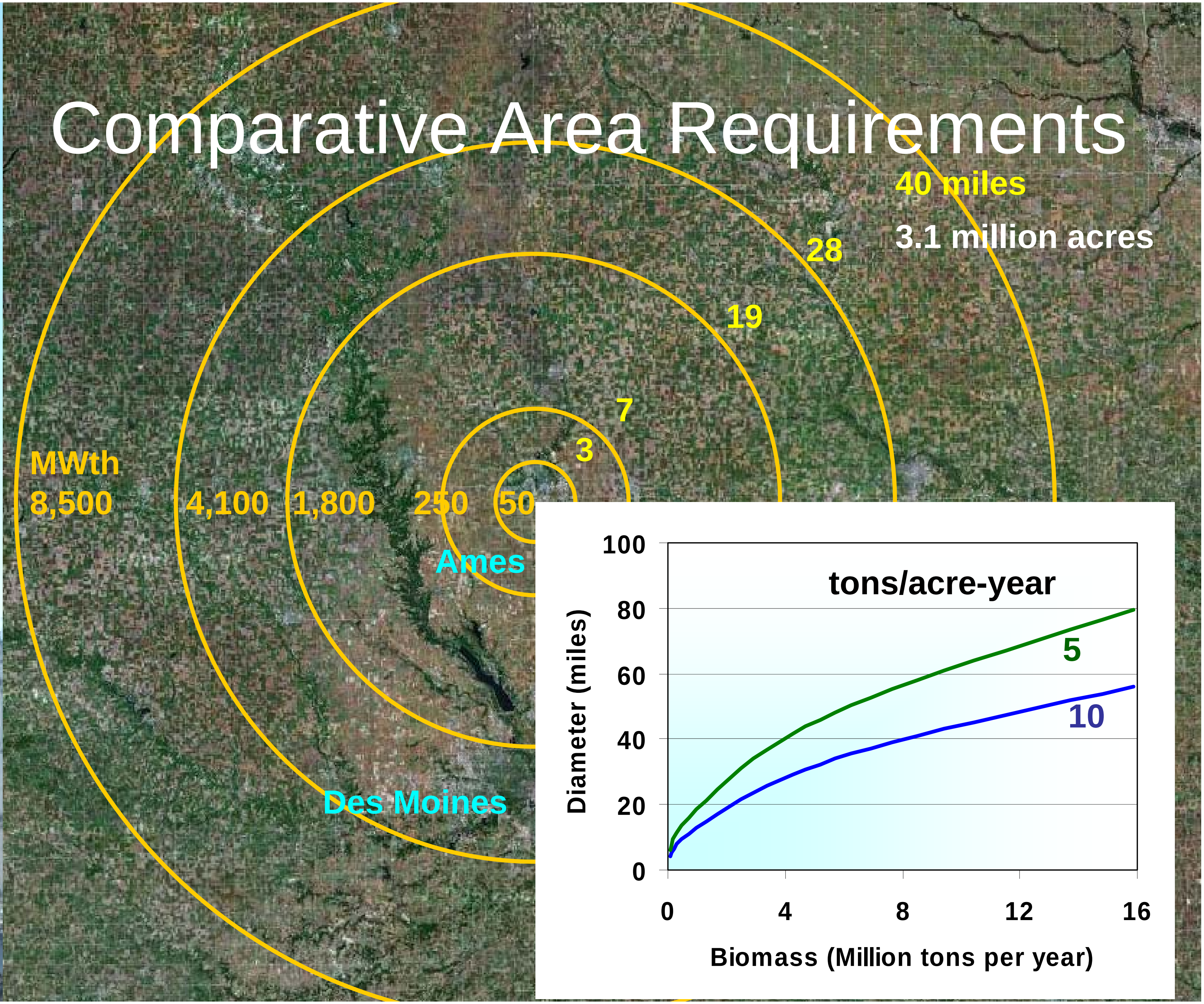
adapted from Boerrigter, 2006

Biofuel Production Costs

Compare:



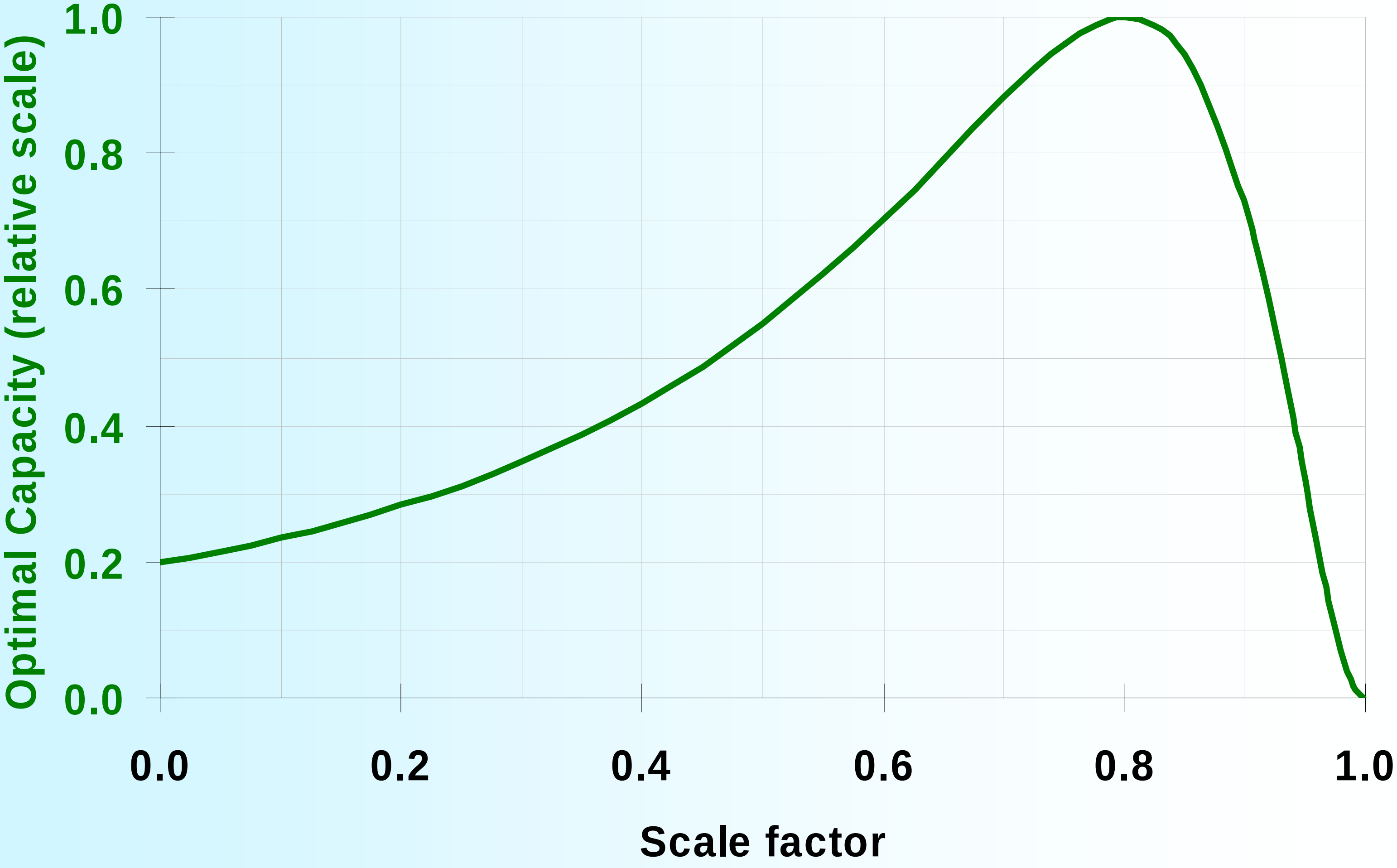
Comparative Area Requirements



Sasol (Secunda/Sasol II and III: 150,000 bbld)

source: Jager, 2003

Relative Impact of Economy of Scale Factor on Optimal Size



Source: Jenkins, 1997

Conclusions

- Thermochemical conversion can be used to provide a wide range of fuels and chemicals from biomass. Coupling thermal and biological conversion in advanced biorefinery concepts can offer advantages for improved utilization and efficiency.
- Large scale demonstration of thermochemical biorefineries still lacking, technical uncertainties remain, especially in gas quality and catalyst performance.
- Good economies of scale in capital cost suggest large optimal sizes for thermochemical facilities (e.g. Fischer-Tropsch). Optimal size is, however, sensitive to scale factor and risk associated with feedstock supply and delivery.
- To process 1.3 billion tons of biomass with thermochemical biorefineries:
  - 145 FT biorefineries at 34,000 bbld capacity needed to supply 1.8 BBOE/year
  - total capital investment in excess of $250 billion

Conclusions

- Substantial greenhouse gas emissions reduction potential
- Large fossil energy ratios
- Some thermochemical fuels (e.g. FT) fungible in existing fuel delivery infrastructure
- Continuing needs in RD&D
  - Feedstock processing
  - Reactor design
  - Gas cleaning and catalyst performance and optimization
  - Process integration and cost reduction
  - Coproduct quality and markets
  - Resource consumption, environmental impacts (e.g. water)
- Large scale implementation of biorefineries should occur as part of overall system optimization, including changes in transportation to increase efficiency and reduce energy demand among multiple energy sources.