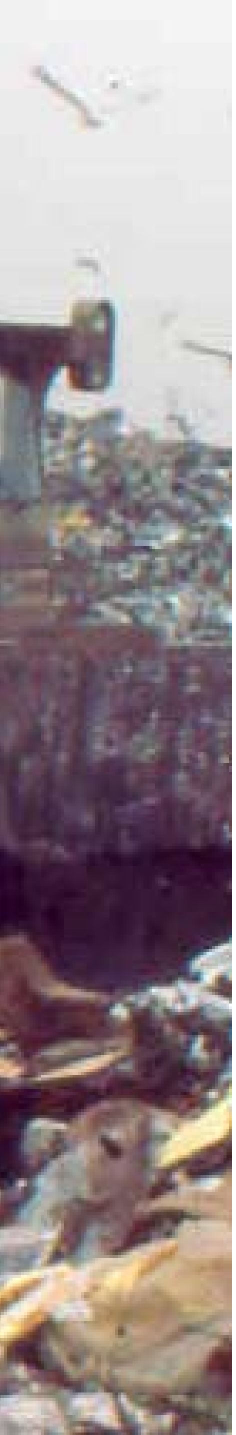

Thermal Technologies for Waste Management

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Principal Biomass and Waste Conversion Pathways

- Collection
  - Separated
  - Mixed
- Processing
- Storage
- Transportation

- Thermochemical Conversion
  - Combustion
  - Gasification
  - Pyrolysis
- Bioconversion
  - Anaerobic/Fermentation
  - Aerobic Processing
  - Biophotolysis
- Physicochemical
  - Esters

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

Thermochemical Conversion

- ***Pyrolysis***—thermal decomposition of organic material through heating
- ***Gasification***—conversion of solids or liquids to fuel- or synthesis-gases through gas-forming reactions
- ***Combustion*** (solids)—exothermic oxidation involving pyrolysis, gasification, and heterogeneous and homogeneous oxidation reactions

Fuels from thermochemical conversion

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)**	**Ethanol** **Other Alcohols** **Liquified-BioMethane (LNG)**	**Vegetable Oils** **Biodiesel (esters)**
Gases	**Producer gas** **Synthesis gas (Syngas)** **Hydrogen**	**Biogas** **(incl. landfill gas, digester gas)** **Biomethane** **Hydrogen**	

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

Combustion of Waste (WTE)

- World statistics:
  - Combustion used to process an estimated 150 million tons per year of MSW
  - Landfilling > 1 Billion tons per year
  - > 600 WTE facilities operating worldwide
  - Since 1995, 164 new WTE facilities have been constructed—none in the US

Region or Country	Million Tons per Year (estimated)
US	30
Europe	55
Japan	40
Rest of World	25

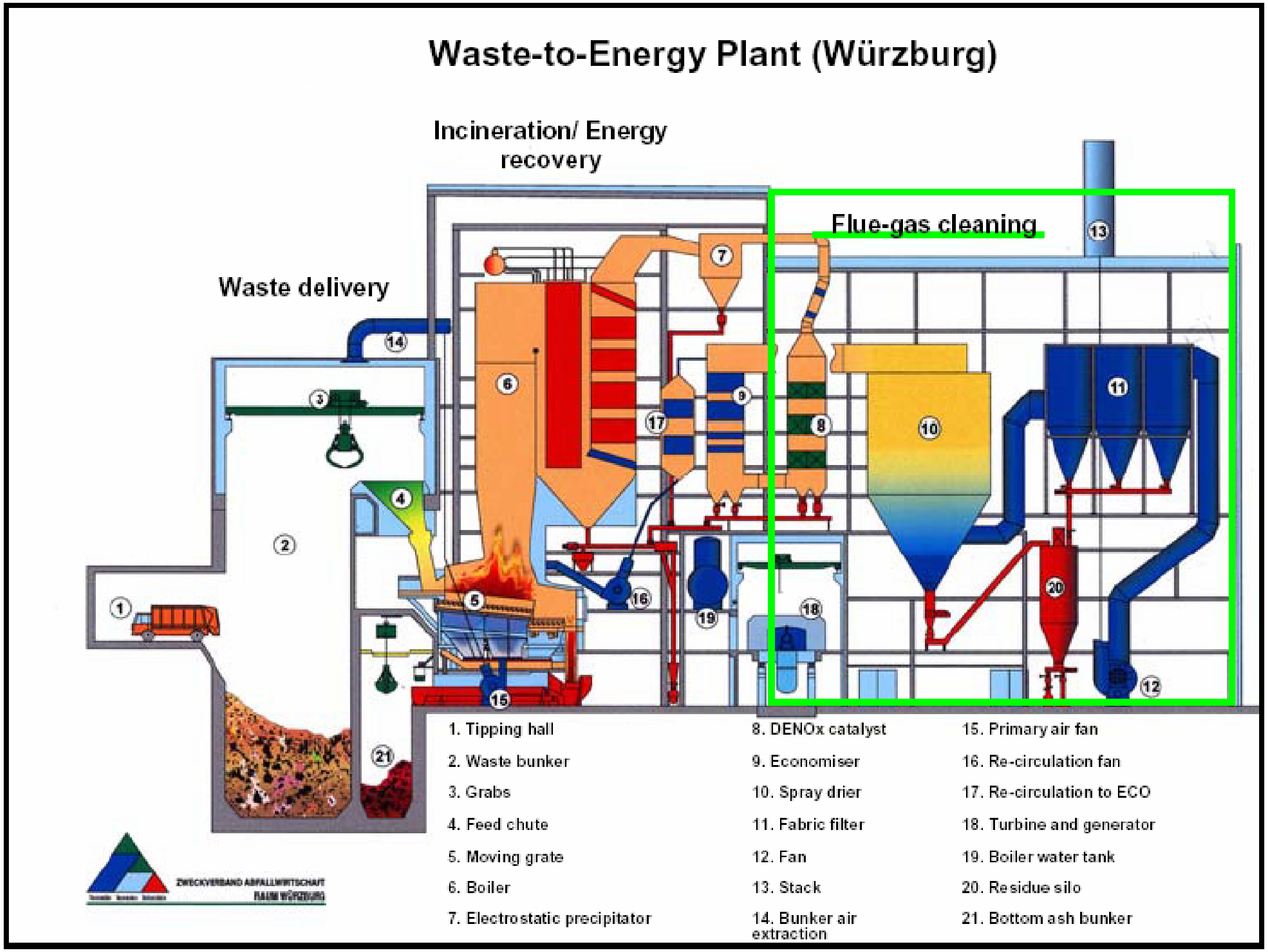
Source: Themelis, 2005; Williams, 2006

MSW Management, 2001

Country/region	Landfilled (%)	Incinerated (%)	Recycled, composted or other treatment (%)
EU-25	54	16	30
EU-15	49	18	33
UK	80	7	12
France	43	32	25
Germany	25	22	53
The Netherlands	8	33	59
Luxembourg	21	44	35
US	56	15	29
Japan	7	77	15

Source: Griffiths and Williams, 2005

WTE Combustion technology



Average Electrical Energy = 550 kWh/ton

Heat available in combined heat and power (CHP) applications

Principal technologies worldwide: Martin Grate, Roller Grate

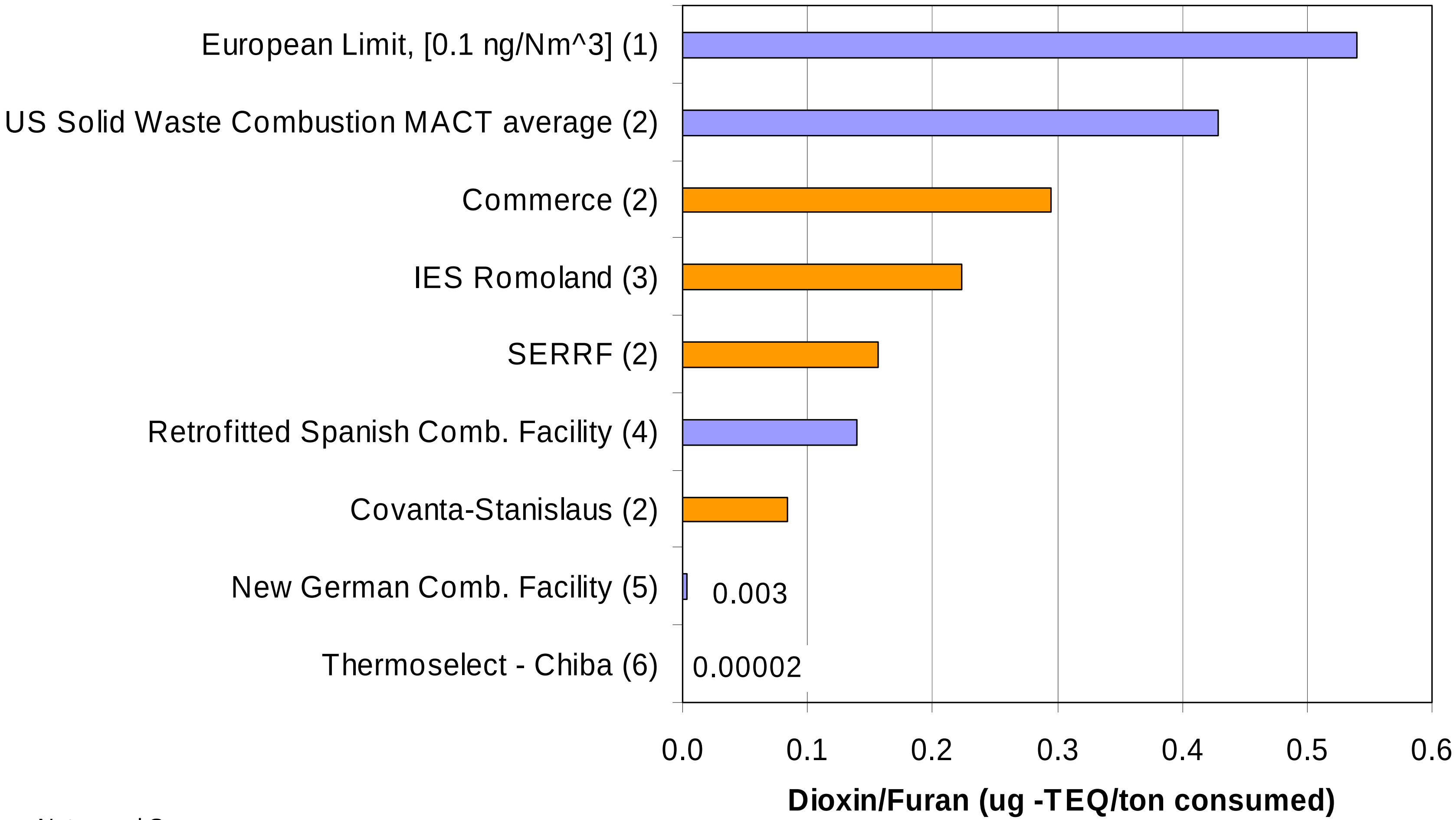
Source: Stengler, 2005; Themelis, 2005

Perceptions and concerns regarding incineration of MSW

- Competition with reduction, reuse, and recycling
  - Per-capita waste generation in California has not declined, total waste generation continues to increase. Amount landfilled in California continues to increase. Holland and Sweden, with large WTE development, see increasing competition from recycling.
- Dioxin emissions
  - MACT standards have substanially reduced (99%) dioxin emissions
  - Dioxin output may in some cases be less than dioxin input in waste. Exposure mechanisms differ.
- Mercury emissions
  - 87% of US anthropogenic mercury emissions from combustion sources
  - WTE accounted for 19% of emissions in 1995, medical waste incineration another 10%, coal fired boilers 33%
  - Emission limits for waste combustion designed to reduce Hg emissions 90% (3 tons/year) from 1995 levels (29.6 tons/year)

Source: EPA, 1997; Williams, 2006; Themelis, 2005; Rensfelt and Ostman, 1996

Dioxin Emissions



Notes and Sources:

1)* assume 0.1 ng TEQ/NM3 (11% O2) and 6000 Nm3/tonne

2)Emissions from Large Municipal Waste Combustion Unties (MWCs) Following MACT Retrofit (Year 2000 Test Data), USEPA Document ID OAR-2003-0072-0013

3)IES Romoland June 2005 source test report. Professional Environmental Services, Inc., Job 1065.001

4)Abad, E., Adrados, M. A., Caixach, J., and Rivera, J. (2002). "Dioxin abatement strategies and mass balance at a municipal waste management plant." Environmental Science & Technology, 36(1), 92-99.

5)MVR Environmental Statement (2005) http://www.mvr-hh.de/eng/elemente/pdfs/MVR_UW_2005_eng.pdf

6)Yamada, S., Shimizu, M., and Miyoshi, F. (2004). "Thermoselect waste gasification and reforming process." Technical Report No. 3 (July), JFE Group, Japan. [Exhaust from reciprocating engine]

Source: Williams, 2006

Gasification

- Gasification—conversion of solids or liquids to fuel- or synthesis-gases through gas-forming reactions
- Principal thermal alternative to combustion now considered

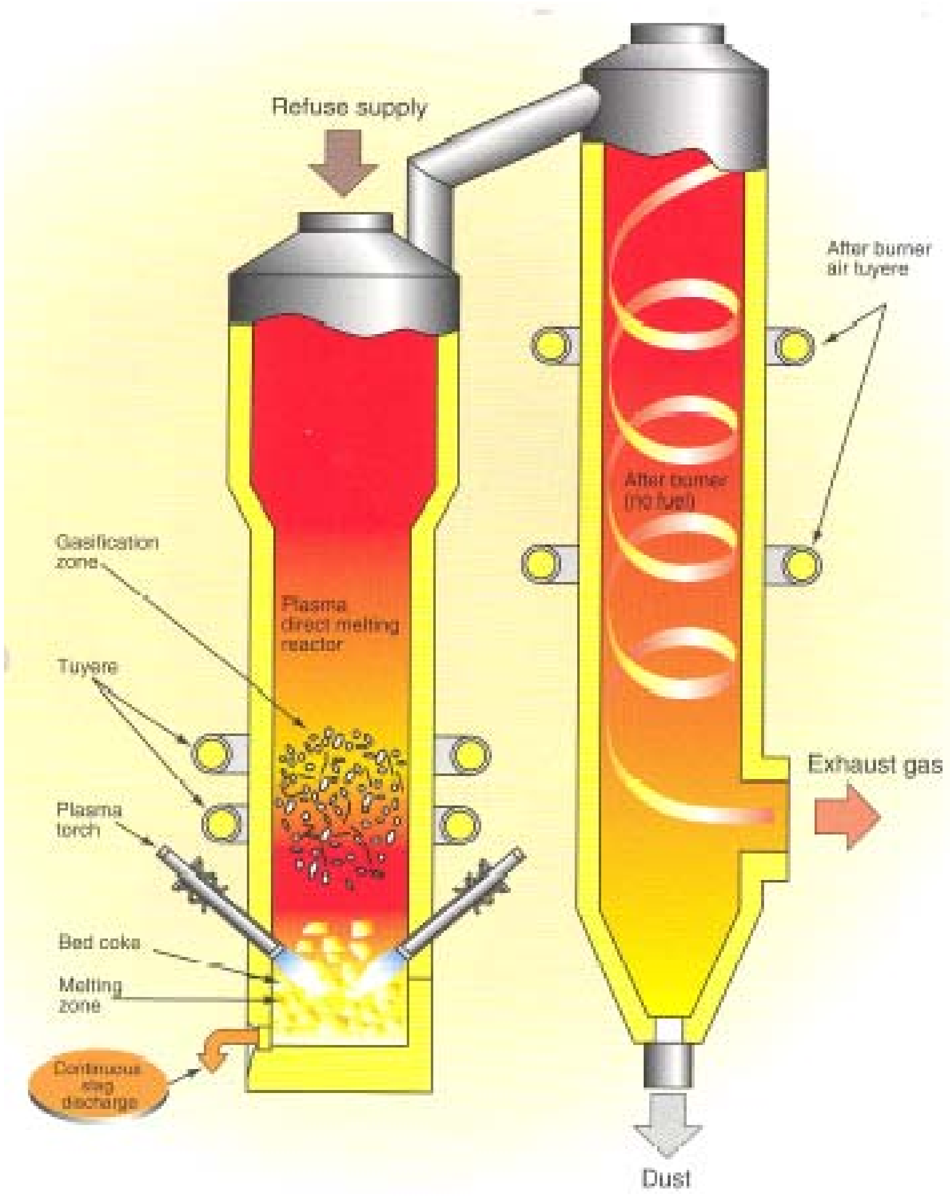
Pyrolysis

- Thermally degrade material w/o the addition of air or oxygen
- Similar to gasification – can be optimized for the production of fuel liquids (pyrolysis oils), with fewer gaseous products (may leave some carbon as char)
- Pyrolysis oil used for (after appropriate post-treatment): liquid fuels, chemicals, adhesives, and other products.
- A number of processes directly combust pyrolysis gases, oils, and char
- Temperature range (typical): 750-1500^{o}F
- Can utilize catalysts to promote reaction (Catalytic cracking)

Pyrolyzer—Mitsui R21

Plasma Arc Systems

- Heating Technique using electrical arc
- Used for combustion, pyrolysis, gasification, metals processing
- Originally developed by SKF Steel in Sweden for reducing gas for iron manufacturing
- Plasma direct melting reactor developed by Westinghouse Plasma Corp.
- Further developed for treating hazardous feedstocks
  - Contaminated soils
  - Low-level radioactive waste
  - Medical waste
- Temperatures sufficient to slag ash
- Plasma power consumption 200-400 kWh/ton
- Commercial scale facilities for treating MSW in Japan



Schematic of Hitachi Metals (PDMR, Westinghouse Plasma Corp.) plasma assisted gasifier and gas burner (Source; Hitachi Metals)

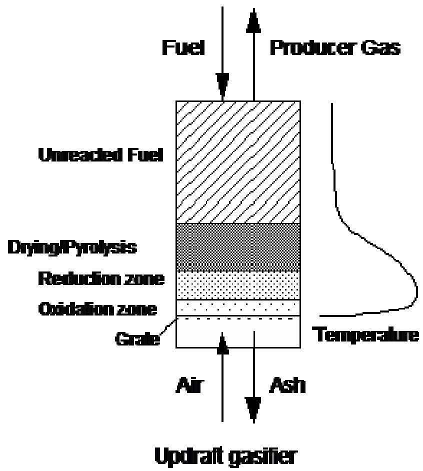
Thermal Gasification

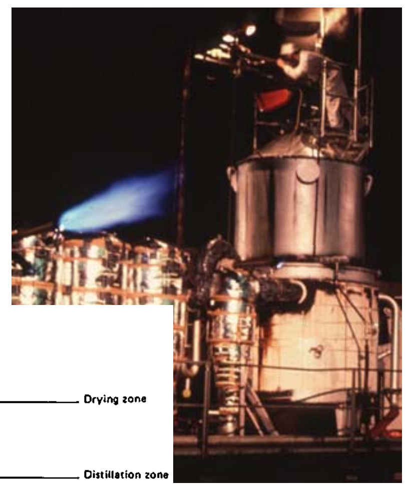
Fuel + Oxidant/Heat

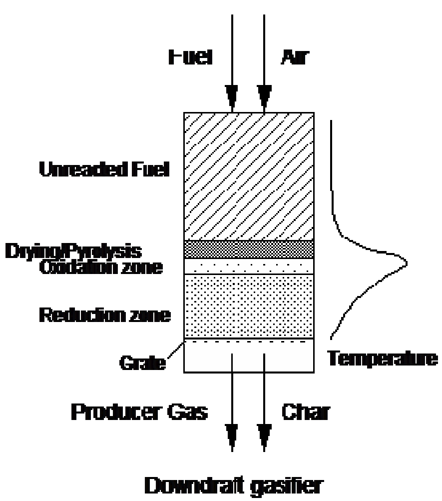
Partial Oxidation/Air or Oxygen
Steam/Carbon Dioxide/Hydrogen
Indirect Heating

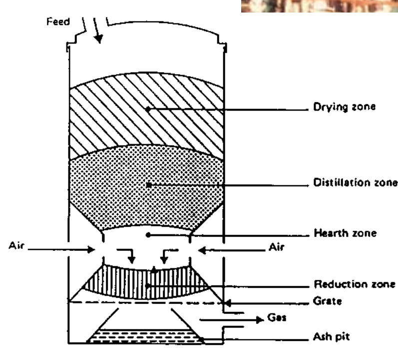
$CO + H_2 + HC + CO_2 + N_2 + H_2O +$
$Char + Tar + PM + H_2S + NH_3 +$
$Other + Heat$

Classification by Reactor Type: Fixed/Moving Beds



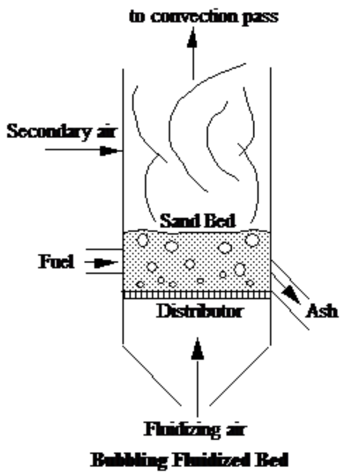




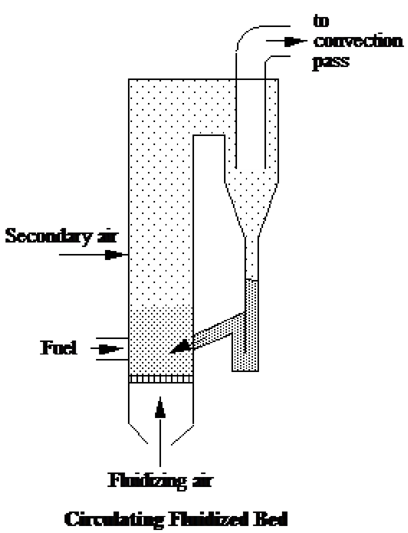


- Updraft
  - Countercurrent
  - High moisture fuel (<60% wet basis)
  - High tar production except with post-reactor catalytic cracking or dual stage air injection
  - Low carbon ash
- Downdraft
  - Cocurrent
  - Moisture < 30%
  - Lower tar than uncontrolled updraft
  - Carbonaceous char
- Crossdraft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

Classification by Reactor Type: Fluidized Beds

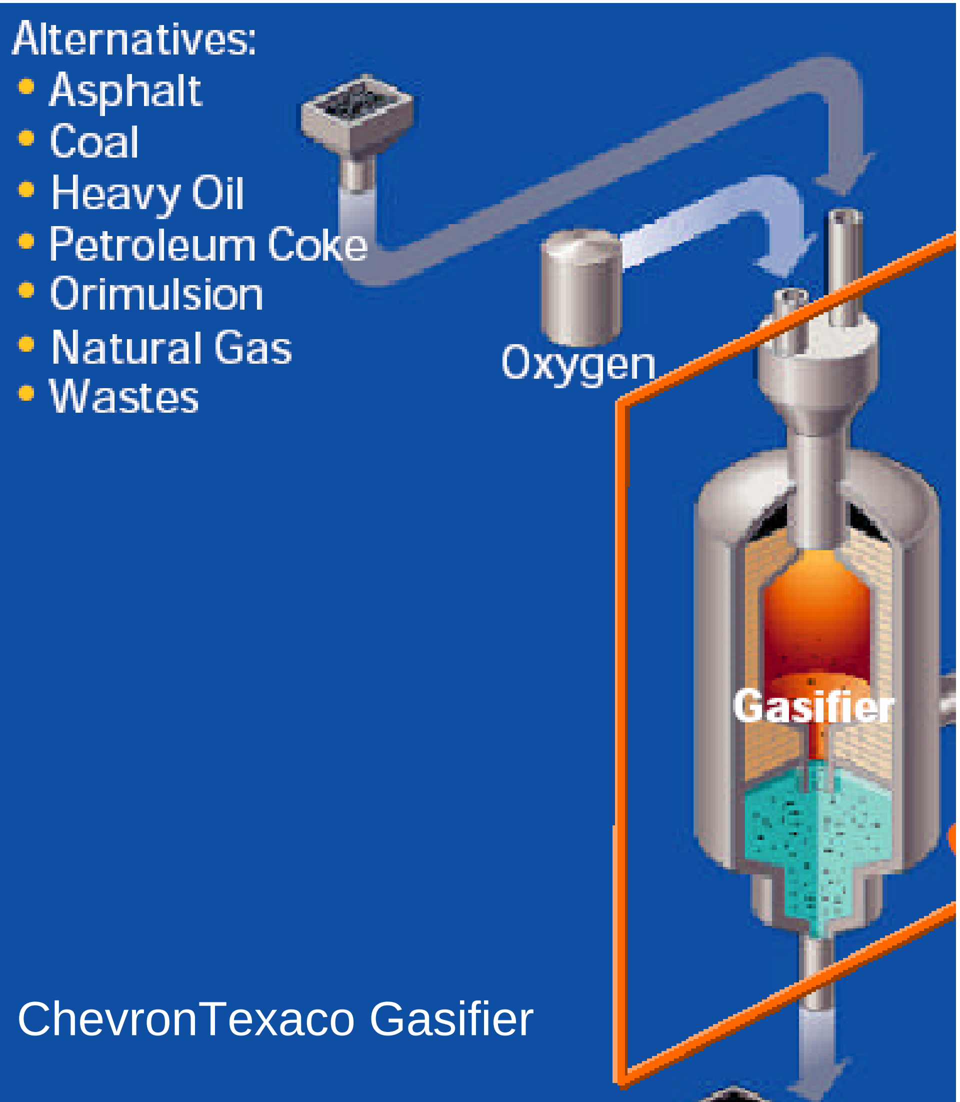


- Bubbling beds
  - Lower velocity
  - Low entrainment/elutriation
  - Simple design
  - Lower capacity and potentially less uniform reactor temperature distribution than circulating beds



- Circulating beds
  - Higher velocity
  - Solids separation/recirculation
  - More complex design
  - Higher conversion rates and efficiencies

Classification by Reactor Type: Entrained Beds



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

Classification by Oxidation Medium

- Air gasification (partial oxidation in air)
  - Generates Producer Gas with low heating value (~150 Btu ft^{-3}) and high N_2 dilution.
- Oxygen gasification (partial oxidation using pure O_2)
  - Generates synthesis gas (Syngas) with medium heating value (~350 Btu ft^{-3}) and low N_2 in gas.
- Steam gasification
  - Generates high H_2 concentration, medium heating value, low N_2 in gas. Can also use catalytic steam gasification with alkali carbonate or hydroxide
- Carbon dioxide
- Hydrogen
- Indirect heated--pyrolysis

Gasification Reactions and Products

Simplified Reaction System for Carbon

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

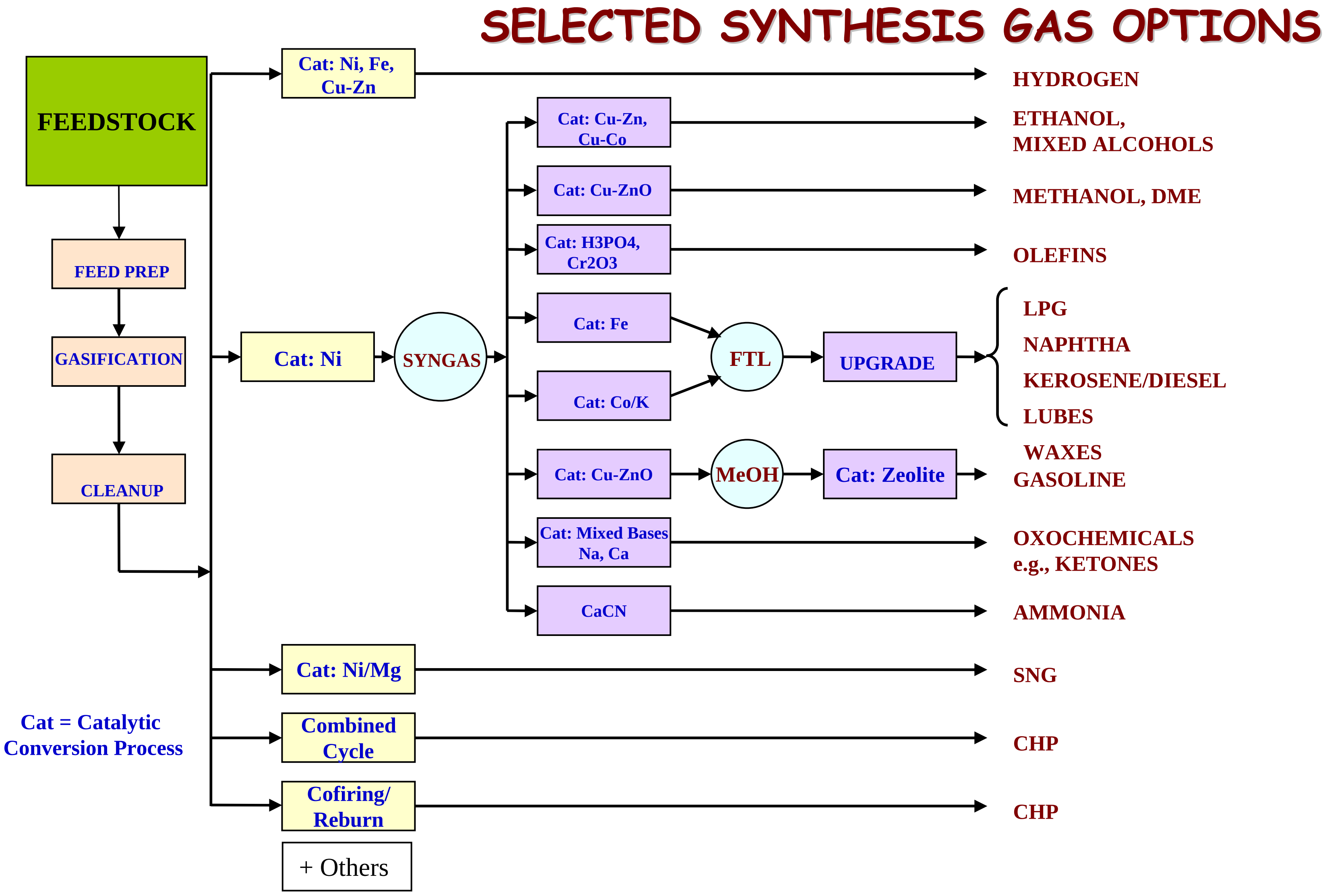
Typical Clean, Dry Gas Composition from air-blown gasifier

	% by volume
CO	22
H_2	14
CH_4	5
H_2O	2
CO_2	11
N_2	46

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}

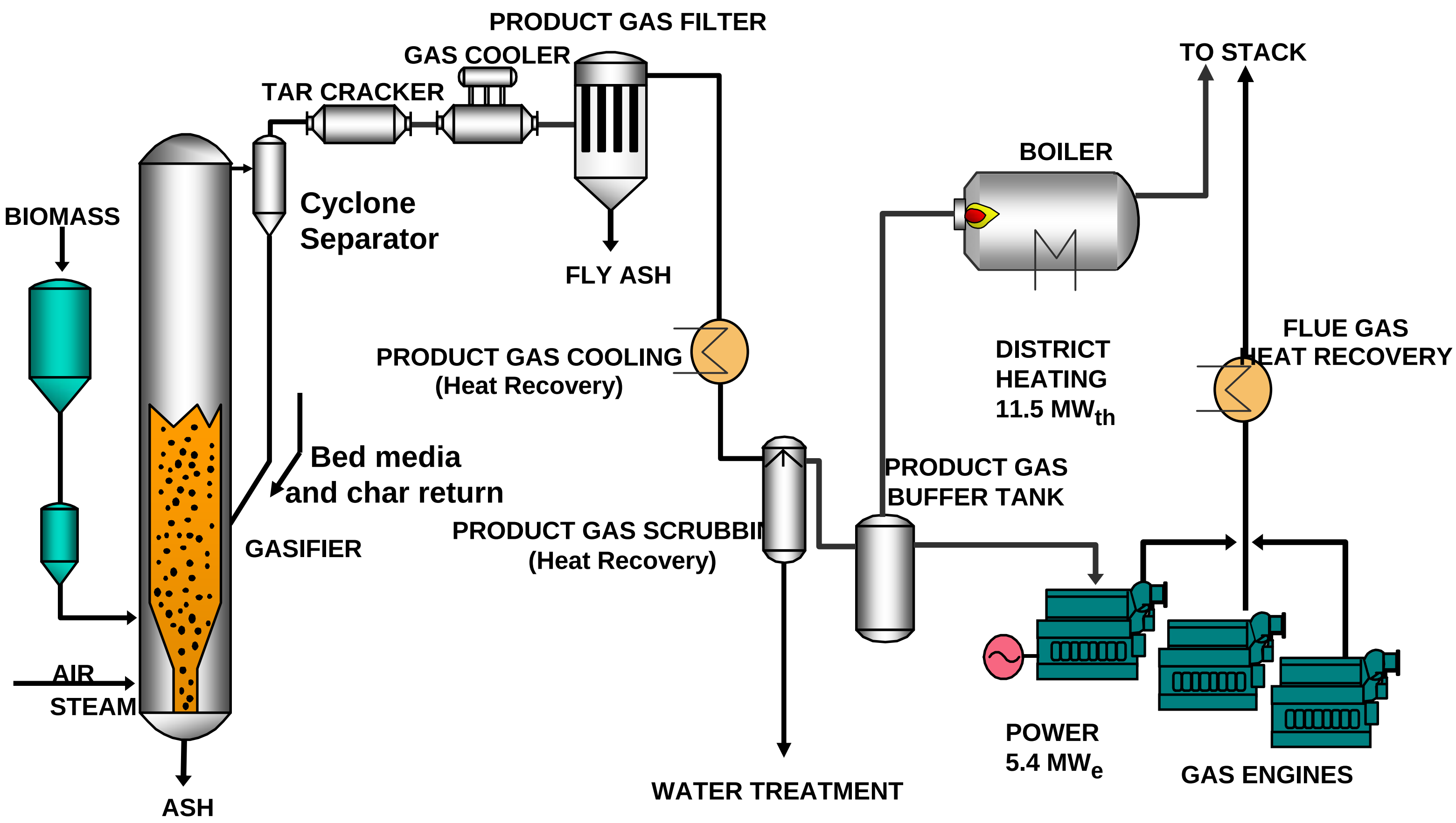
Syngas Options



Source: NREL

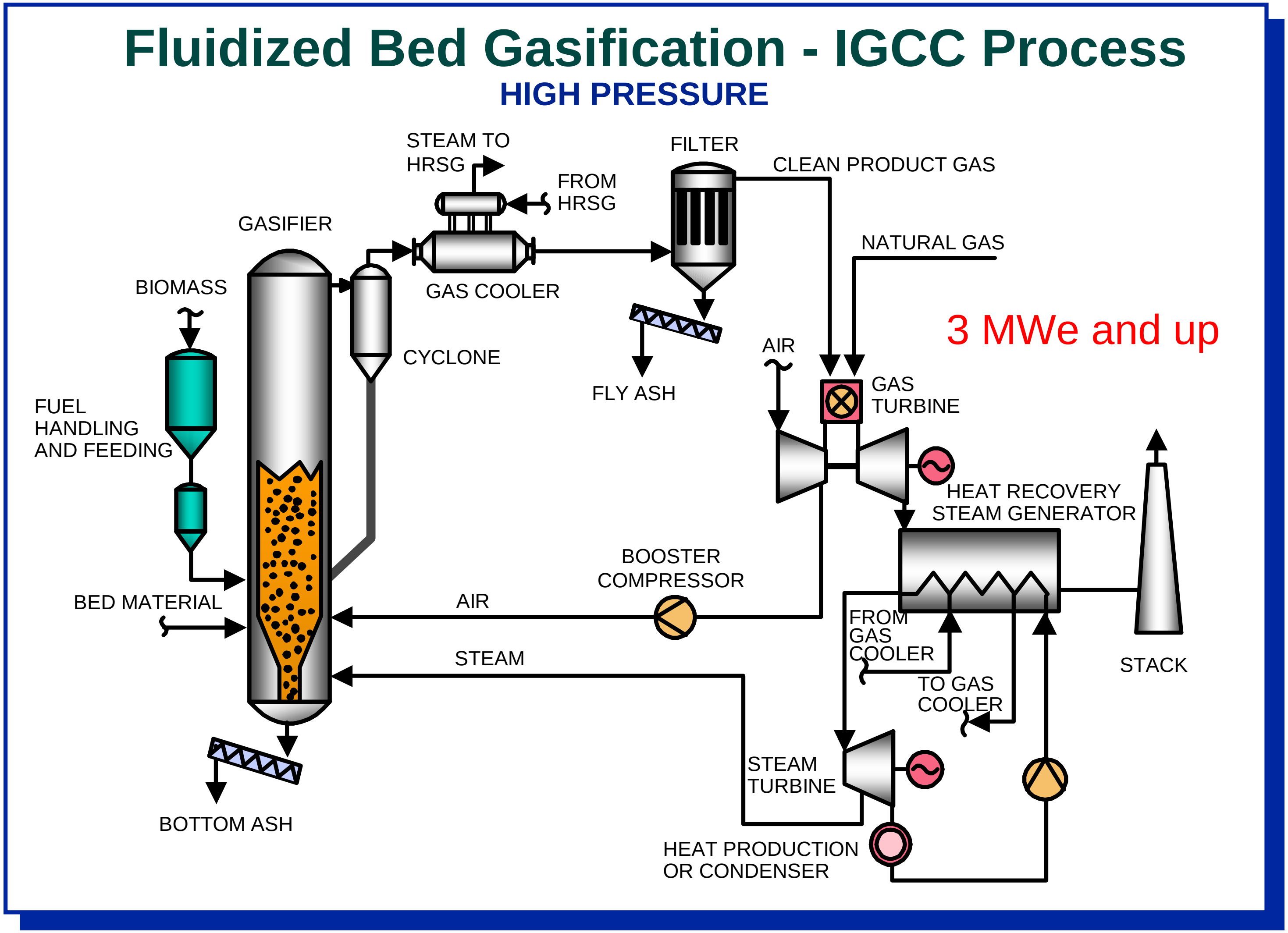
CFB with gas conditioning—Engine Gensets

(Carbona Skive Project, Denmark)



Courtesy Carbona Corporation

BIGCC Power Generation



BTL: Biomass To Liquids

Fischer-Tropsch Synthesis

Fe, Co

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

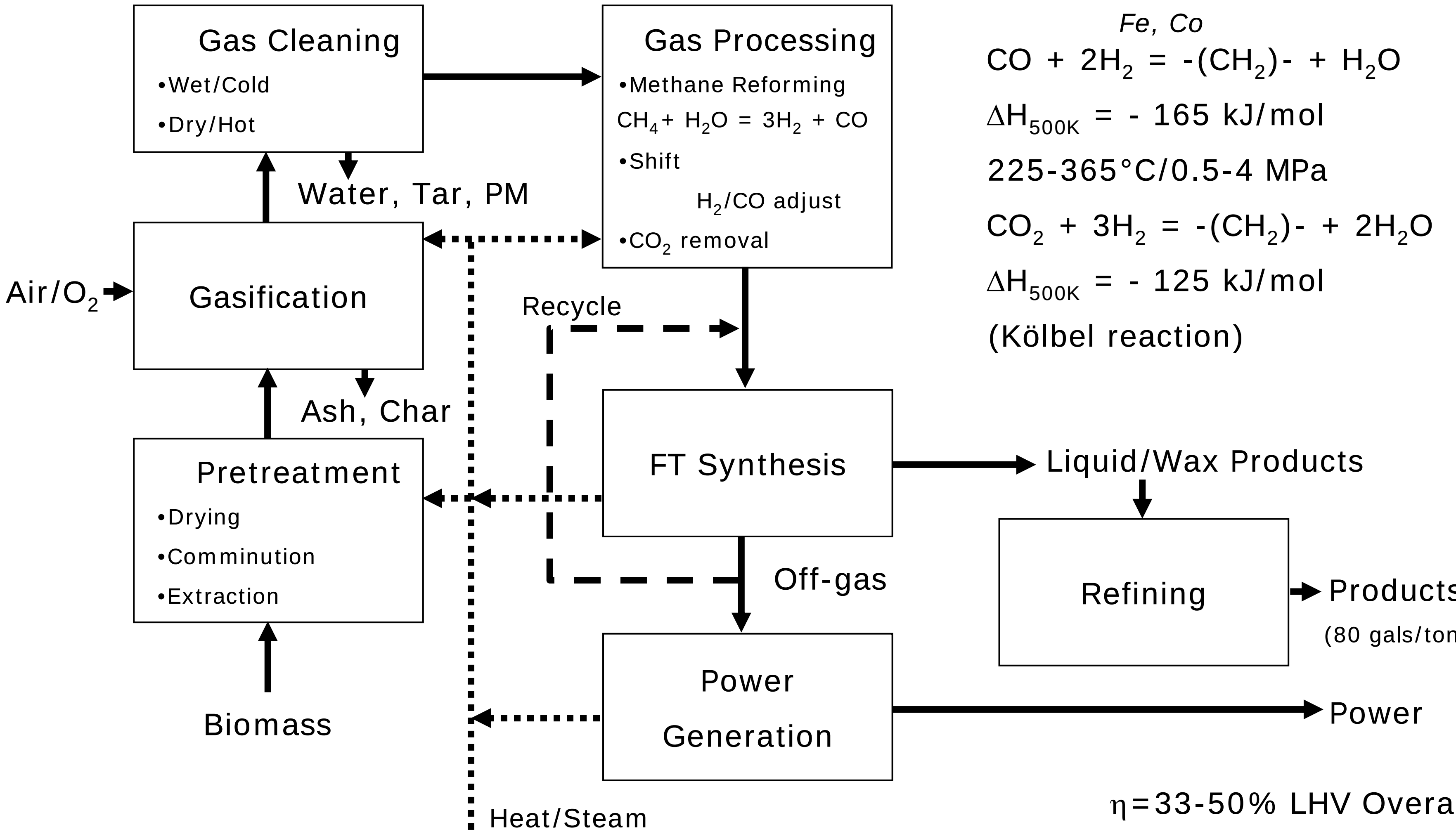
$\Delta H_{500K} = -165$ kJ/mol

225-365°C/0.5-4 MPa

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

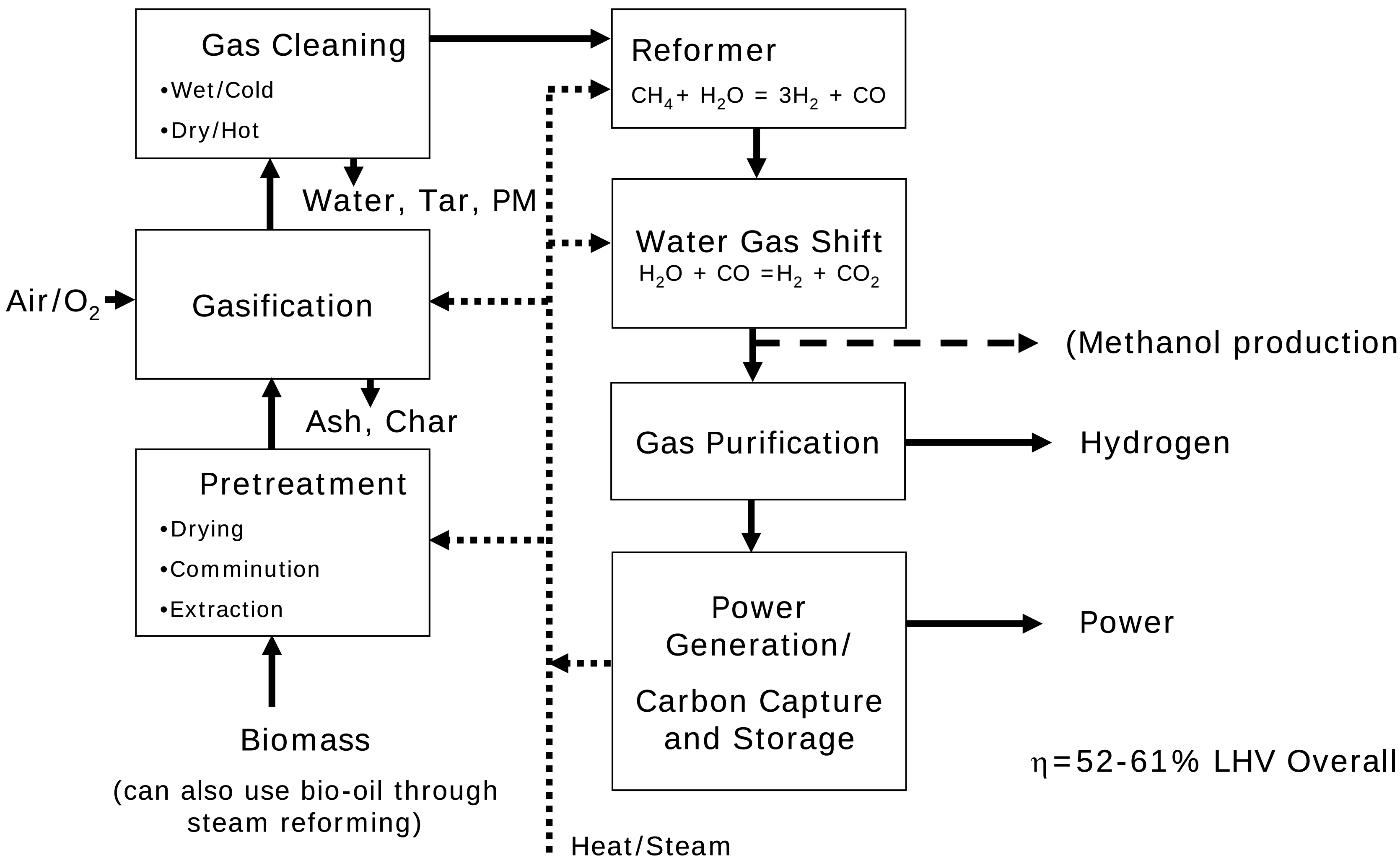
$\Delta H_{500K} = -125$ kJ/mol

(Kölbel reaction)



η=33-50% LHV Overall

Biomass To Hydrogen: Gasification



Advantages of Gasification

- Produces fuel gas for more versatile application in power generation and chemical synthesis.
- Potential for higher efficiency conversion using integrated gasifier combined cycles compared with conventional Rankine steam cycle power systems.
- Typically lower temperatures than direct combustion thus decreases potential alkali volatilization, fouling, slagging, and bed agglomeration (fluidized beds) although for high alkali, high ash fuels, slagging and bed agglomeration can be problems. Can also reduce heavy metal volatilization.
- Lower volume of gas requiring treatment to reduce NOx and SOx emissions compared to combustion flue gas.
- Fuel nitrogen evolved principally as NH_3 and sulfur as H_2S, more readily removed than NOx and SO_2 in combustion systems.
- Applications for power generation at smaller scales than direct combustion systems although gas cleaning is primary concern and expense

Gasification Constraints

- Gas cleaning required for use of fuel gas in engines, turbines, and fuel cells
  - For reciprocating engines, tar and particulate matter removal are primary concerns, tar removal difficult to achieve. Reactor designs influence tar production, some newer two stage gasifiers reduce tar but cleaning is still an issue. Need for cool gas to maintain engine volumetric efficiency leads to tar condensation and waste water production for wet scrubbing systems. Engine derating for gas from air-blown reactors.
  - For gas turbines, alkali concentration in gas must be kept low (typically less than 1 ppmv), need for hot gas cleaning to maintain high efficiency. Alkali typically removed by condensing on particles and hot filtering at temperatures ~1,300°F.
  - Fuel cells require clean gas and alkaline, phosphoric acid, and PEM types intolerant of high CO. Molten carbonate and solid oxide fuel cells internally reforming and developmental for gasification systems.

Gasification Constraints

- Generates carbonaceous solid (char)
  - Low grade carbon, can be activated to improve value.
  - Dual-reactor and similar systems burn char to provide additional heat to process (e.g. FERCO dual fluidized bed tested in Vermont--based on Bailie twin reactor concept).
- Individual reactors limited in scale, multi-reactor systems needed for large power or refinery systems
- Advanced IGCC systems using pressurized reactors need pressure feeding systems
- For lower tar reactors, moisture content limited (<30%), requires feedstock drying.
- Particle size distribution important for proper fuel handling and material flow—added expense for fuel processing

Fate of N, S, Cl in gasification

- Fuel N principally converted to NH_3 and N_2
  - 20 to 70% conversion to NH_3
  - Concentrations from 600 to 6,000 ppmv depending on fuel N
  - HCN, other species present at lower concentrations
  - Need to remove to avoid high NOx emissions during gas combustion
  - At sufficiently low NH_3 concentrations, gas can be used in reburning applications to reduce NOx from solid-fuel direct combustion systems
  - Ammonia a principal product from syngas
- Fuel S principally converted to H_2S, can be scrubbed.
- Fuel Cl mostly evolved as HCl, can interfere with sulfur removal (e.g. reaction with zinc and iron based sorbents).

History of Gasification-WTE

- Thirty years of development
- 20 processes, 13 tested at capacities > 10 tons per day, 5 tested at 1 to 5 tons per day
- Early designs—
  - Did not envision need for feedstock separation
  - Heterogenity of feed underestimated, lack of compositional data
  - Scale-up too fast
  - Lack of regard for chemical complexity
  - Did not adequately address gas cleaning

Source: Rensfelt and Ostman, 1996

Separation and Gas Cleaning for Gasification Systems

A.											
WASTES	-	-	-	-	-	-	-	Incineration	-	Flue gas cleaning
B.											
WASTES	-	Separation	-	-	-	-	-	Incineration	-	Flue gas cleaning
C.											
WASTES	-	-	-	Gasification	-	-	-	Combustion	-	Flue gas cleaning
D.											
WASTES	-		-	Gasification	-	Gas cleaning	-	Combustion	-	-
E.											
WASTES	-	Separation	-	Gasification	-	-	-	Combustion	-	Flue gas cleaning
F.											
WASTES	-	Separation	-	Gasification	-	Gas cleaning	-	Combustion	-	-

Source: Rensfelt and Ostman, 1996

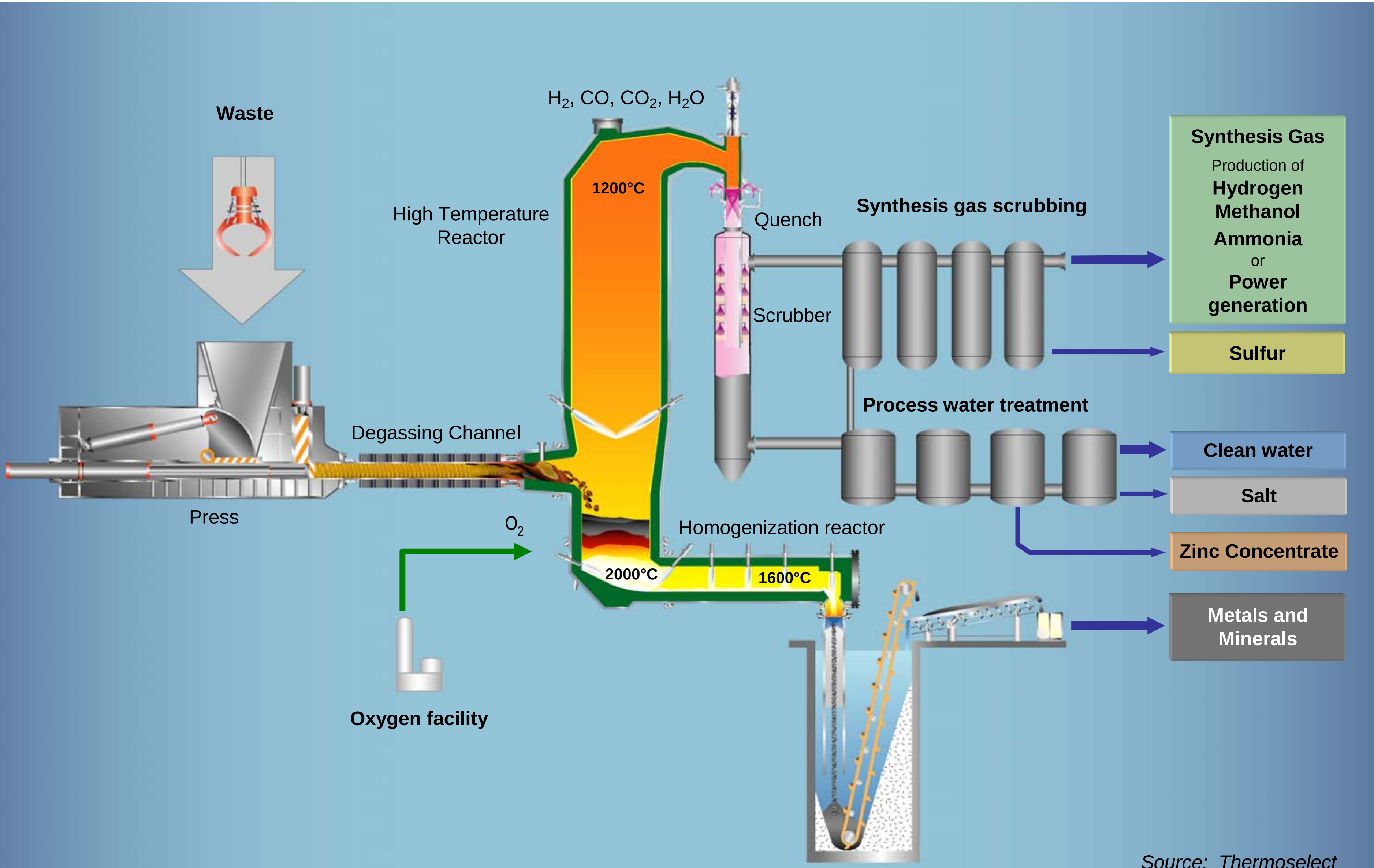
MSW Gasifier Development

- High temperature
  - Higher investment costs, lower efficiencies
- Separation, pre-processing of feed
  - RDF in fluidized beds, reduced Cl concentrations
  - High temperature fixed beds for mixed wastes
- More sophisticated materials handling
- Ash slagging/ash vitrification
- Intermediate gas cleaning

Selected MSW Gasification Developers

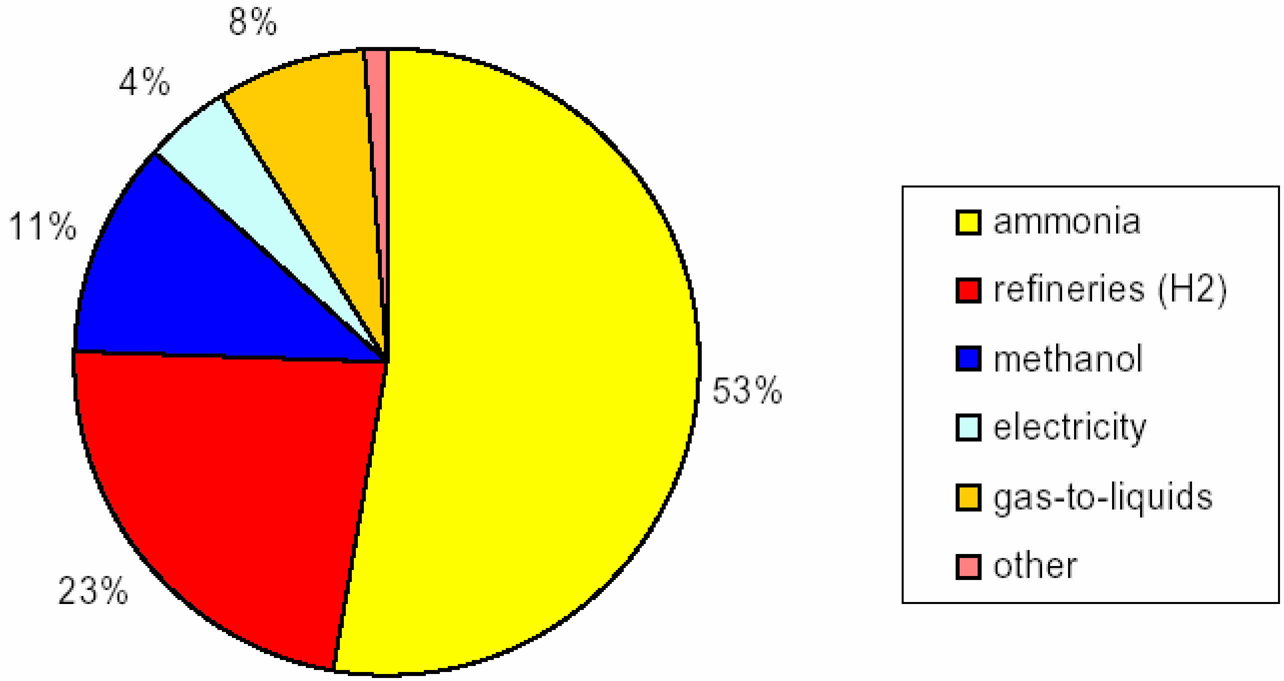
- Nippon Steel (fixed bed O_2 blown)
- Ebara-Alstom (derived from Bailie twin reactor concept)—air blown fluidized bed with cyclonic combustor
- Hitachi Metals Plasma Arc
- Thermoselect—combined pyrolysis and high temperature slagging gasifier
- Greve-TPS/Ansaldo (CFB on RDF)

Thermoselect technology



Source: Thermoselect

World Syngas Market—6 EJ/y



Transportation fuel production via GtL – 0.5 EJ/y (Fischer-Tropsch: Sasol in South Africa, Shell Bintulu, Malaysia)

Source: IEA

Conclusions

- Combustion remains predominant thermal technology for MSW conversion with realized improvements in emissions
- Gasification and pyrolysis systems now in commercial scale operation but industry still emerging
- Improved environmental data needed on operating systems
- Comprehensive environmental or life cycle assessments should be completed