THERMAL CONVERSION 101

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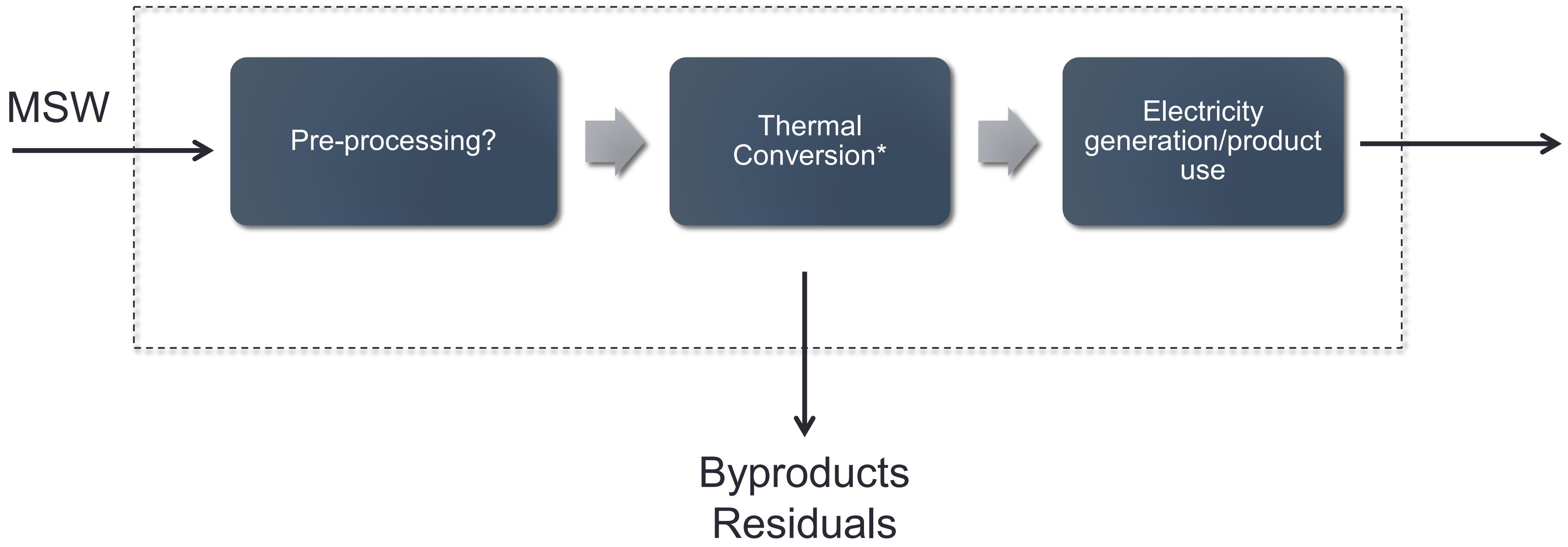
Module Outline

- Introduction
- Review of waste chemical properties
- Discussion of thermal conversion techniques
  - Waste to energy
  - Gasification
  - Pyrolysis
  - Hydrothermal carbonization
- Module wrap-up

Thermal Conversion

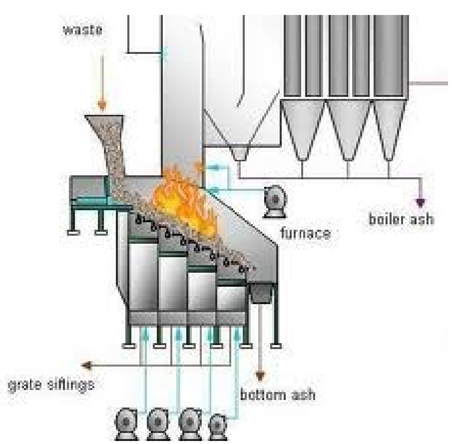
- Use of heat to rapidly transform wastes into fuels, byproducts and/or power



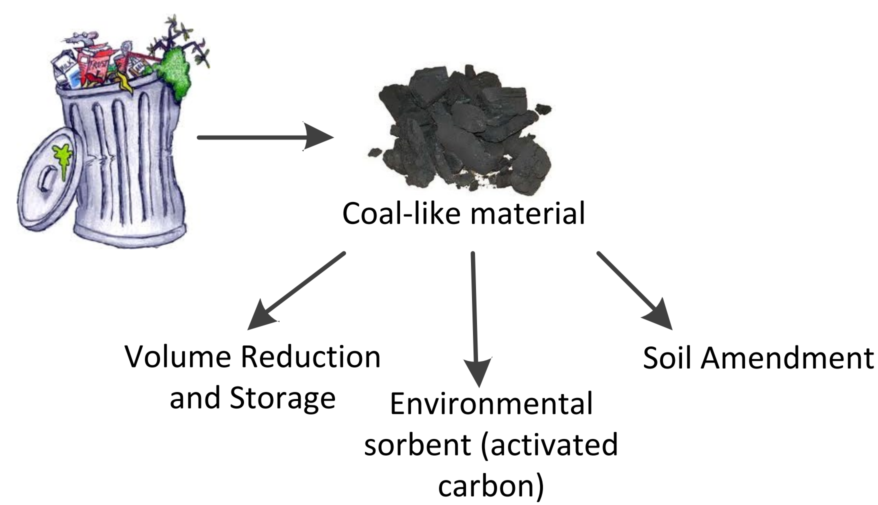
*Organic and carbon containing wastes

Why Thermal Conversion?

- Diversion from landfills
- Waste volume reduction
- Conversion to useful products
  - Oil, char, gas, heat
- Energy generation (offset fossil fuels)
- Sustainability



Beneficial Material Generation



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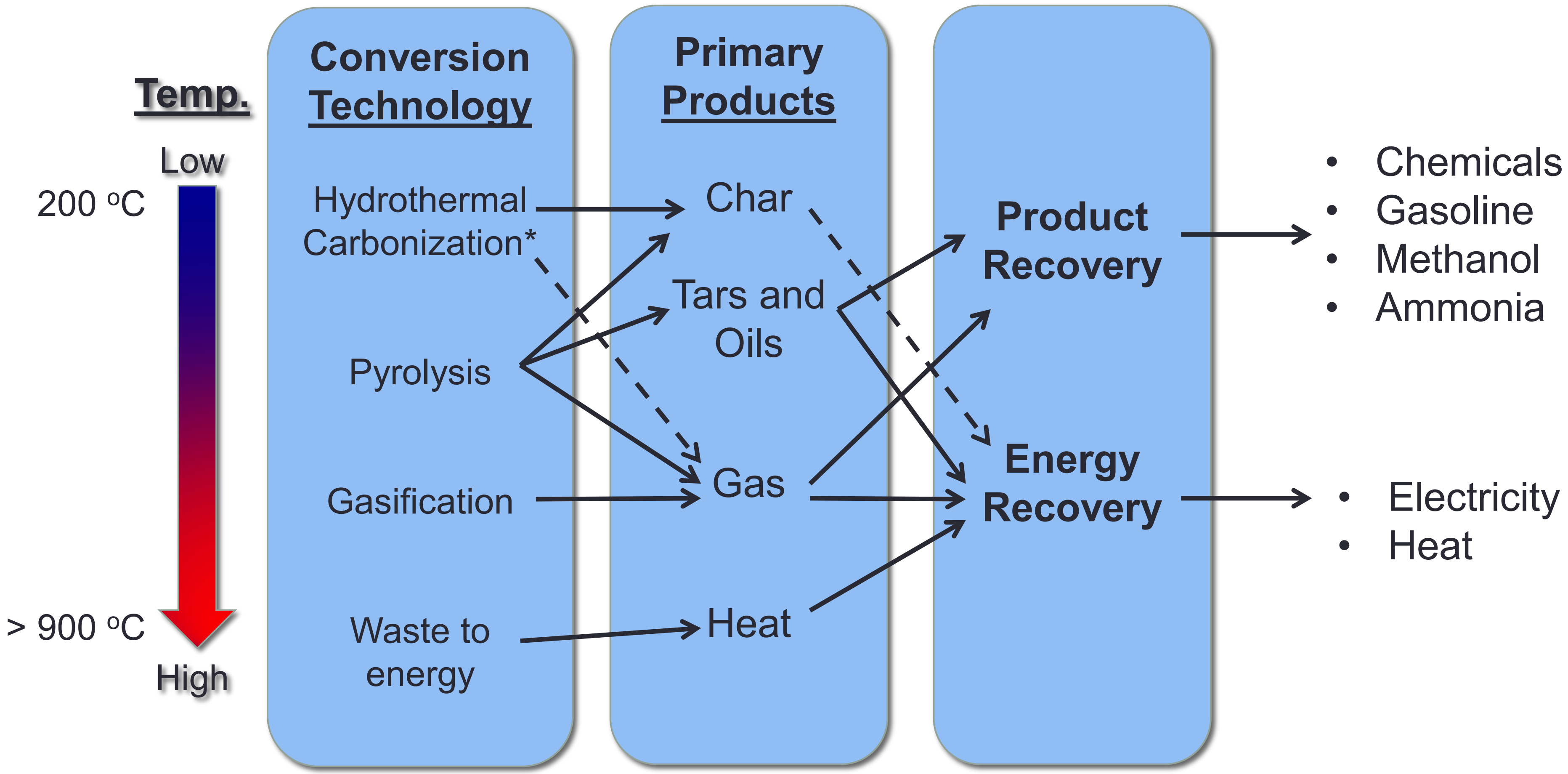
Thermal Conversion Techniques



**possible recovery of chemicals in liquid-phase, not necessarily tar or oil*

Thermal Conversion Techniques

	Hydrothermal Carbonization	Pyrolysis	Gasification	Combustion
Temperature	< 350 °C	< 500 °C	> 500 °C	> 900 °C
Atmosphere	air or inert	Oxygen-free	Limited oxygen; air	Oxygen; air
Pressure	autogenous	variable	variable	low
Feedstock Moisture Content	wet – add water to achieve high moisture conditions (i.e., 20% solids)	Relatively dry (MSW water content is typically 20%, by wt. If using a wet feedstock (swine waste), it is often dried)		
Solid Product	char	char	char	ash
Main Gaseous Products	CO_2 (small total quantity of gas)	H_2, CO, CO_2, CH_4	H_2, CO, CO_2, CH_4	CO_2, N_2
Liquid Products	water waste, tar and oil	oil; tar	oil	none
Potential Recovery Products	char, and possibly gas, liquid	tar/oil, gas and char	gas, oil and char	Heat in combustion gas

Thermal Conversion Processes

Bryan – do you have any of these numbers?

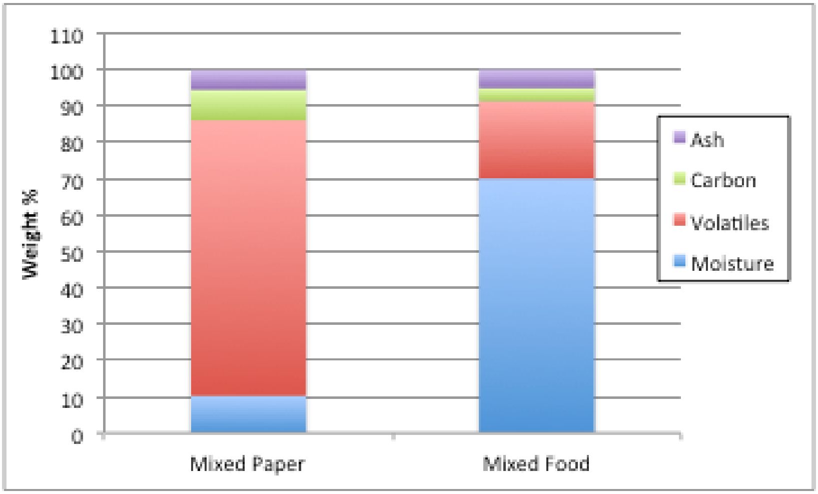
Process	Number in the US
Waste-to-energy	
Pyrolysis	
Gasification	
Hydrothermal carbonization	

Review of Waste Chemical Properties

- Ultimate and proximate analysis
- Fusing point of ash
- Energy content
- LHV vs HHV
- Basis of analysis

Proximate Analysis

- Moisture (temperature held at 105 ^{o}C for 1 hour)
- Volatile combustible matter (temperature increased to 950 ^{o}C in a closed crucible)
- Fixed carbon (combustible residue from volatile combustible matter step)
- Ash (weight of residue after combustion at 950 ^{o}C in an open crucible)



Ultimate Analysis

- Laboratory technique to determine the elemental composition (C, H, N, O, S, moisture and ash) of the waste
- Necessary to assess the suitability of the waste as a fuel and for predicting emissions from thermal conversion techniques

$\rightarrow$ $C_{760}H_{1980}O_{870}N_{13}S$

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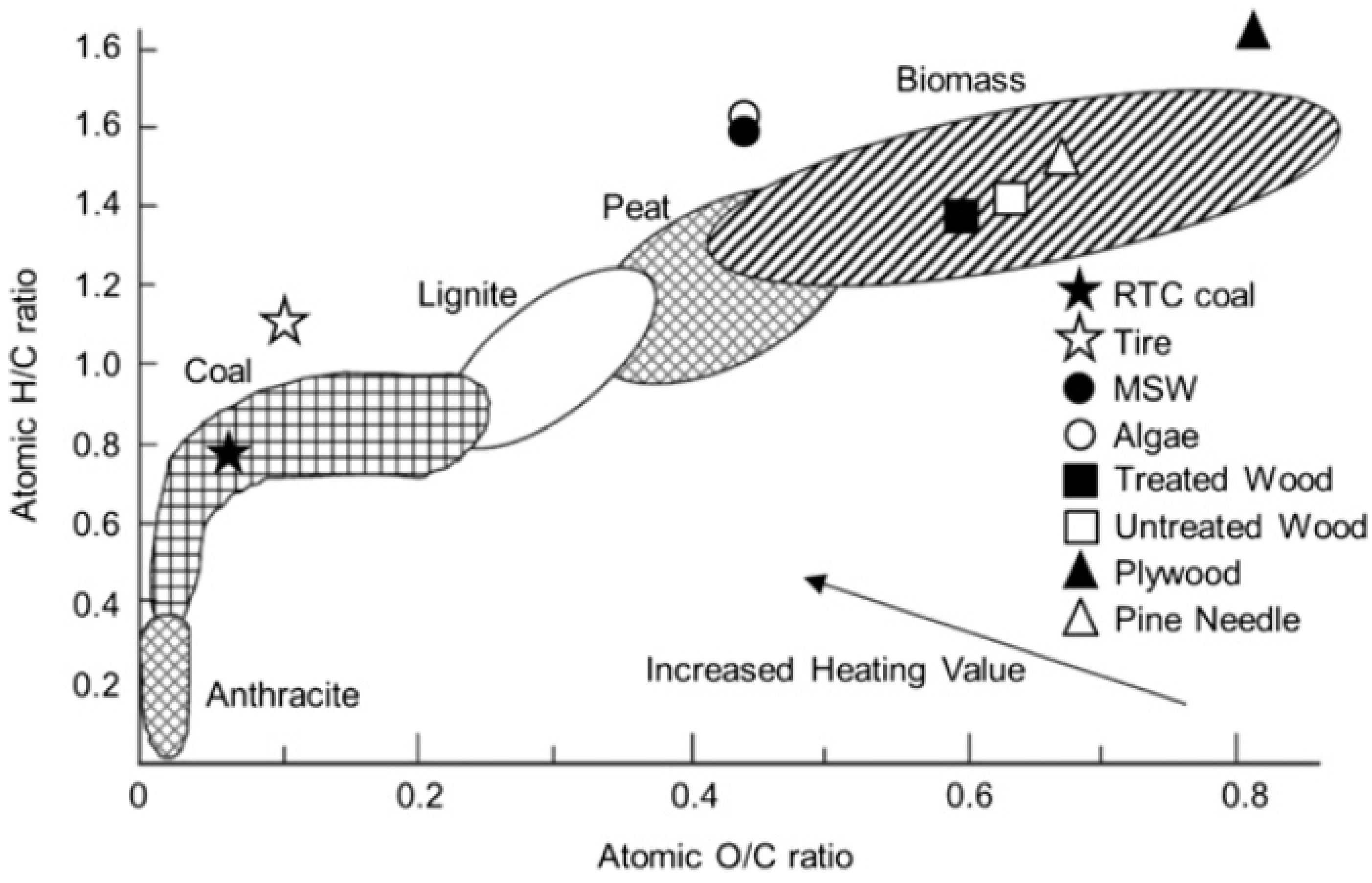
Van Krevelen Diagram



Taken from: Janajreh et al. (2012). Plasma gasification process: Modeling, simulation and comparison with conventional air gasification. Energy Conversion and Management, in press.

Fusing Point of Ash

- The temperature in which the ash resulting form the burning of MSW forms a solid by fusion and aggregation
- Typical temperatures: 1100 – 1200 ^{o}C

http://www.joveincement.com/images/EditorUpload/Cement_Clinker.jpg

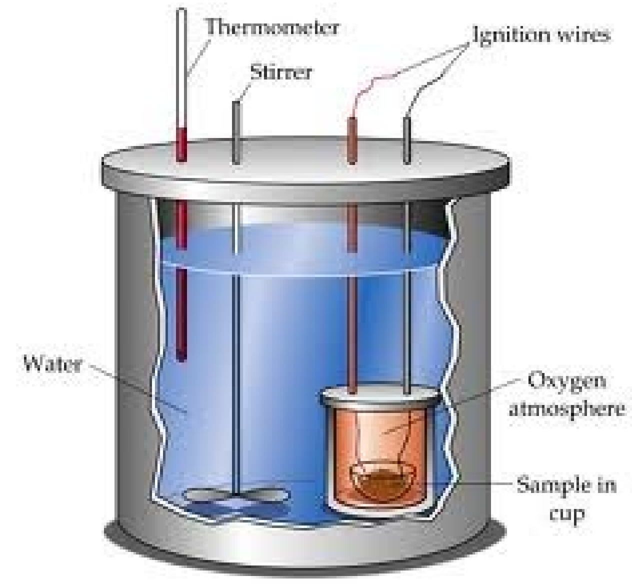
Energy Content

- Determined by:
  - Using a boiler as a large calorimeter
  - Laboratory-scale bomb calorimeter
  - Calculation based on ultimate or proximate analysis
- Calculation

  1. Dulong equation

$$\frac{BTU}{lb} = 145C + 610(H - \frac{1}{8}O) + 40S + 10N$$

where: C, H, O and S and N = % of each element, by weight.



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  2. Model based on proximate analysis:

Kcal/kg = 45B - 6W

B = Combustible volatile matter in MSW (%)

W = Water, percent weight on dry basis

HHV vs LHV

- HHV = higher heating value
  - Gross calorific value or gross energy
  - Includes the energy used to vaporize water
  - HHV assumes all the water component is in liquid state at the end of combustion
- LHV = lower heating value
  - Net calorific value
  - Excludes the energy used to vaporize water

$$LHV = HHV - 10.55(W + 9H)$$

Where:
LHV = lower heating value if fuel in BTU/lb
HHV = higher heating value of fuel in BTU/lb
W = Weight % of moisture in fuel
H = Weight % of hydrogen in fuel

Basis of Analysis

- Important to ensure all terminology is on the same basis
  - ar = as received (includes moisture)
  - db = dry basis
  - daf = dry ash free basis

- Conversion between these:

Conversion from ar to db:

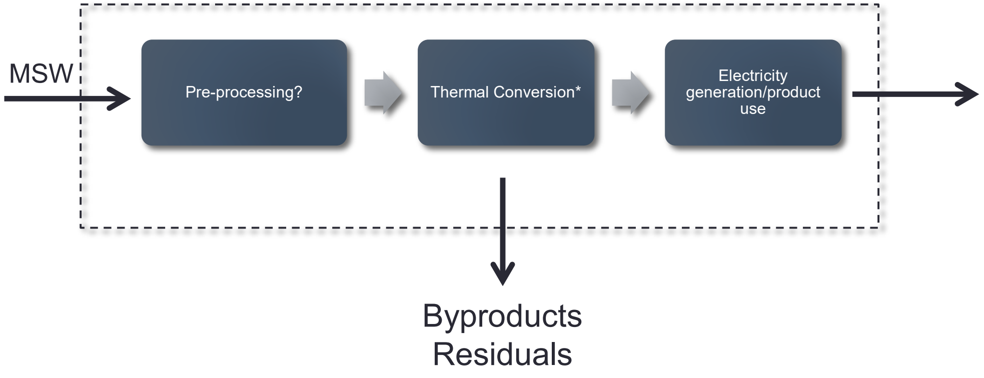
$$\text{db} = \text{ar}\left(\frac{100}{100\text{-}\%\text{Moisture}}\right)$$

Conversion from db to daf:

$$\text{daf} = \text{db}\left(\frac{100}{100\text{-}\%\text{Ash}}\right)$$

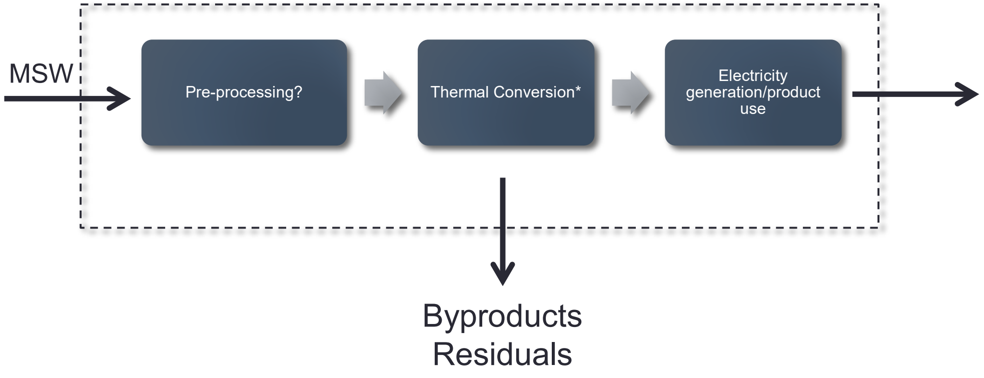
Thermal Conversion Technologies

- Waste to Energy
- Gasification
- Pyrolysis
- Hydrothermal Carbonization

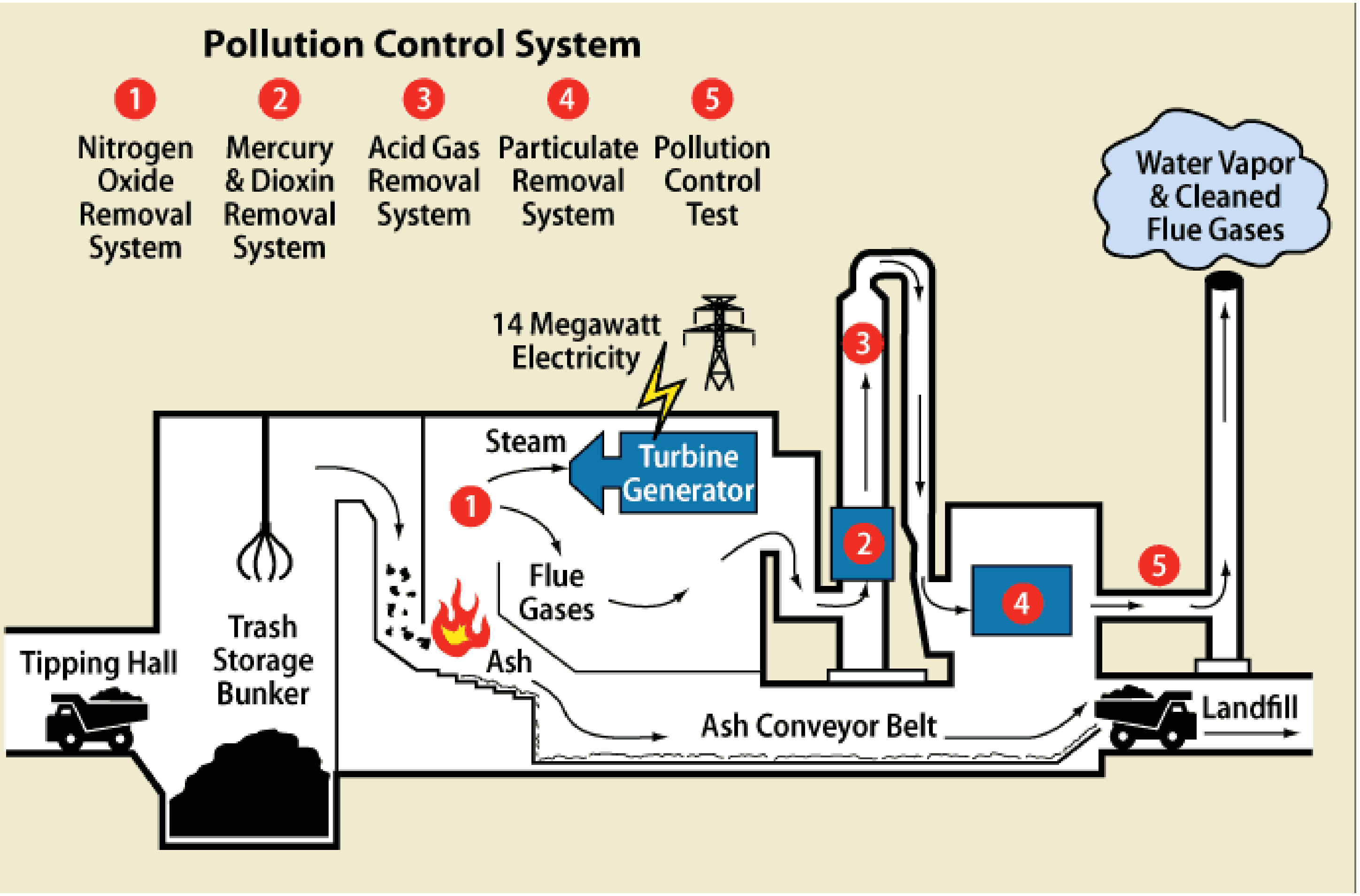


Thermal Conversion Technologies

- **Waste to Energy** → **Proven at field-scale**
- Gasification
- Pyrolysis
- Hydrothermal Carbonization



Waste to Energy



Source: http://www.window.state.tx.us/specialrpt/energy/renewable/images/exhibit18-1.png

Waste to Energy

- Thermal processing of solid waste by chemical oxidation with stoichiometric or excess amounts of air
- End products depend on waste composition

$$C + O_2 \rightarrow CO_2$$

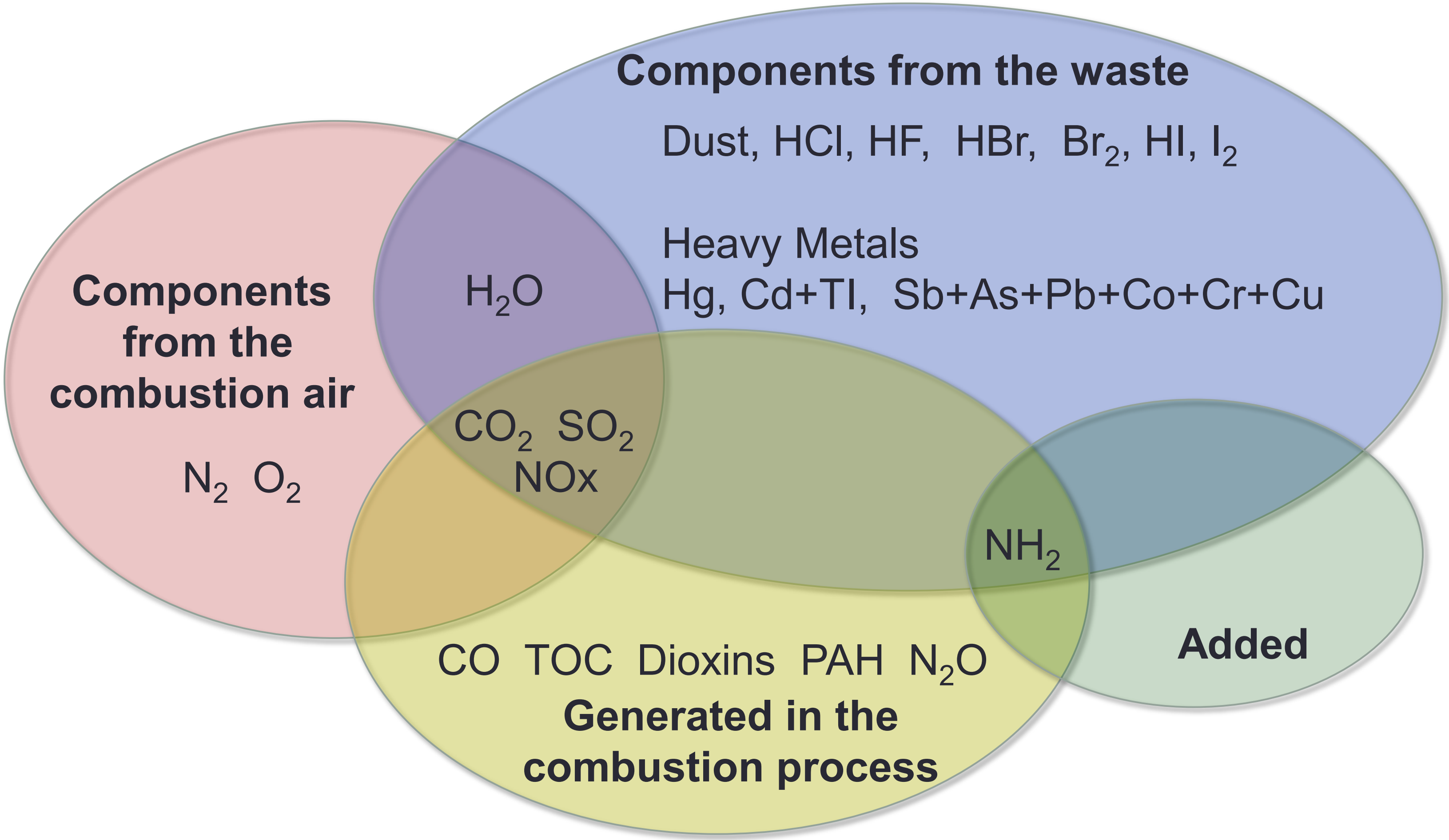
$$2H_2 + O_2 \rightarrow 2H_2O$$

$$S + O_2 \rightarrow SO_2$$

- Primary End Products: nitrogen gas, carbon dioxide, water vapor, ash, heat
- Operational Temperatures: 1450 – 1800 ^{o}F

Waste to Energy

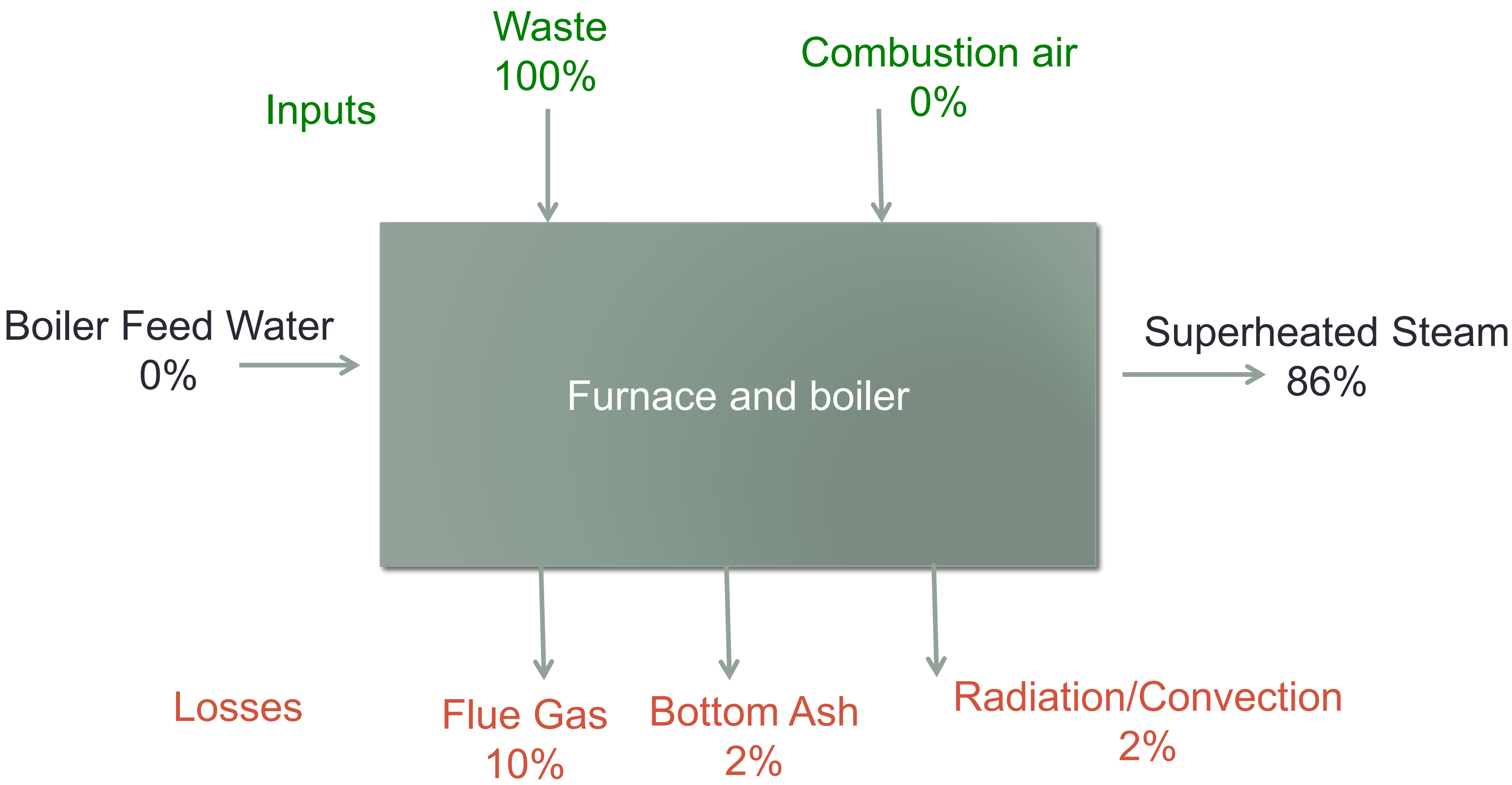
- Combustion products in flue gas



Source: Dalager and Reiman (2011). Incineration: Mass Balances. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Waste to Energy

- Typical energy balance



Source: Hulgaard and Vehlow (2011). Incineration: Process and Technology. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Waste to Energy

- Energy Recovery
  - Hot water for district heating
  - Process steam for various industries
  - Electricity or combined heat and power
- Depends on existing infrastructure, consumption, and economics

Energy Utilization	Recovery		Overall Efficiency
Heat only	Heat	75-90 (100)*	75-90 (> 100)*
Steam only	Steam	75-90	75-90
Power only	Power	25-35	25-35
Combined steam and power	Steam Power	60-75 15 - 20	75-90
Combined heat and power	Heat Power	60-65 (85)* 20-27	80-92 (>100)*

**With flue gas condensation*

Source: Hulgaard and Vehlow (2011). Incineration: Process and Technology. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Waste to Energy

- Solid residues

Type of Residue	Typical Amt Produced (kg/t of waste incinerated)
Bottom Ash	150-300
Grate Siftings	~5
Boiler Ash	~5
Economizer Ash	No data
Fly Ash	10-30
Flue gas cleaning residues:	
Dry process	20-60
Semidry process	15-30
Wet process	0.5-3.0 (sludge) 1-4 (gypsum)

Source: Hjelmar, Johnson, and Comans. (2011). Incineration: Solid Residues. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Waste to Energy

- Pre-treatment options
  - Removal of bulky items
  - Mixing of low and high heating value waste
  - Shredding
  - Screening
  - Removal of metallic iron

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Waste to Energy

- Types of facilities
  - Mass burn
  - Refuse derived fuel
- Different technologies
  - Moving grate
  - Rotary kiln
  - Fluidized bed

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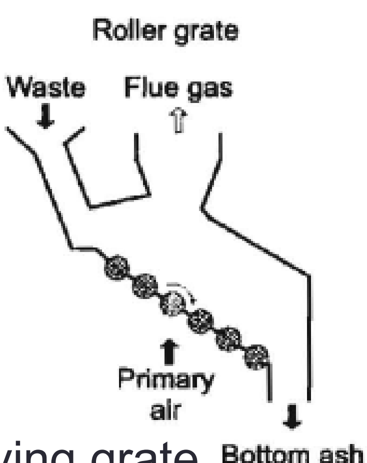
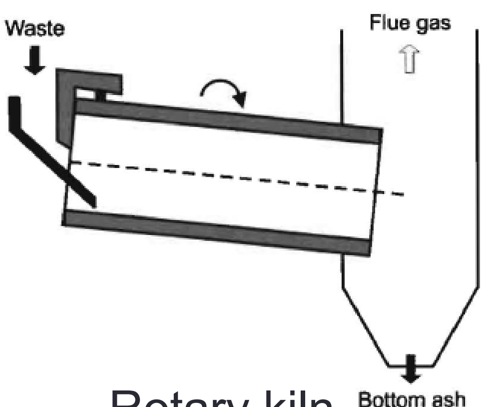
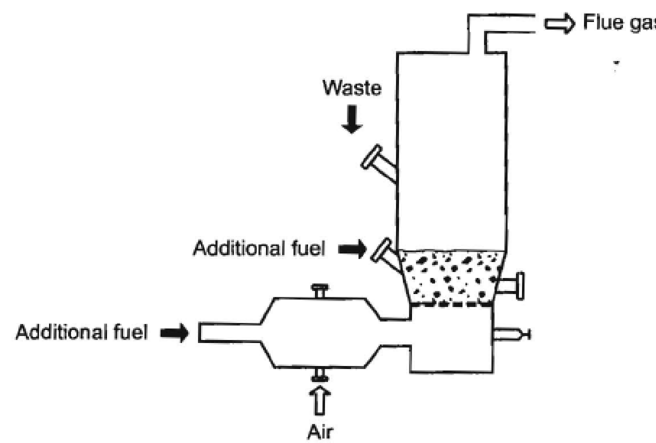


Moving grate



Rotary kiln



Fluidized bed

Waste to Energy: Advantages

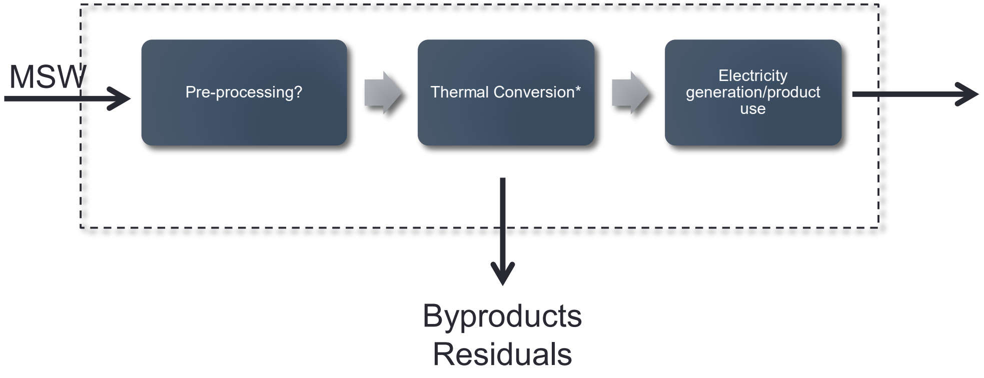
- Volume and weight reduced (approx. 90% vol. and 75% wt. reduction)
- Waste reduction is immediate, no long term residency required
- Air discharges can be controlled
- Ash residue is usually non-putrescible, sterile, inert
- Cost can be offset by heat recovery/ sale of energy

Waste to Energy: Disadvantages

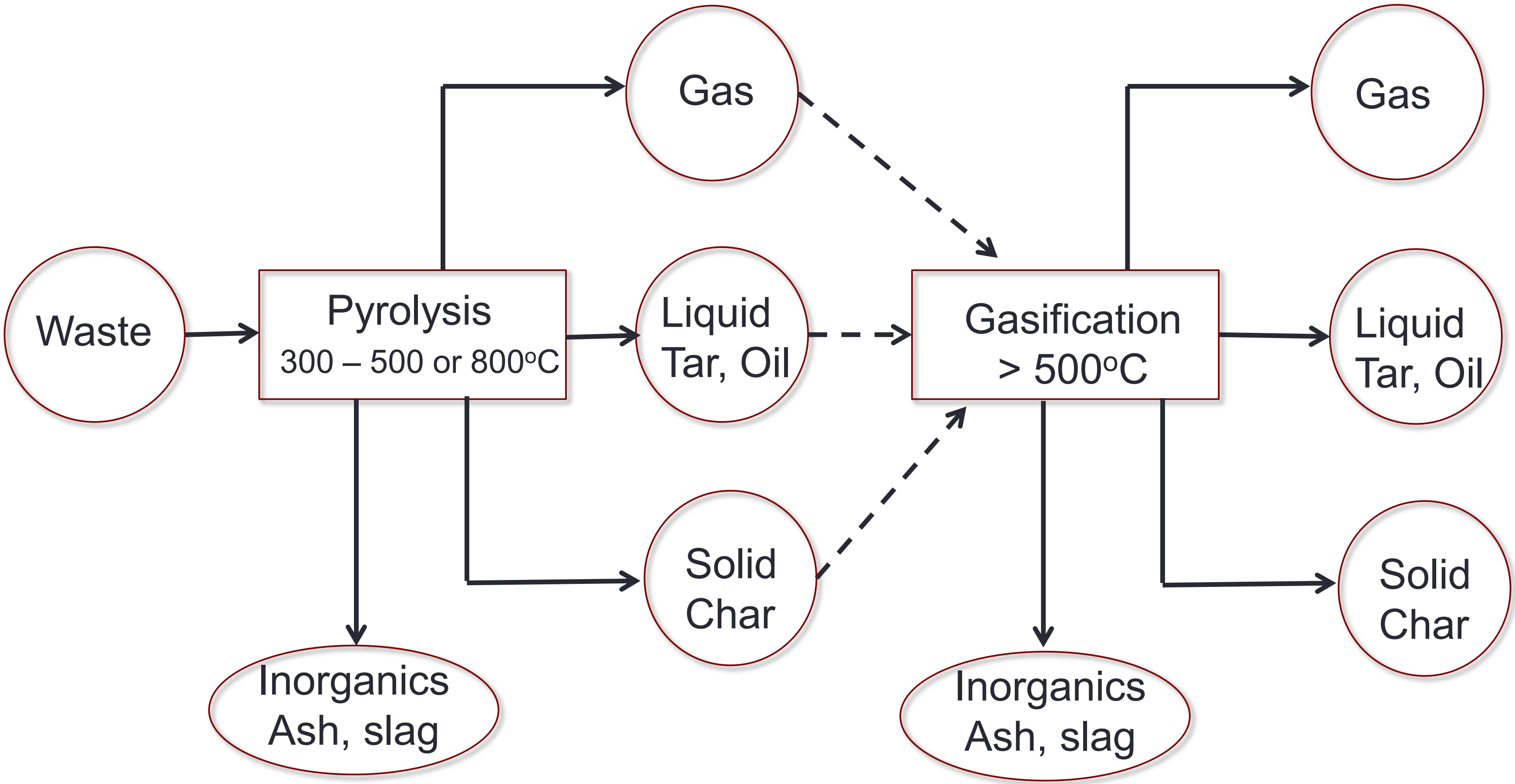
- High capital cost
- Skilled operators are required
- Some materials are noncombustible
- Some material require supplemental fuel
- Volume of gas from incineration is 10 x as great as other thermochemical conversion processes, greater cost for gas cleanup/pollution control
- Public disapproval

Thermal Conversion Technologies

- Waste to energy
- **Gasification**
- **Pyrolysis**
- Hydrothermal carbonization

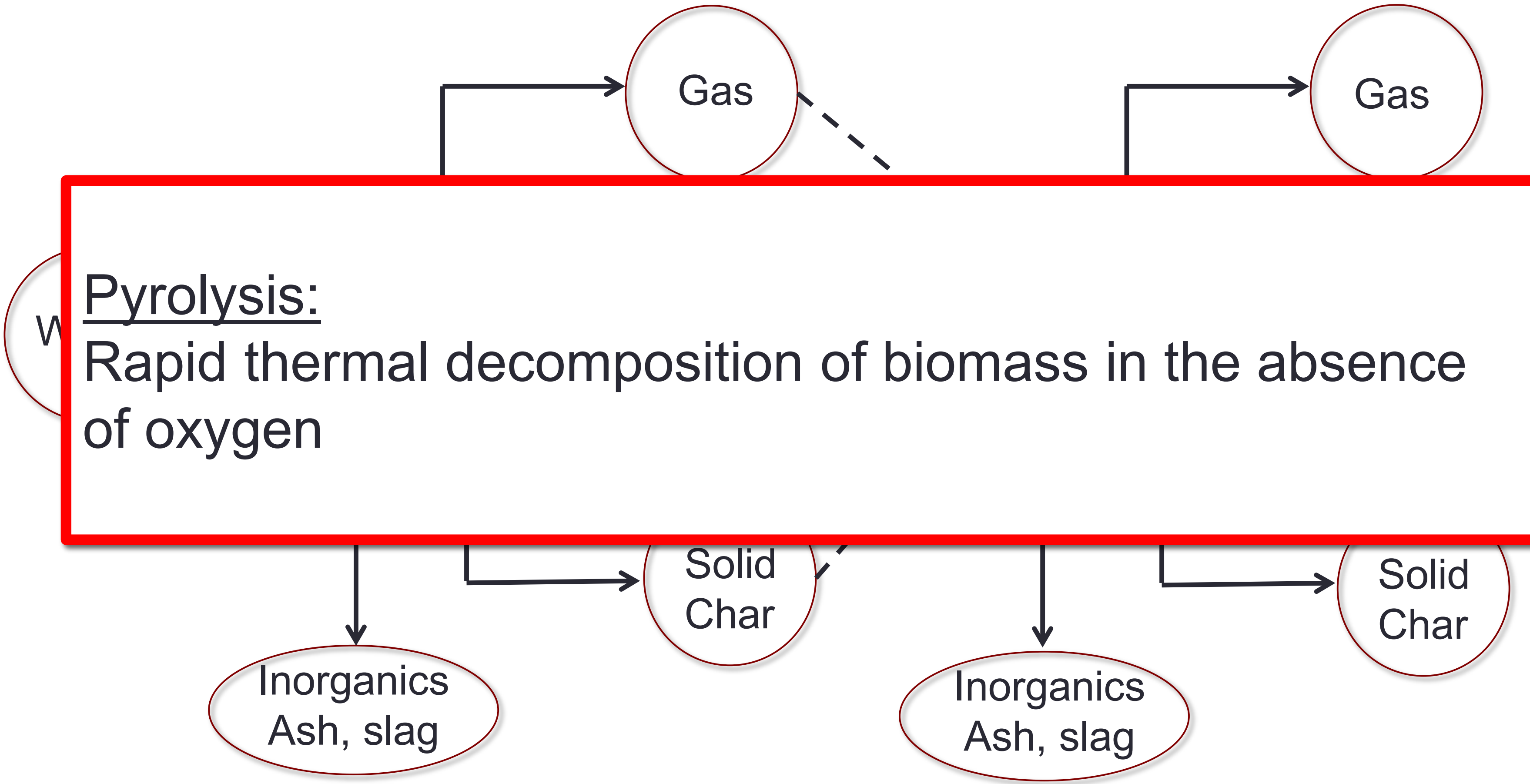


Gasification and Pyrolysis



Pyrolysis and gasification often occur sequentially. Temperature range differentiates between the two

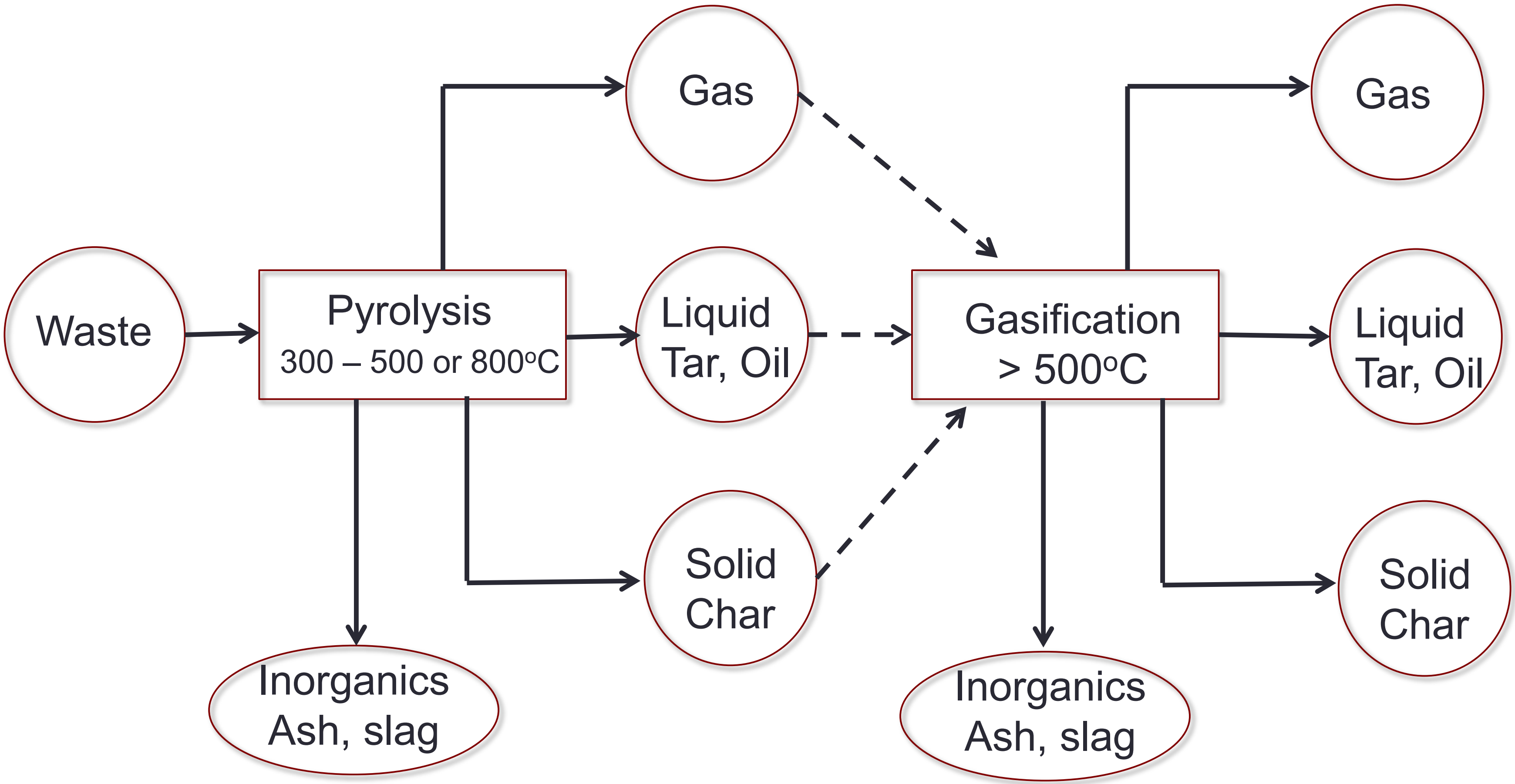
Gasification and Pyrolysis



<u>Pyrolysis:</u>
Rapid thermal decomposition of biomass in the absence of oxygen

Pyrolysis and gasification often occur sequentially. Temperature range differentiates between the two

Gasification and Pyrolysis



Pyrolysis and gasification often occur sequentially. Temperature range differentiates between the two

Gasification and Pyrolysis

<u>Gasification:</u>

- Conversion of solid or liquid feedstock into useful and convenient gaseous fuel or chemical feedstock under less than stoichiometric oxygen that can be burned to release energy or used for production of value-added chemicals
- Gasification adds hydrogen and strips carbon from the feedstock to produce a gas with a high H/C ratio

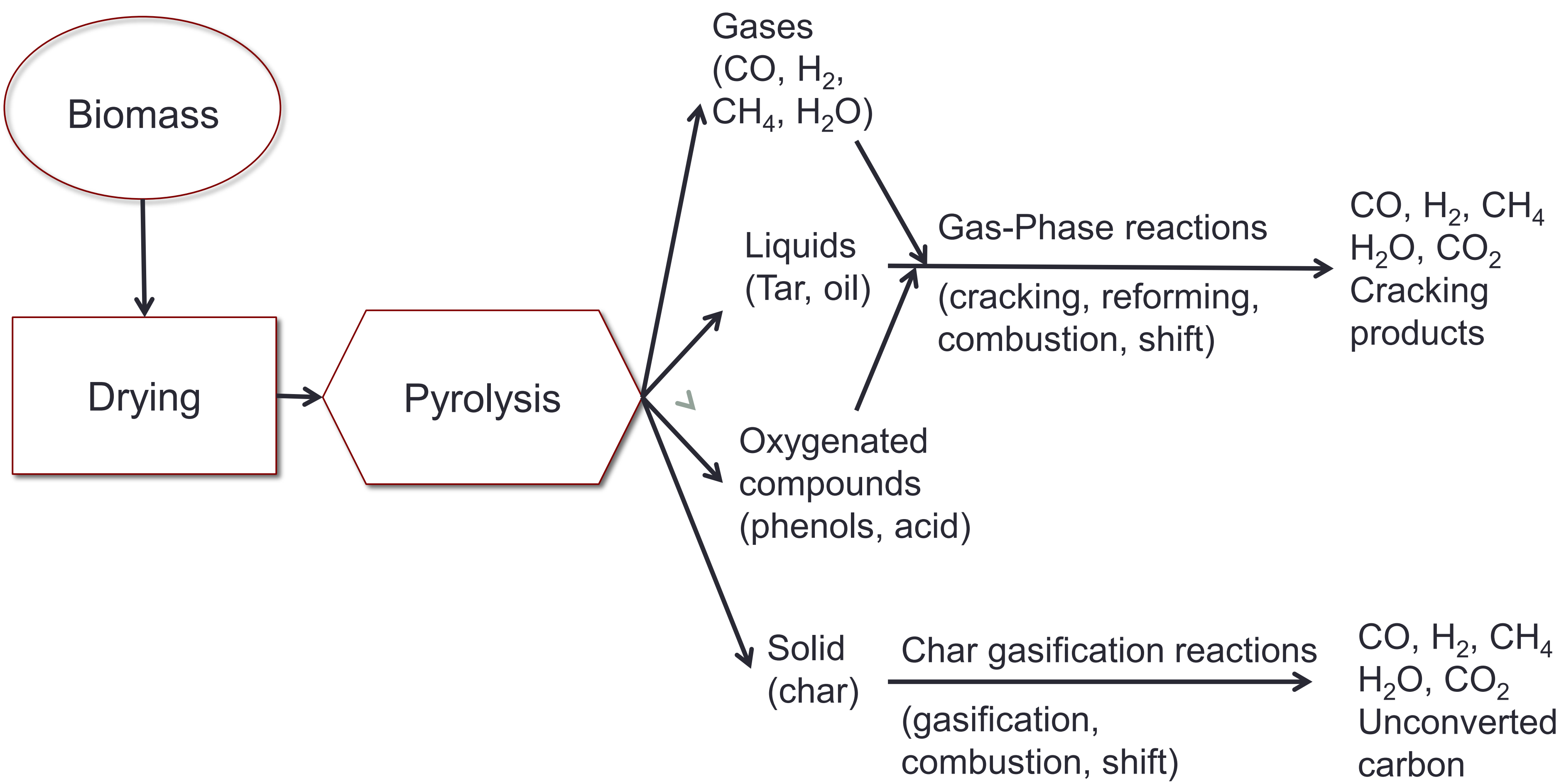
Inorganics
Ash, slag

Inorganics
Ash, slag

Pyrolysis and gasification often occur sequentially. Temperature range differentiates between the two

Gasification and Pyrolysis

Reaction Mechanisms



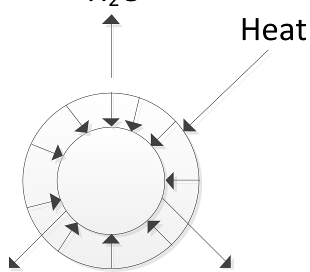
Gasification and Pyrolysis: Temperature

Temp. Range (°C)	Chemical Reactions
100 - 120	Thermal drying, dehydration
250	Deoxidation, desulfurization, molecular splitting of water and carbon dioxide, splitting of hydrogen sulfide
340	Breakage of bonds of aliphatic compounds, splitting of methane
380	Carbonization
400	Breakage of carbon-oxygen and carbon-nitrogen bonds
400 - 600	Decomposition of bituminous compounds into oils and tars
600	Cracking of bituminous compounds into heat resistant compounds (gaseous, short-chained hydrocarbons), formation of aromatic compounds (e.g., benzene)
> 600	Olefin, reaction of ethylene to cyclohexane, thermal aromatization to benzene and higher-volatility aromatic compounds

Source: Astrup and Bilitewski. (2011). Gasification and pyrolysis. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Gasification and Pyrolysis: Reactions

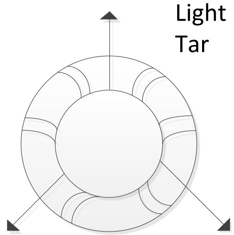
Heating and Drying



Thermal front penetrates particle

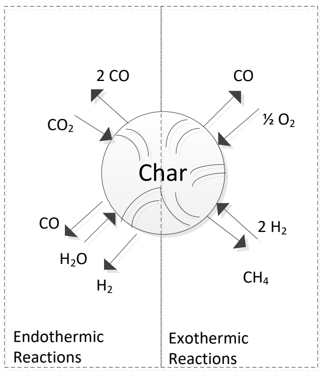
Pyrolysis

Volatile gases released:
CO, CO2, H2, H2O
Light hydrocarbons
Tar



Porosity increases

Gas-Solid Reactions



Gas-Phase Reactions

$CO + H_2O \rightarrow CO_2 + H_2$

$CO + 3H_2 \rightarrow CH_4 + H_2O$

Gasification and Pyrolysis: Reactions

Important Pyrolysis and Gasification Reactions.

	Description	Reaction energy (kJ/mol)	Effect of temperature increase	Effect of pressure increase
Solid–gas reactions				
$C + 1/2O_2 \rightarrow CO$	Partial combustion	110.6	To right	To left
$C + O_2 \rightarrow CO_2$	Combustion	393.8	—	—
$C + 2H_2 \rightarrow CH_4$	Hydrogenation	79.9	To left	To right
$C + H_2O \rightarrow CO + H_2$	Water -gas	−131.4	To right	To left
$C + CO_2 \rightarrow 2CO$	Boudouard	−172.6	To right	To left
Gas–gas reactions				
$CO + H_2O \rightarrow CO_2 + H_2$	Shift	41.2	To left	—
$CO + 3H_2 \rightarrow CH_4 + H_2O$	Reforming	201.9	To left	To right
Secondary solid–gas reactions				
Tar + $H_2O \rightarrow CO + H_2$	Steam reforming	—	—	—
Tar + $H_2 \rightarrow$ hydrocarbons + gas	Hydro cracking	—	—	—
Tar + catalyst → char + gas	Cracking	—	—	—

Source: Astrup and Bilitewski. (2011). Gasification and pyrolysis. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Gasification and Pyrolysis Products

- Product composition varies dramatically depending on operational parameters and feedstock composition.

Process	Solid		Liquid		Gas	
	%, wt.	Energy (MJ/kg)	%, wt.	Energy (MJ/kg)	%, wt.	Energy (MJ/m^3)
Pyrolysis	20 – 50 Metal, glass, sand, ash	10 – 35	30 – 50 Tar, oil, water	5 - 15	20 – 50 H_2, CH_4, CO, CO_2, volatiles	3 - 12
Gasification	30 – 50 Ash	NA	10 – 20 Tar, oil	NA	30 – 85 Similar to pyrolysis, more CO_2	3 - 12

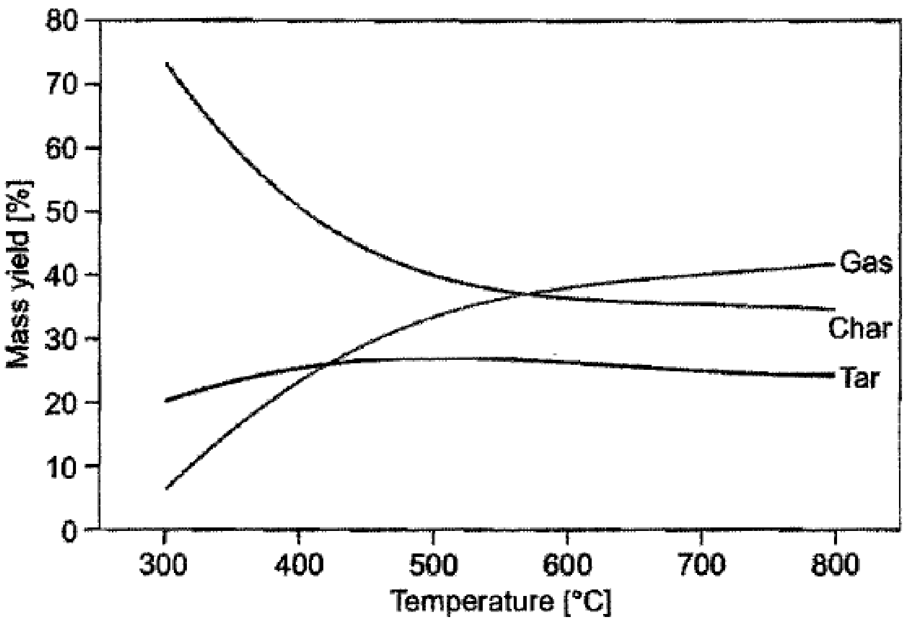
Sources:
Astrup and Bilitewski. (2011). Gasification and pyrolysis. In: Solid Waste Technology and Management, Ed. By T.H. Christensen
Lu, Jordan, Berge (2012). Thermal conversion of municipal solid waste via hydrothermal carbonization: comparison of carbonization products to products from current waste management processes. Waste Management, in press.

Pyrolysis and Gasification: Input Feedstock Composition

- Physical and chemical properties influence heterogeneous reactions between the solid and gas phases, char and ash formation, and quality of outputs
  - Moisture content
  - Particle size
  - Particle size distribution
- Higher organic matter generally correlates with higher energy content
- Metals significantly influence output and need for gas cleaning
- Mixed, unprocessed MSW can be difficult, generally needs to be pretreated
  - Reduce the nondegradable fraction
  - Reduce particle size
  - Homogenize waste

Gasification and Pyrolysis: Important Process Parameters

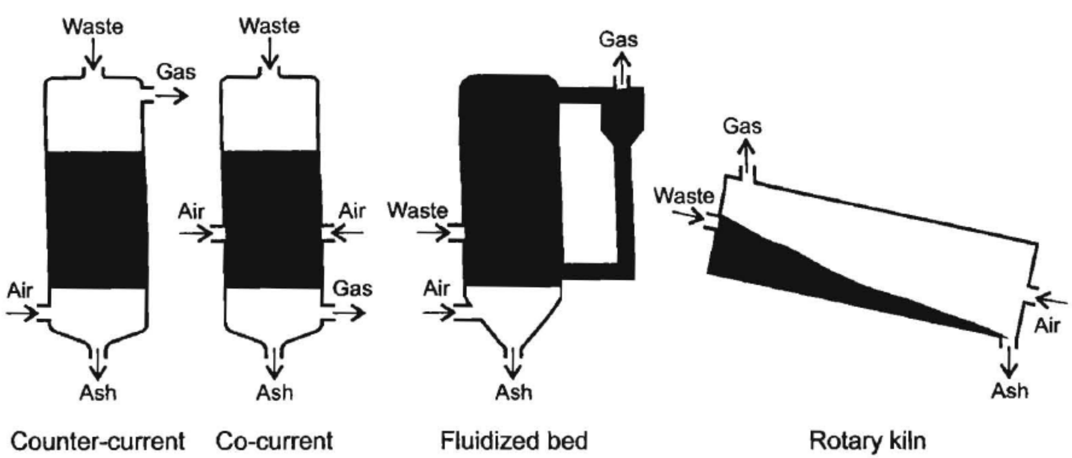
- Temperature
  - Higher temperatures = higher carbon conversion and less tar
  - Higher temperatures may result in lower gas-phase energy
  - In pyrolysis, higher temperatures yield more gas and less liquid



Source: Astrup and Bilitewski. (2011). Gasification and pyrolysis. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Gasification and Pyrolysis: Important Process Parameters

- Heating rate
  - Slow rate and low temperatures = more char
  - Moderate rate and moderate temperatures = equali distribution of pyrolysis products
  - High rate and high temperature = more liquid
  - Slow rate and high temperatures = more gas output
- Pressure
  - High pressure increases gas yield
- Technology

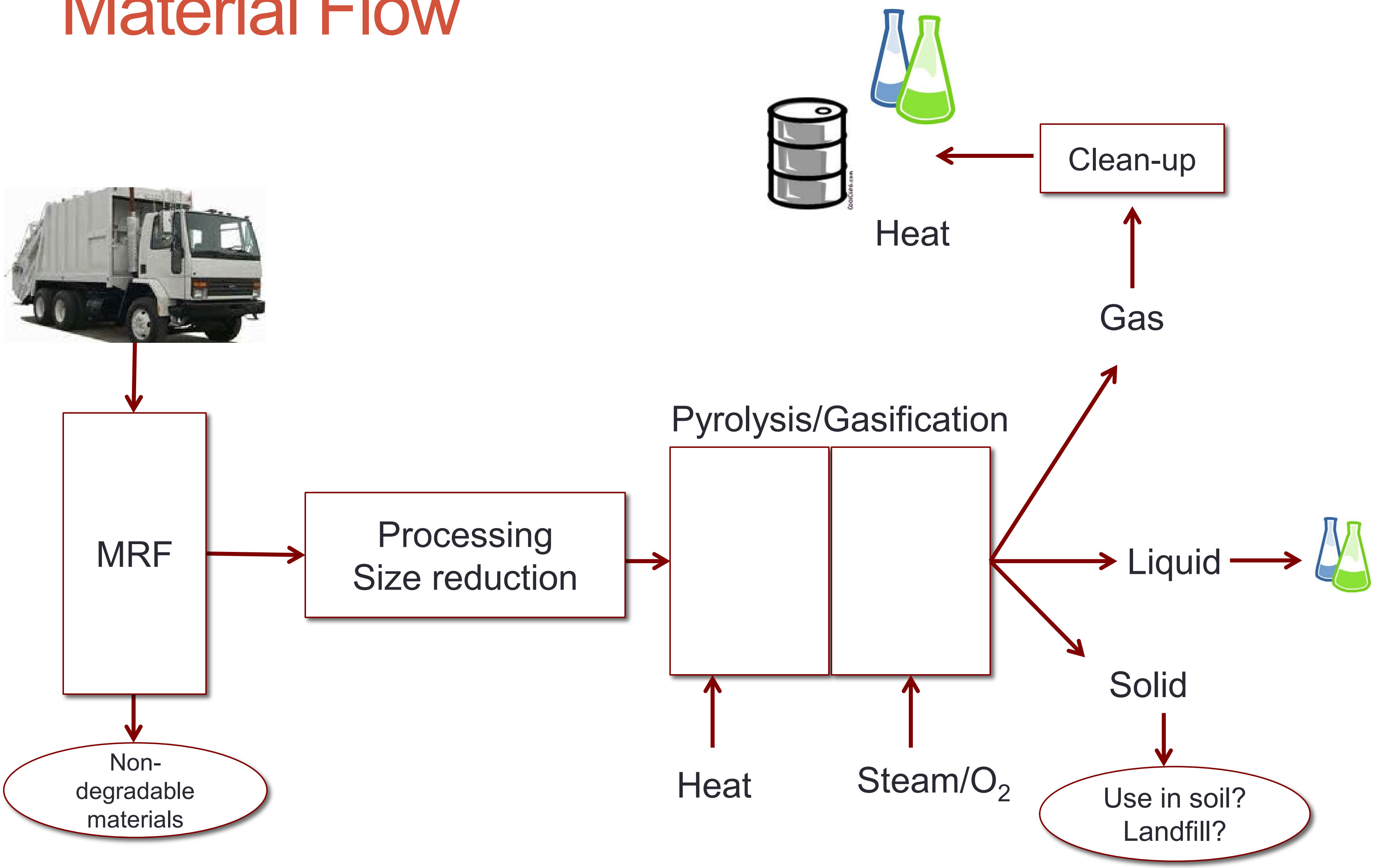


Source: Astrup and Bilitewski. (2011). Gasification and pyrolysis. In: Solid Waste Technology and Management, Ed. By T.H. Christensen.

Gasification and Pyrolysis: Energy Recovery

- Recovery for heat and/or electricity production
- Clean syngas can be used to generate electricity via a gas turbine
- "Dirty" gas can be combusted in a boiler
- Conversion to electricity efficiencies range form 10 – 20%
- Heat recovery efficiencies range from 60-85% of input energy

Gasification and Pyrolysis: Possible Material Flow



Gasification and Pyrolysis: Advantages

- Possibility to recover chemical energy as hydrogen or other chemical feedstocks
- Less need for flue gas cleaning
- Potentially better options for CO_2 capture
- Potentially lower emissions of dioxins
- Improved quality of solid residues

Gasification and Pyrolysis: Disadvantages

- Homogeneous fuels are required
- Complicated to operate
  - Slagging
  - Tar production
  - Contaminants in gas
- Commercial application is lacking

Variations of Gasification and Pyrolysis

- Plasma Arc
  - Conversion of organic matter to syngas via an electric arc
  - Temperatures > 4000°C
  - Residual materials immobilized in vitrified mass
  - Gas heating value output/electricity input = 21.4
- Torrefaction
  - Mild pyrolysis (230 – 300°C)
  - Improves energy density by reducing O/C ratio
  - H_2O is removed
  - Carbon content increases
  - 90% of biomass energy remains in char
  - Char is brittle

http://1.bp.blogspot.com/-dBa5ttbCPGM/TgwWTlhg2NI/AAAAAAAACnQ/FJTHtpkQcyI/s1600/plasma-2.JPG

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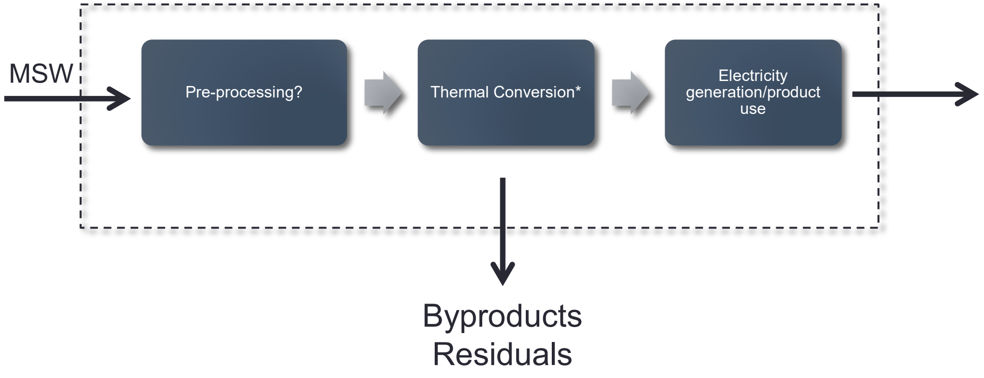
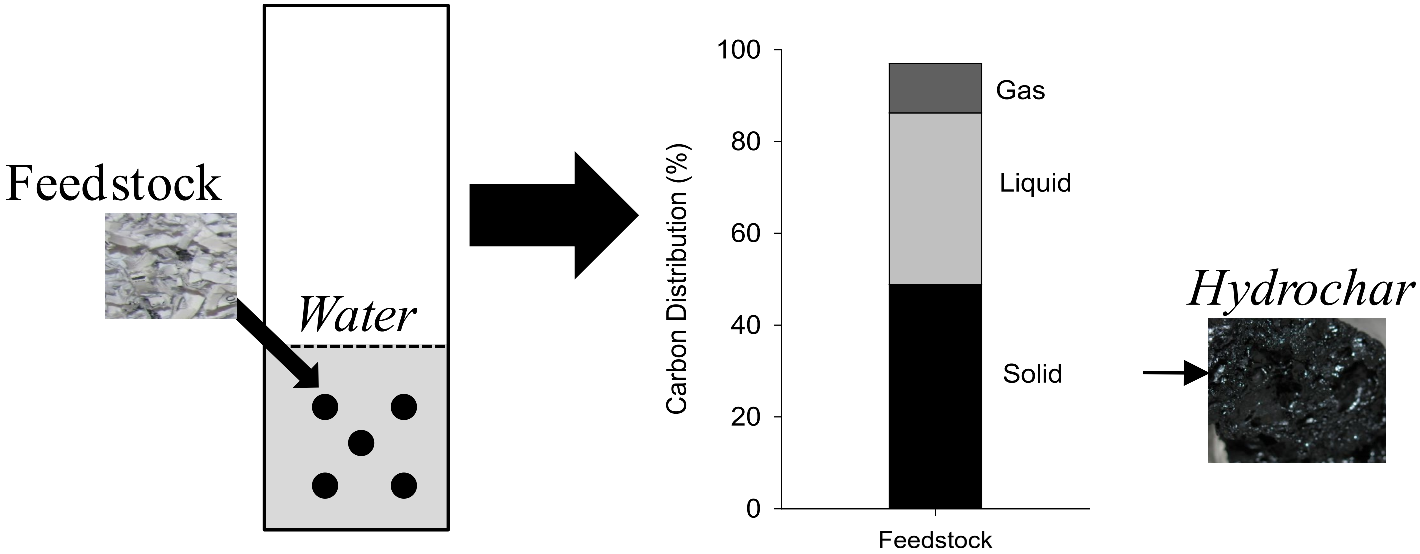
Thermal Conversion Technologies

- Waste to energy
- Gasification
- Pyrolysis
- **Hydrothermal carbonization**



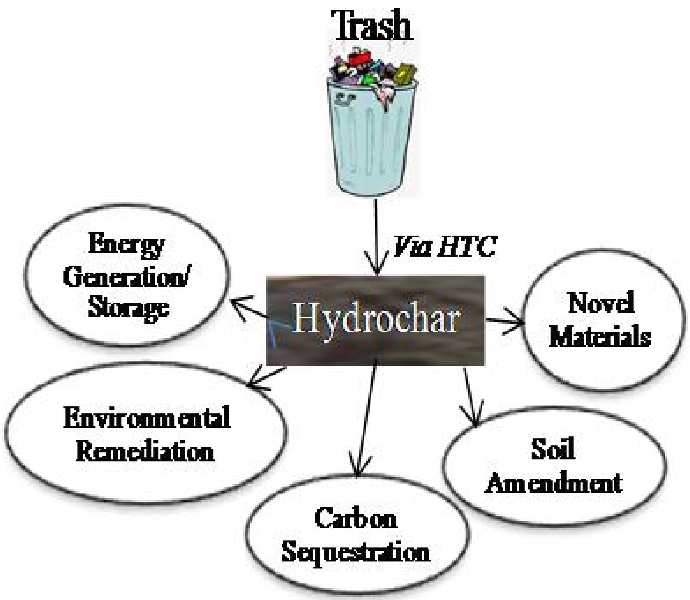
Hydrothermal Carbonization

- HTC is a wet, relatively low temperature (180 – 350 ^{o}C) thermal conversion process
- Reaction occurs at autogenous pressures (i.e., whatever the system will generate)
- Create a carbonaceous reside called “hydrochar”



Hydrothermal Carbonization as a Waste Management Tool

- Conversion of waste to useful products
  - Energy source
  - Novel nanomaterials
  - Activated carbon
- Reduction of fugitive gas emissions



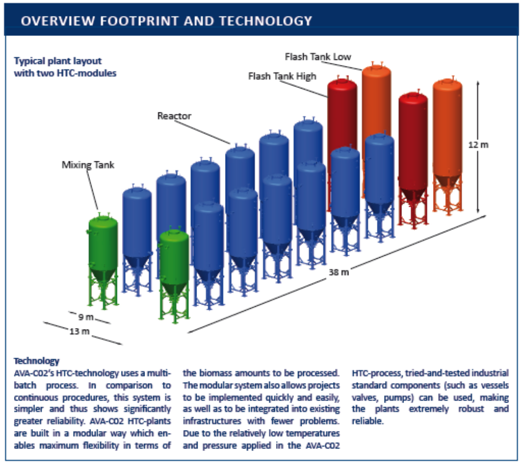
Hydrothermal Carbonization

- New potential waste management technique

WASTE management world.

Council Backs 'First of Kind' Waste to Energy Facility in U.S.

INGELIA develops the first floor hydrothermal carbonization of biomass



TerraNova energy

CLEAN energy beyond COAL

Hydrothermal Carbonization

An innovative process for utilization of humid waste biomass for energy production

Max Planck Institute of Colloids and Interfaces

Sustainable Materials for Energy Storage, Catalysis and Separation Science

Hydrothermal Carbonization

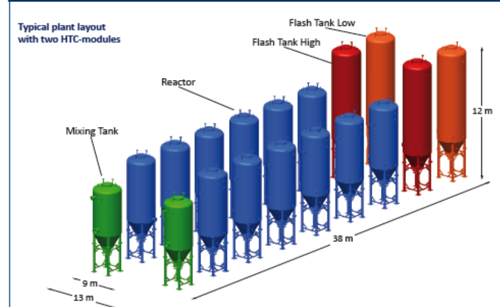
- New potential waste management technique

WASTE management world

Council Backs 'First of Kind' Waste to Energy Facility in U.S.

INGELIA develops the first floor hydrothermal carbonization of biomass

OVERVIEW FOOTPRINT AND TECHNOLOGY



Technology

AVA-CO2's HTC-technology uses a multi-batch process. In comparison to continuous procedures, this system is simpler and thus shows significantly greater reliability. AVA-CO2 HTC-plants are built in a modular way which enables maximum flexibility in terms of the biomass amounts to be processed. The modular system also allows projects to be implemented quickly and easily, as well as to be integrated into existing infrastructures with fewer problems. Due to the relatively low temperatures and pressure applied in the AVA-CO2 HTC-process, tried-and-tested industrial standard components (such as vessels valves, pumps) can be used, making the plants extremely robust and reliable.

TerraNova energy

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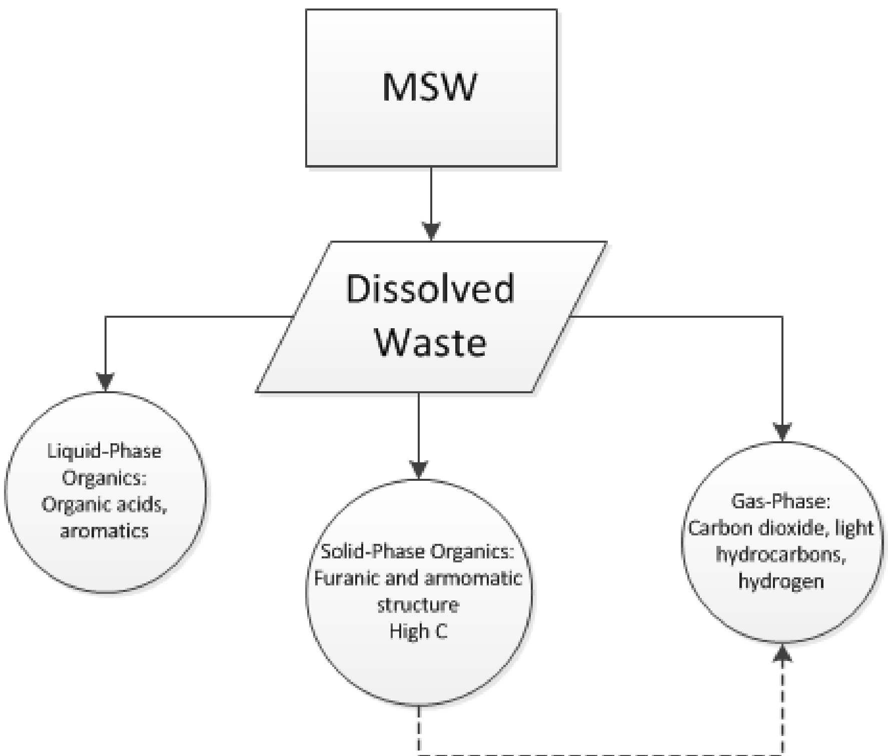
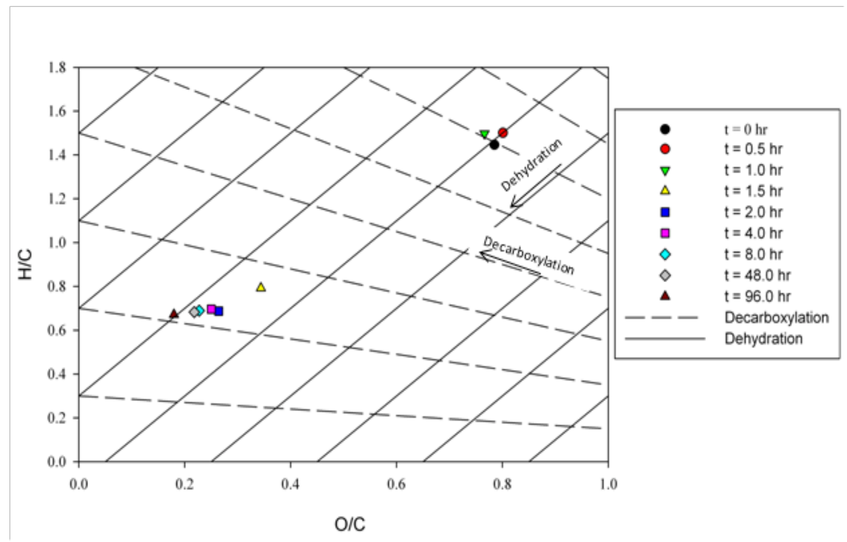
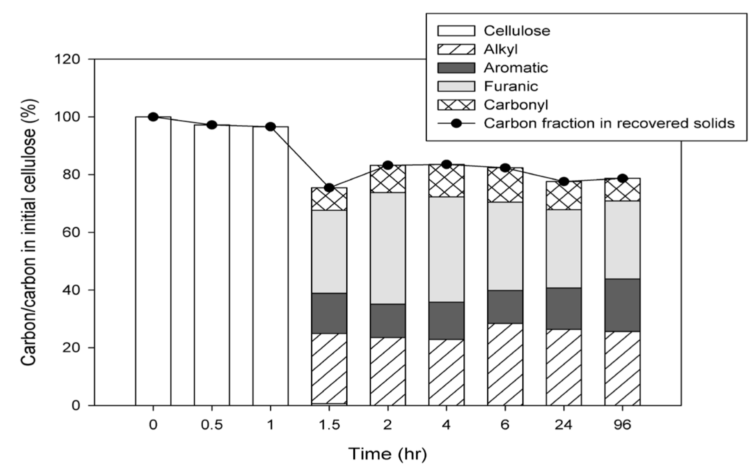
Hydrothermal Carbonization Mechanisms

- Hypothesized Mechanisms

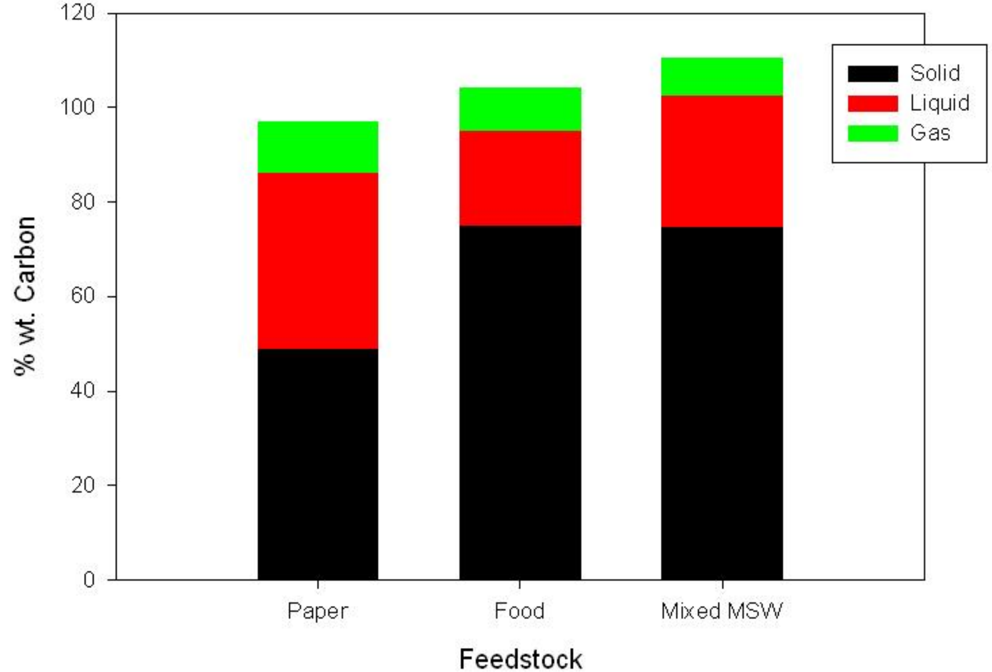






Source: Lu, X., Pellechia, P.J., Flora, J.R.V., Berge, N.D. (submitted, 2012). Influence of reaction time and temperature on product formation associated with the hydrothermal carbonization of cellulose. Submitted to *Environmental Science and Technology.*

Hydrothermal Carbonization: Influence of Waste Input




Paper


Food


Mixed MSW


Plastic

% of biomass energy retained in char depends on waste material (75 – 100%)

Berge, N.D., Ro, K.S., Mao, J., Flora, J.R.V., Chappell, M., Bae, S. (2011). Hydrothermal Carbonization of Municipal Waste Streams. *Environmental Science and Technology* 45(13), 5696-5703.

Hydrothermal Carbonization Products

- Product composition varies dramatically depending on operational parameters and feedstock composition.

Process	Solid		Liquid		Gas	
	%, wt.	Energy (MJ/kg)	%, wt.	Energy (MJ/kg)	%, wt.	Energy (MJ/m^3)
Pyrolysis	20 – 50 Metal, glass, sand, ash	10 – 35	30 – 50 Tar, oil, water	5 - 15	20 – 50 H_2, CH_4, CO, CO_2, volatiles	3 - 12
Gasification	30 – 50 Ash	NA	10 – 20 Tar, oil	NA	30 – 85 Similar to pyrolysis, more CO_2	3 - 12
Hydrothermal carbonization	**50 - 80**	**18 - 36**	**5 - 20**	**Not Avail**	**2 – 5** **Mostly CO_2; some energy-rich hydrocarbons**	**Not Avail**

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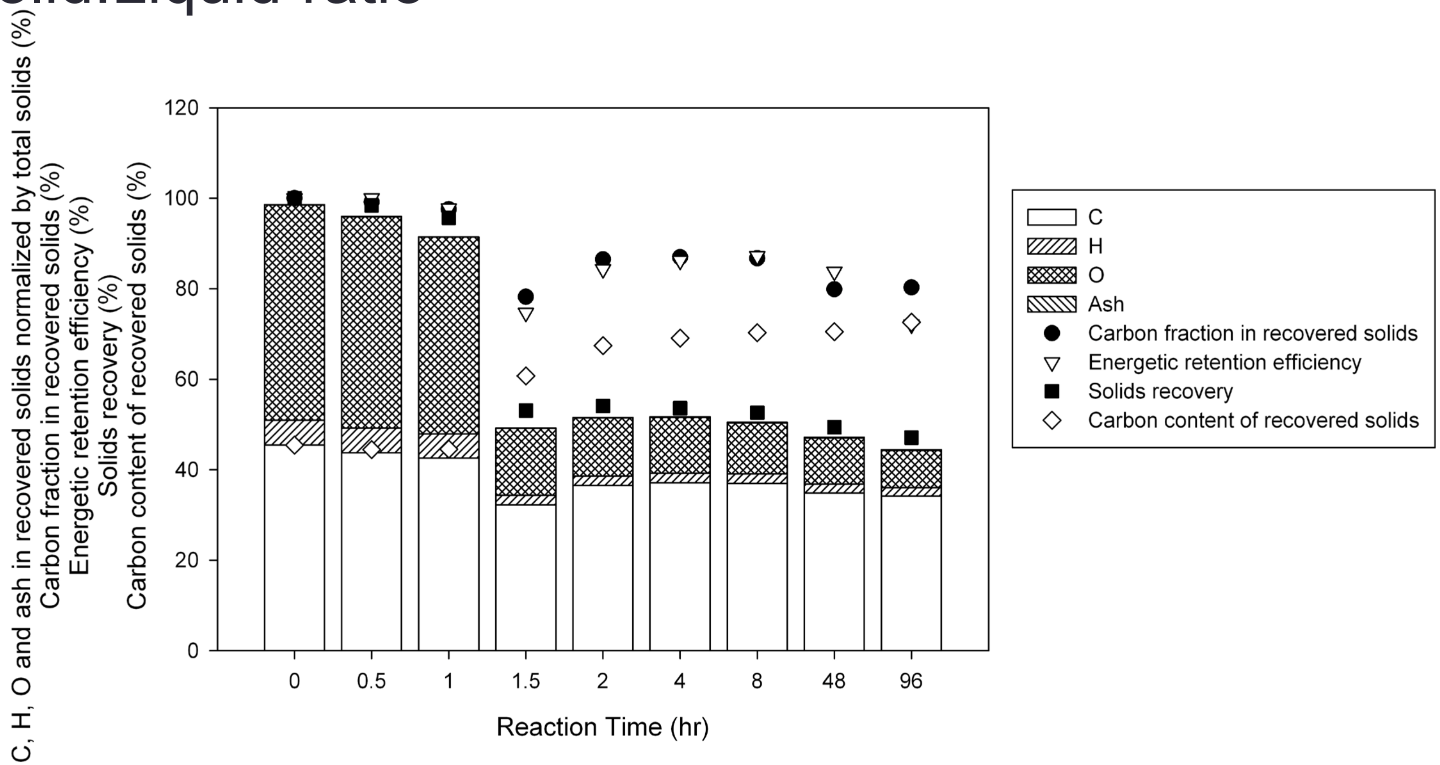
Hydrothermal Carbonization: Process Parameters

- Temperature
- Time
- Solid:Liquid ratio



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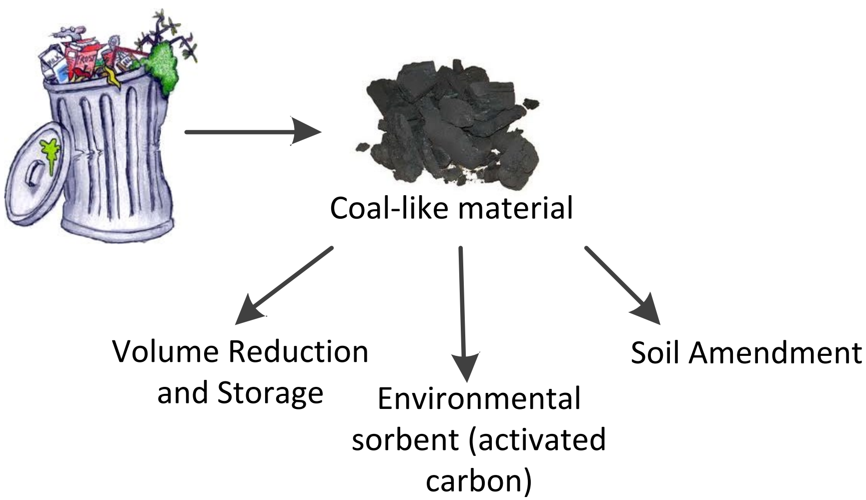
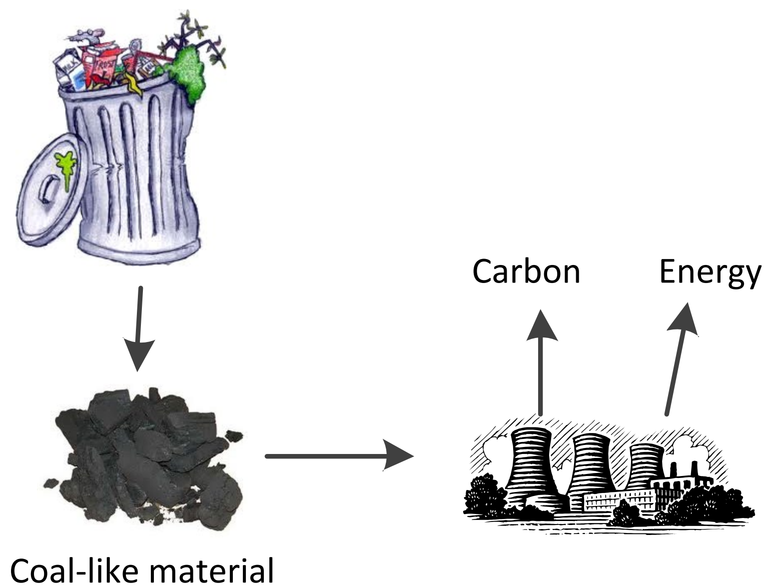
Hydrothermal Carbonization: Comparison to Waste Management Processes

- Benefits depend on char use:
  - Material Generation
  - Energy Source

Beneficial Material Generation



Energy Generation



Hydrothermal Carbonization: Energy Derived from Products

Potential Energy Generation from Waste Management Processes (10^{-3} MJ/g waste)[1]

Waste Material	Landfilling[2]	Composting	Anaerobic Digestion[5]	Incineration	HTC[3]
Paper	5.7	0	-	12.9	7.8
Food	1.98	0	2.6 – 3.6	5.43[4]	11.94
Mixed MSW	2.1	0	-	15.5	9.76

[1] assuming 100% conversion to energy and energy content of methane is 38 MJ/m^3
[2] using gas calculations with gas collection efficiencies reported in Table 3
[3] maximum energy over a 120 hr period
[4] based on typical food waste, with a moisture content of 70%.
[5] based on the maximum amount of biogas measured at anaerobic digestion facilities reported by Levis et al. (2010): 136 m^3 gas/Mg waste and assuming 50 – 70% of the gas is methane; 100% of the gas is collected

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[2]usin ... ble 3

[3]max ...

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Note: Carbon is no longer sequestered!

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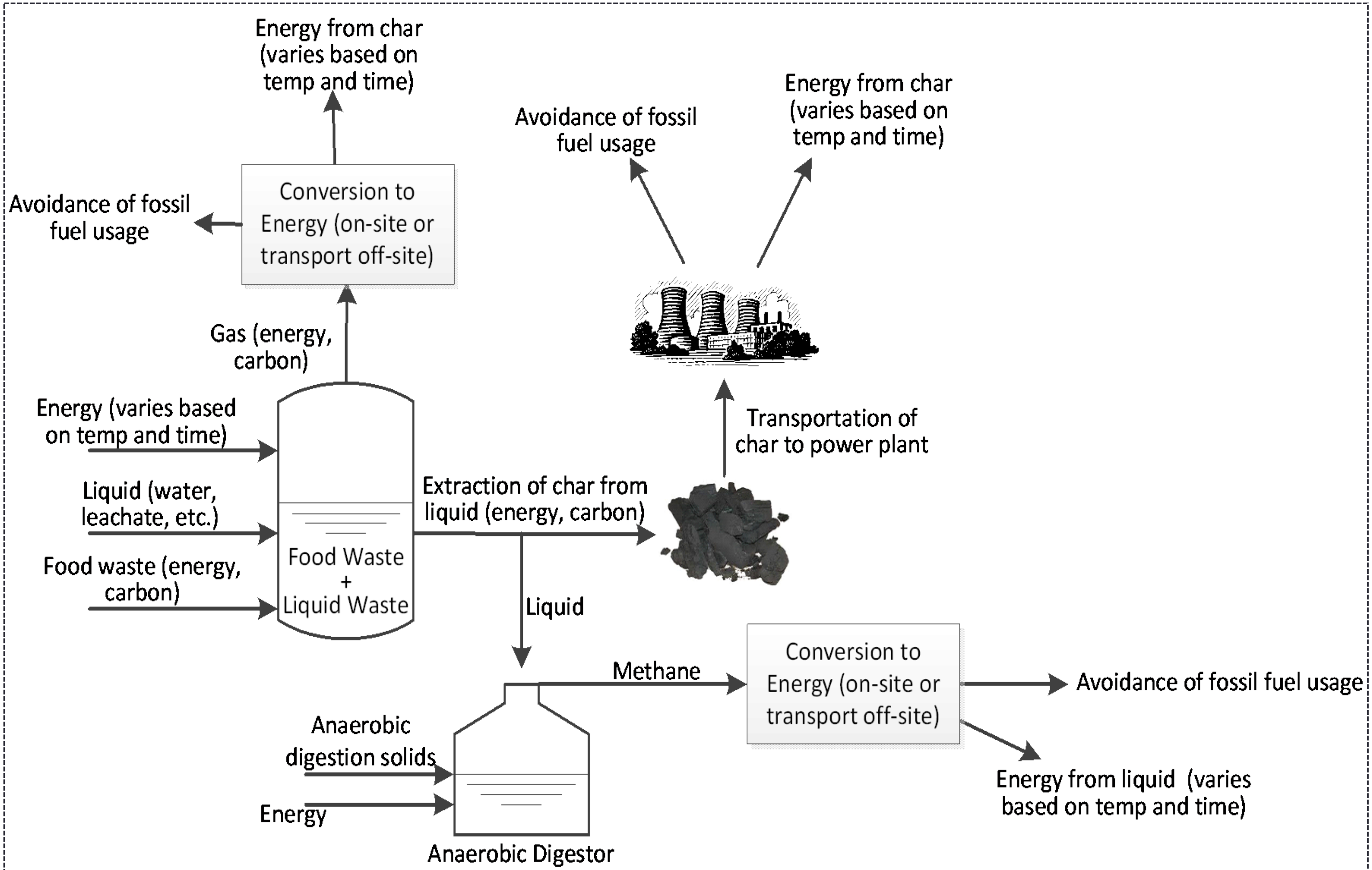
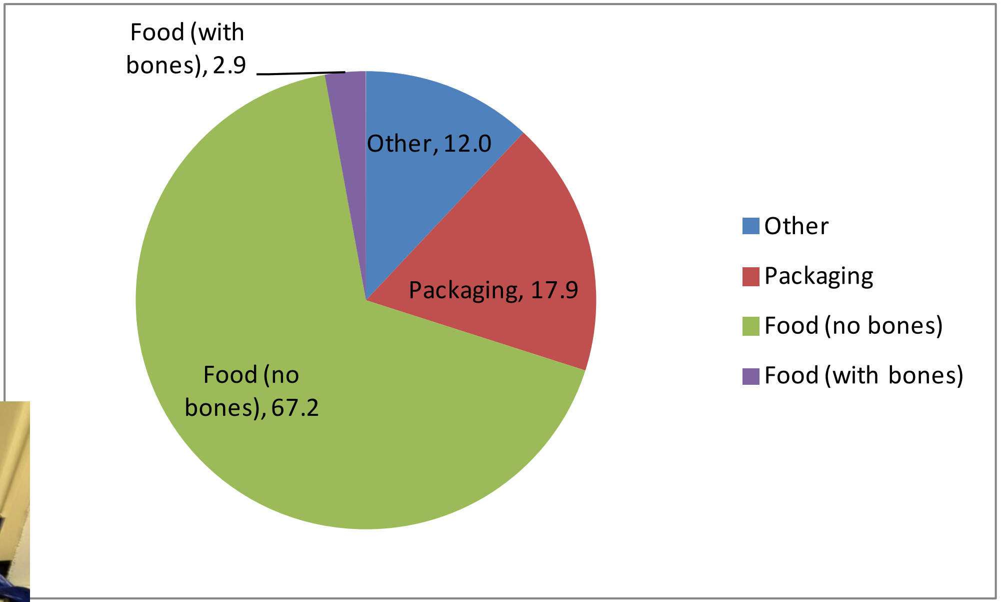
Hydrothermal Carbonization: Process Schematic



When to Use Hydrothermal Carbonization?

- Waste diversion?
  - Food waste



Environmental Research & Education Foundation

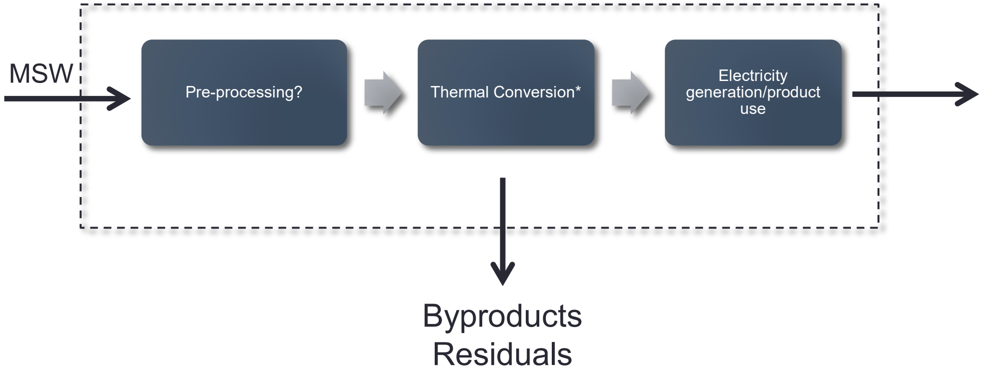
Lighting a path to sustainable waste management practices

Hydrothermal Carbonization: Advantages and Disadvantages

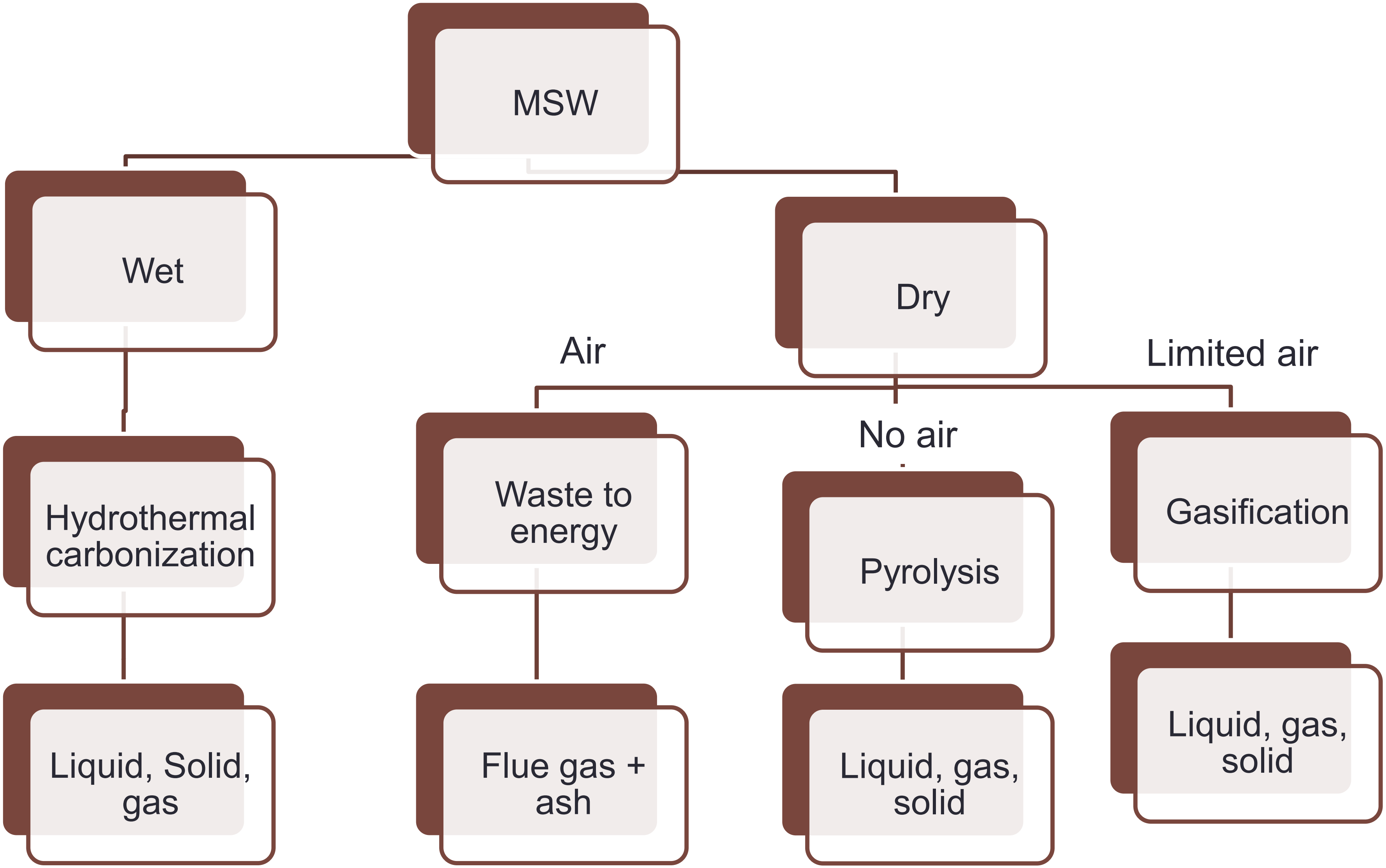
- Advantages
  - Wet feedstock, no drying required
  - Retain large portion of carbon in solid
  - High energy density char
  - Waste volume and mass reduction
- Disadvantages
  - Not yet applied at commercial scale
  - Waste pre-processing?
  - Skilled operator needed

Thermal Conversion Technologies

- Waste to Energy
- Gasification
- Pyrolysis
- Hydrothermal Carbonization



Summary of Conversion Technologies



Thermal Conversion Techniques

	Hydrothermal Carbonization	Pyrolysis	Gasification	Combustion
Temperature	< 350 °C	< 500 °C	> 500 °C	> 900 °C
Atmosphere	air or inert	Oxygen-free	Limited oxygen; air	Oxygen; air
Pressure	autogenous	variable	variable	low
Feedstock Moisture Content	wet – add water to achieve high moisture conditions (i.e., 20% solids)	Relatively dry (MSW water content is typically 20%, by wt. If using a wet feedstock (swine waste), it is often dried)		
Solid Product	char	char	char	ash
Main Gaseous Products	CO_2 (small total quantity of gas)	H_2, CO, CO_2, CH_4	H_2, CO, CO_2, CH_4	CO_2, N_2
Liquid Products	water waste, tar and oil	oil; tar	oil	none
Potential Recovery Products	char, and possibly gas, liquid	tar/oil, gas and char	gas, oil and char	Heat in combustion gas

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Process	Solid		Liquid		Gas	
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Waste to Energy	15 – 20	NA	NA	NA	80 - 90	12 - 16
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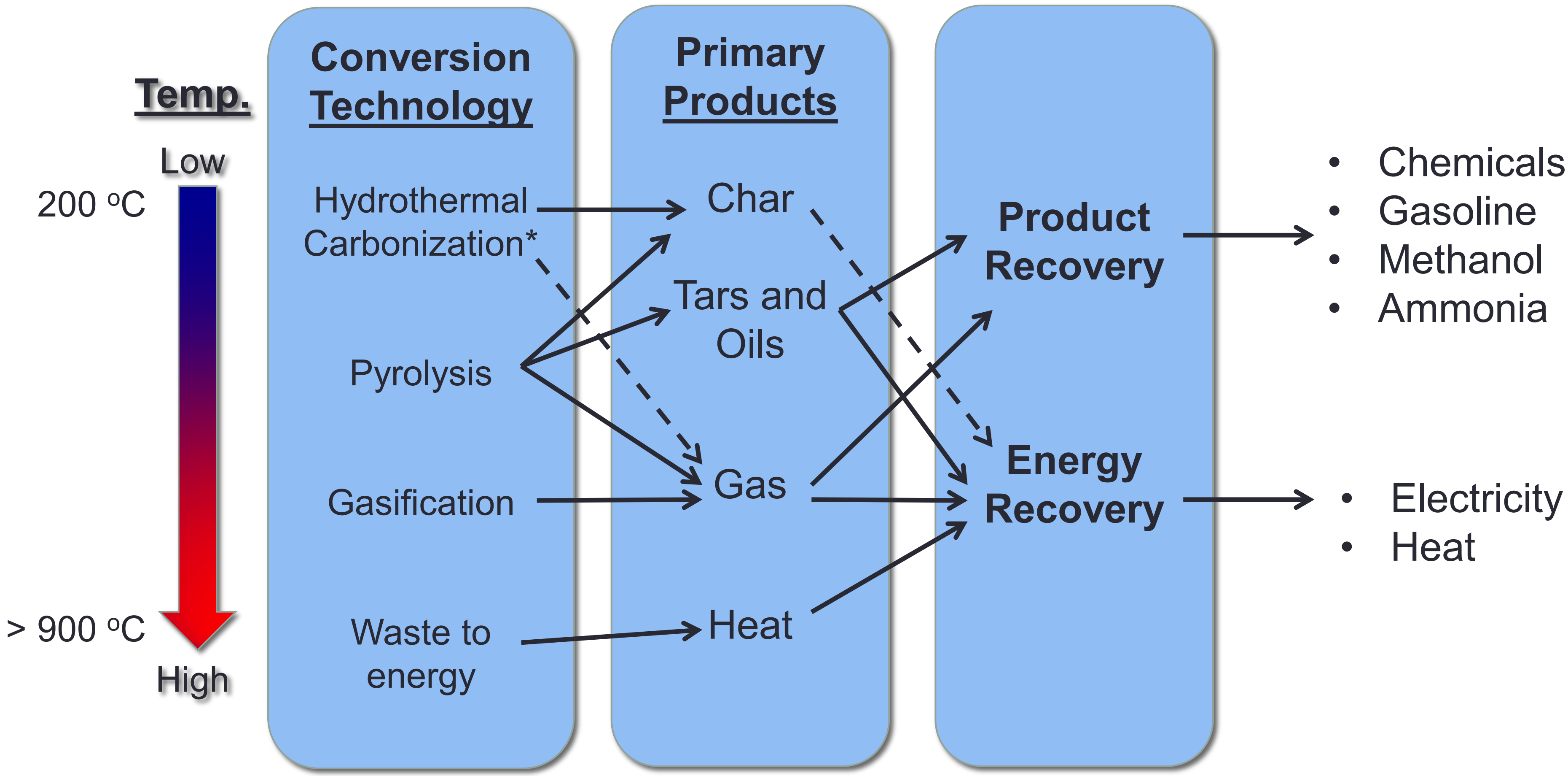

**possible recovery of chemicals in liquid-phase, not necessarily tar or oil*

Thermal Conversion Processes

- As collected MSW vs separated waste?
- Diversion from landfills?
  - Potential for lower C emissions
  - Potential for more energy recovery
  - Lower NOx, SOx and PM emissions

THANK YOU

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