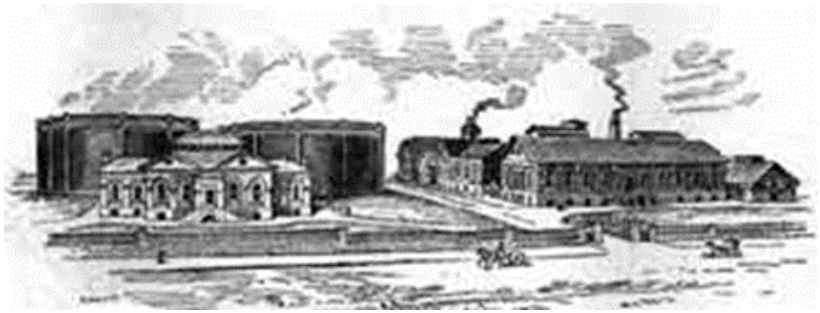
Gasification Tutorial Clearwater Conference 2023 Update

Ronald W. Breault
NETL, DOE
Morgantown, WV



200+ years



- Baltimore, Maryland began the first commercial unit 1816

Valmet Gasifier for Biomass and Waste

Outline

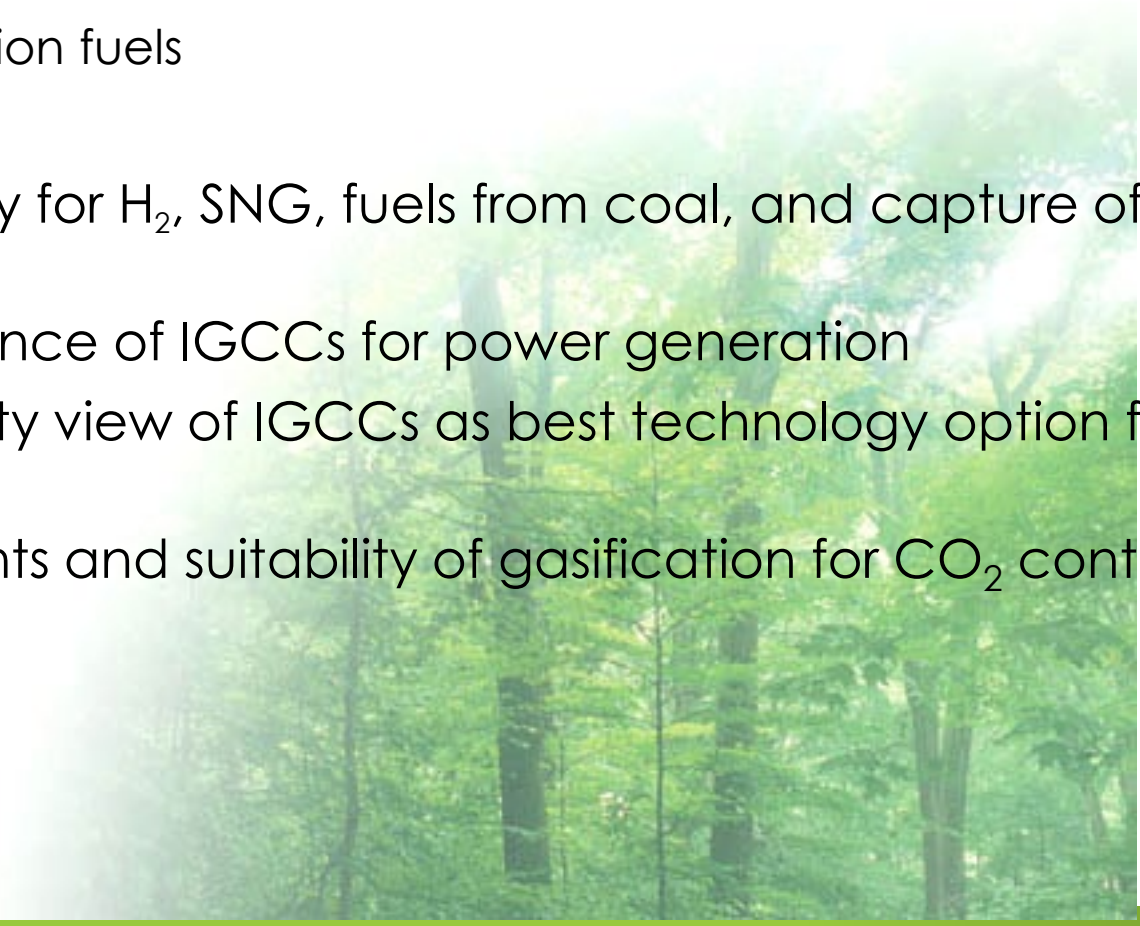
- Background/History
- Comparison with Combustion
- IGCC Efficiency
- Gasifiers – by Developer
- Biomass and Waste Gasification
- Additional Slides
  - Hydrodynamics and Kinetics
  - Typical Gas Compositions
  - Acid Gas Control

Citations

- Breault, R. W. "Gasification Processes Old and New: A Basic Review of the Major Technologies" *Energies* **2010**, *3*(2), 216-240; **https://doi.org/10.3390/en3020216**
- Shadle, L.J., Breault, R.W. (2012). Integrated Gasification Combined Cycle (IGCC). In: Chen, WY., Seiner, J., Suzuki, T., Lackner, M. (eds) Handbook of Climate Change Mitigation. Springer, New York, NY. https://doi.org/10.1007/978-1-4419-7991-9_40
- Shadle, L.J., Breault, R.W., Bennett, J. (2017). Gasification Technology. In: Chen, WY., Suzuki, T., Lackner, M. (eds) Handbook of Climate Change Mitigation and Adaptation. Springer, Cham. https://doi.org/10.1007/978-3-319-14409-2_40
- Shadle, L.J., Indrawan, N., Breault, R.W., Bennett, J. (2022). Gasification Technology. In: Lackner, M., Sajjadi, B., Chen, WY. (eds) Handbook of Climate Change Mitigation and Adaptation. Springer, Cham. https://doi.org/10.1007/978-3-030-72579-2_40
- Biomass and Municipal Solid Waste (MSW) Gasification | netl.doe.gov, https://netl.doe.gov/research/Coal/energy-systems/gasification/gasifipedia/biomass-msw
- Breault, R. W., 2012 Gasification Tutorial
- Breault, R. W., 2008 Gasification Tutorial

Why the Interest in Gasification?

- Continuing high price of fuels
  - Natural gas & Highway transportation fuels
- Energy Security
- Gasification is baseline technology for H_2, SNG, fuels from coal, and capture of CO_2 for sequestration
- Excellent environmental performance of IGCCs for power generation
- Growing environmental community view of IGCCs as best technology option for coal systems
- Carbon management requirements and suitability of gasification for CO_2 control



What is Gasification?

NATIONAL ENERGY TECHNOLOGY LABORATORY

Gasification converts any carbon-containing material into synthesis gas, composed primarily of carbon monoxide and hydrogen (referred to as syngas)

Syngas can be used as a fuel to generate electricity or steam, as a basic chemical building block for a large number of uses in the petrochemical and refining industries, and for the production of hydrogen.

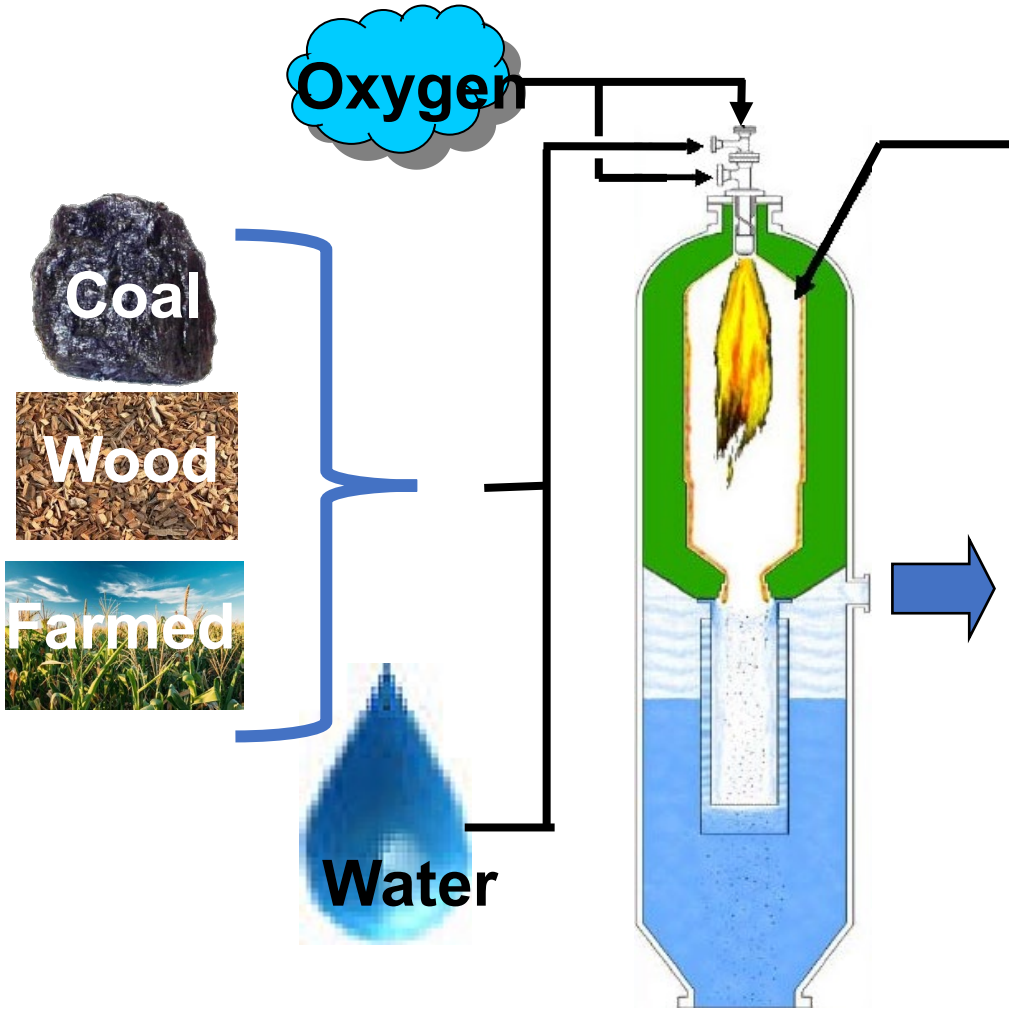
Gasification adds value to low- or negative-value feedstocks by converting them to marketable fuels and products.







Gasification is



Extreme Conditions:

- 500 psig or more
- 1700 to 2,600 Deg F
- Corrosive slag and H_2S gas

Products (syngas)

CO (Carbon Monoxide)

H_2 (Hydrogen)

[CO/H2 ratio can be adjusted]

By-products

H_2S (Hydrogen Sulfide)

CO_2 (Carbon Dioxide)

Slag (Minerals from Coal)

Gas Clean-Up Before Product Use

Key Definitions

- Town Gas: **a gaseous product manufactured from coal, containing approximately 50% hydrogen, with the rest comprised of mostly methane and carbon dioxide, with 3% to 6% carbon monoxide.**
- Synthesis Gas (Syngas): **mixture of hydrogen and carbon monoxide**
- Synthetic Natural Gas: **mixture mainly of methane made from syngas**
- Producer Gas: **partial oxidation of coke with humidified air.**
- Water Gas: **equal amounts of hydrogen and carbon monoxide**

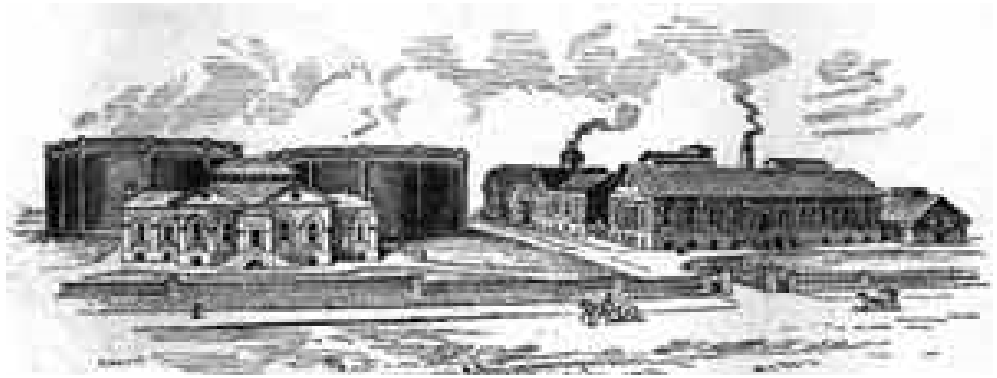
History of Gasification

Town gas, a gaseous product manufactured from coal, supplies lighting and heating for America and Europe.

Town gas is approximately 50% hydrogen, with the rest comprised of mostly methane and carbon dioxide, with 3% to 6% carbon monoxide.

First practical use of town gas in modern times was for street lighting

The first public street lighting with gas took place in Pall Mall, London on January 28, 1807



Baltimore, Maryland began the first commercial gas lighting of residences, streets, and businesses in 1816

History of Gasification

NATIONAL ENERGY TECHNOLOGY LABORATORY

Used during World War II to convert coal into transportation fuels (Fischer – Tropsch)

Used extensively in the last 50+ years to convert coal and heavy oil into hydrogen – for the production of ammonia/urea fertilizer

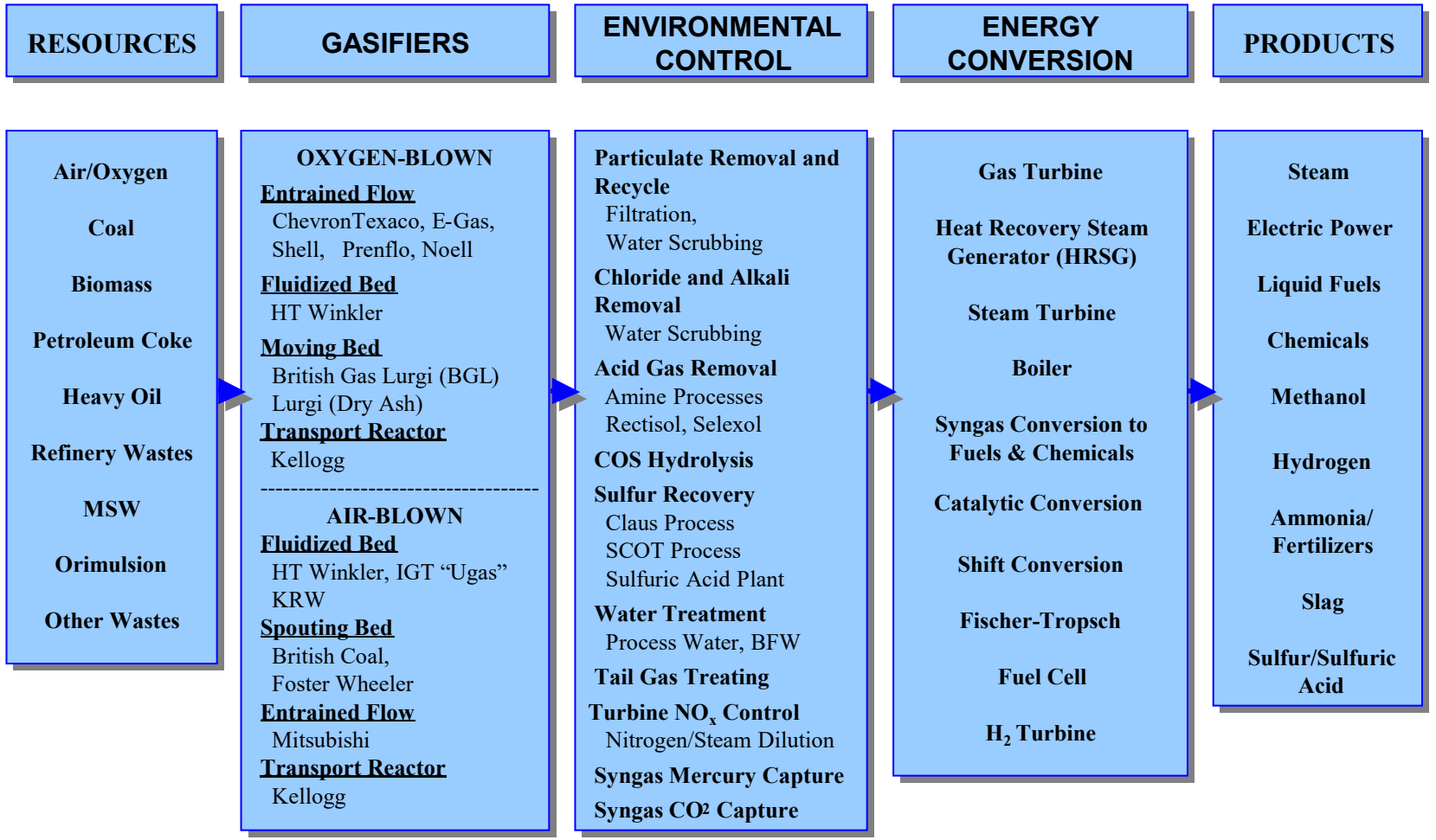
Chemical industry (1960's)

Refinery industry (1980's)

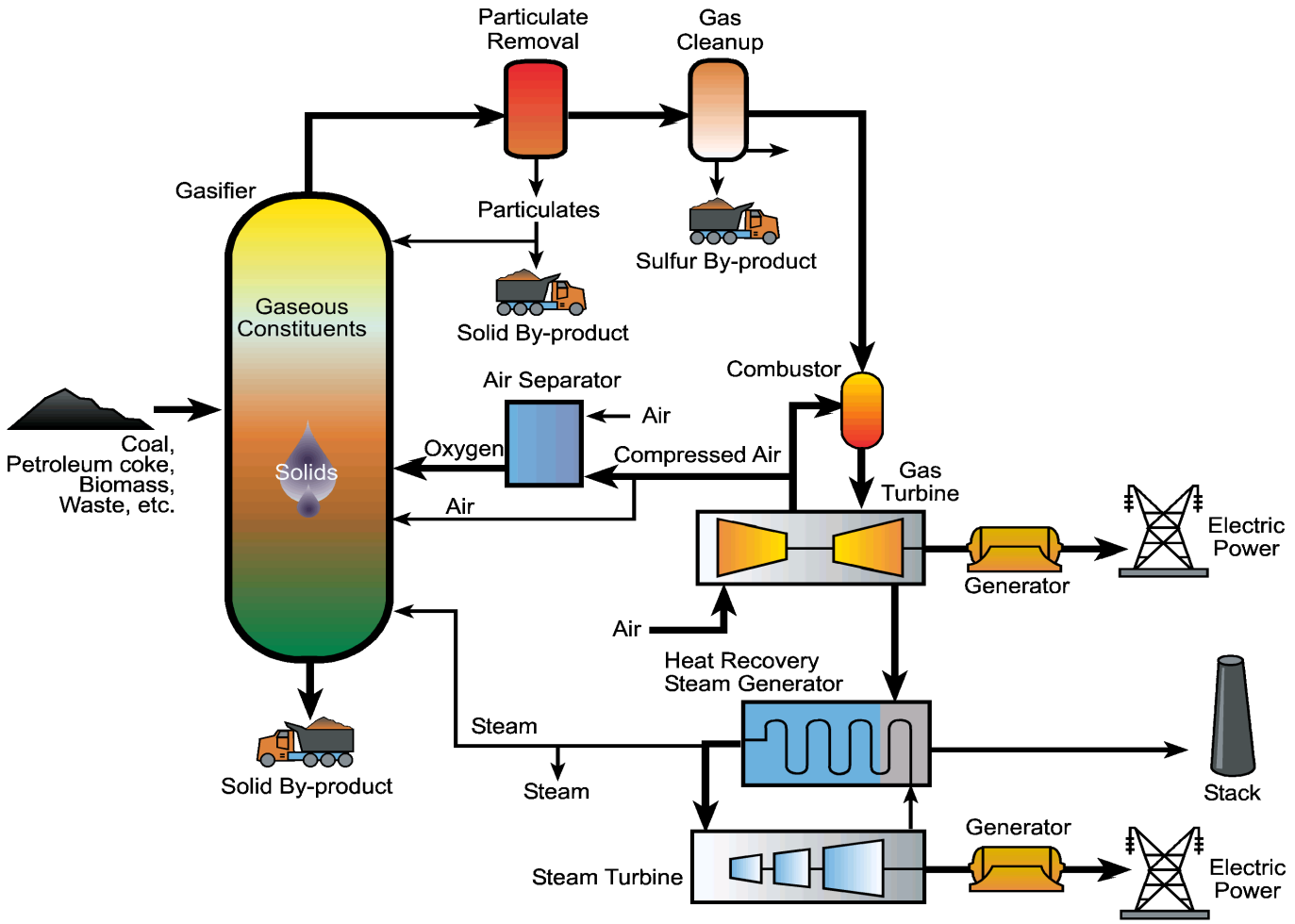
Global power industry (Today)



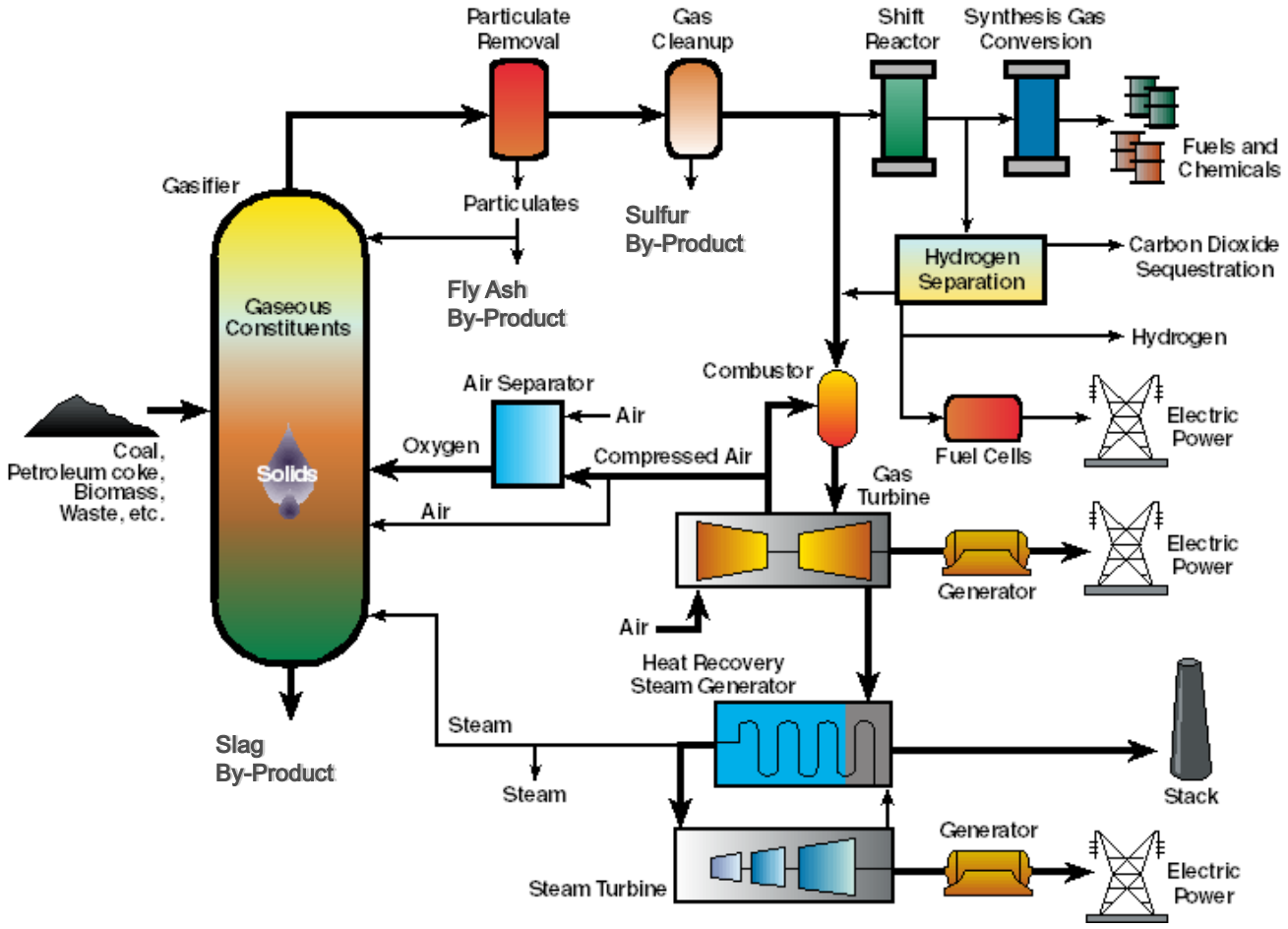
Gasification-Based Energy Conversion Systems



Integrated Gasification Combined Cycle (IGCC)



Gasification-Based Energy Production System Concepts



Gasification Chemistry











Gasification with Oxygen

$C + {}^1/_2\ O_2 \rightarrow CO$

$\Delta H = -3{,}922$ Btu/lb C

Combustion with Oxygen

$C + O_2 \rightarrow CO_2$

$\Delta H = -14{,}111$ Btu/lb C

Gasification with Carbon Dioxide

$C + CO_2 \rightarrow 2CO$

$\Delta H = 6267$ Btu/lb C

Gasification with Steam

$C + H_2O \rightarrow CO + H_2$

$\Delta H = 4750$ Btu/lb C

Gasification with Hydrogen

$C + 2H_2 \leftrightarrow CH_4$

$\Delta H = -2672$ Btu/lb C

Water-Gas Shift

$CO + H_2O \leftrightarrow H_2 + CO_2$

$\Delta H = -650$ Btu/lb CO

Methanation

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$

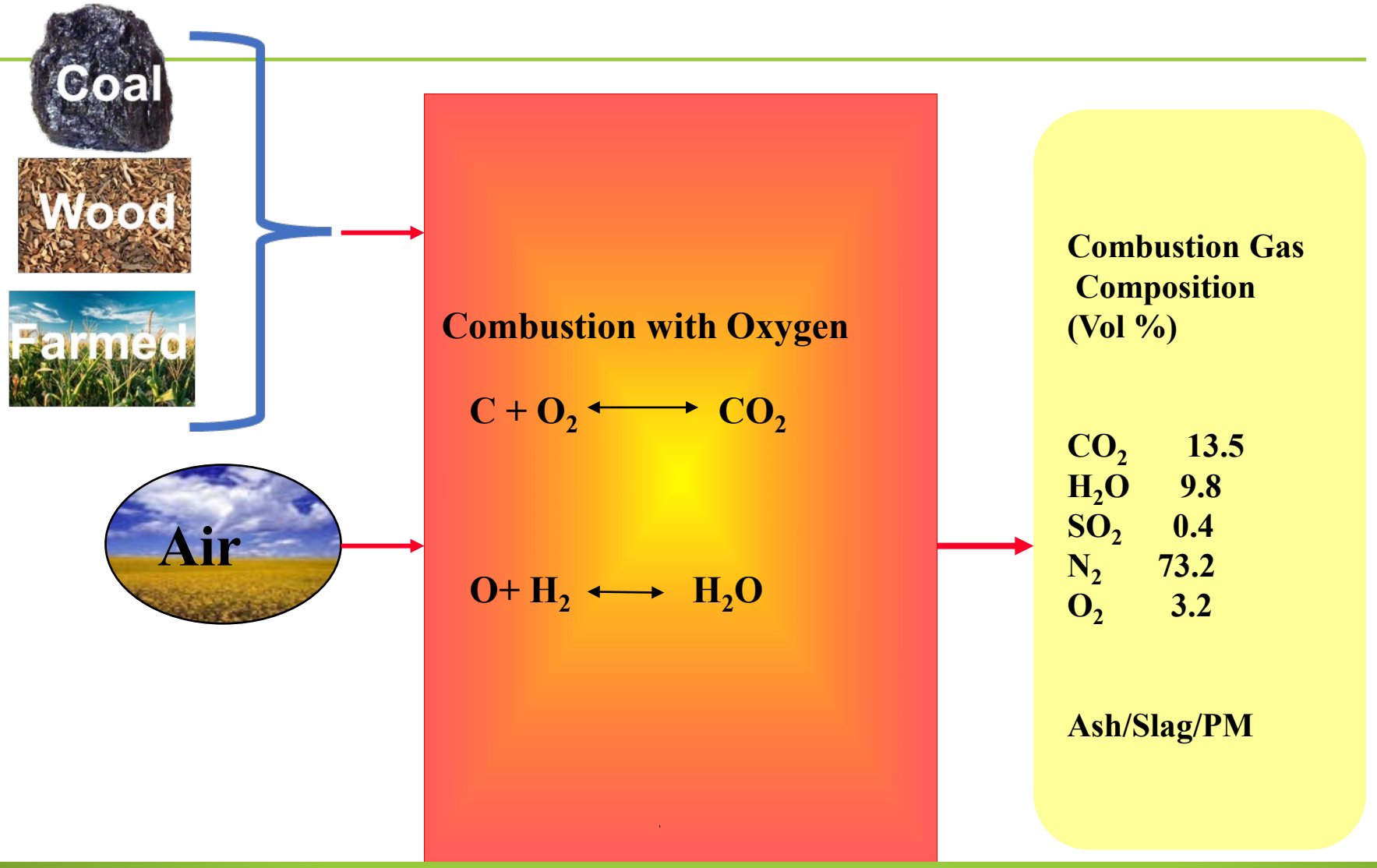
$\Delta H = -3181$ Btu/lb CO

Gasifier Gas Composition (Vol %)

H_2	25 - 30
CO	30 - 60
CO_2	5 - 15
H_2O	2 - 30
CH_4	0 - 5
H_2S	0.2 - 1
COS	0 - 0.1
N_2	0.5 - 4
Ar	0.2 - 1
NH_3 + HCN	0 -0.3

Ash/Slag/PM

Combustion Chemistry



Contrasts Between Combustion & Gasification

	Combustion	Gasification
chemical process	full oxidation	partial oxidation
chemical environment	excess oxygen (air) - oxidizing	oxygen-starved - reducing
primary product	heat (e.g., steam)	syngas (CO & H2)
"downstream" products	electric power	electric power, pure H2, liquid fuels, chemicals
current application	dominates coal-fired power generation worldwide	mostly chemicals and fuels, power generation demonstrated
efficiency	35-37% (HHV)	39 -42% HHV
emissions	~ NSPS	~ 1/10 NSPS
capital cost	$1000-1150/kW	competitive
maturity / risk	high experience, low risk	reliability needs improved

Environmental Contrasts

	Combustion	Gasification
sulfur converted to…	SO2	H2S
sulfur capture	flue gas scrubbers, boiler limestone injection	absorbed in physical solvents
sulfur disposal	gypsum sold for wallboard	sold as H2SO4 or elemental S
nitrogen converted to…	NOx	traces of NH3 in syngas (syngas combustion produces low levels of NOX)
NOx control	low-NOx burners, staged combustion, plus SCR/SNCR	low NOx combustors plus diluents
C is converted to…	Directly to CO2	CO in syngas
CO2 control	post-combustion removal from diluted stream (higher cost)	pre-combustion removal from concentrated stream

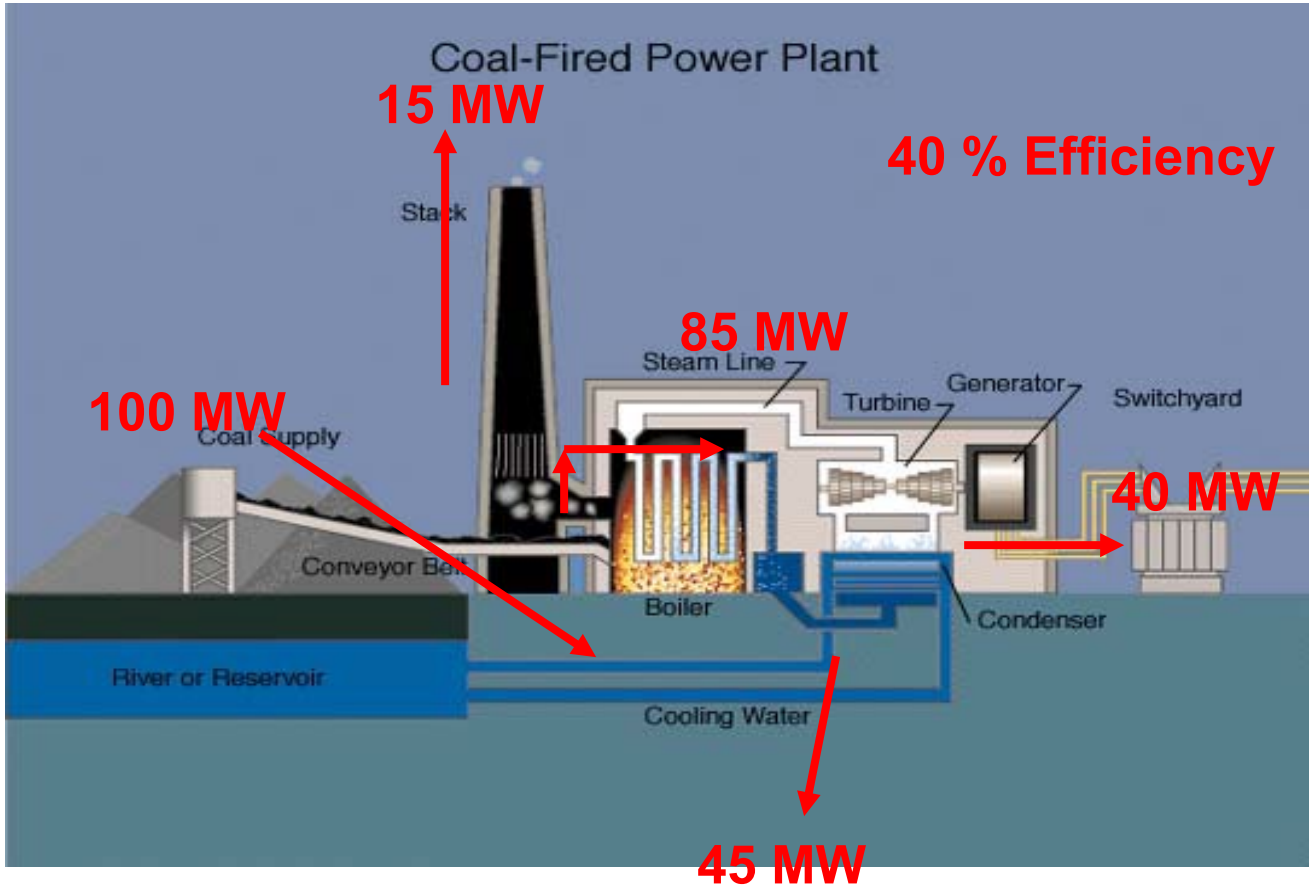
Fundamental Comparison of IGCC with Advanced PC-Fired Plant

	IGCC	PC
• Operating Principles	Partial oxidation	Full Oxidation
• Fuel Oxidant	Oxygen	Air
• Temperature	≤ 3000 F	≤ 3200 F
• Pressure	400-1000 psi	Atmospheric
• Sulfur Control	Concentrate gas	Dilute gas
• Nitrogen Control	Not needed	Pre/post combustion
• Ash Control	Low Vol slag	Fly/bottom ash
• Trace Elements	Slag Capture	ESP/Stack
• Wastes/Byproducts	Several Markets	Limited Markets
• Performance - eff. (%)	42-45	35-42

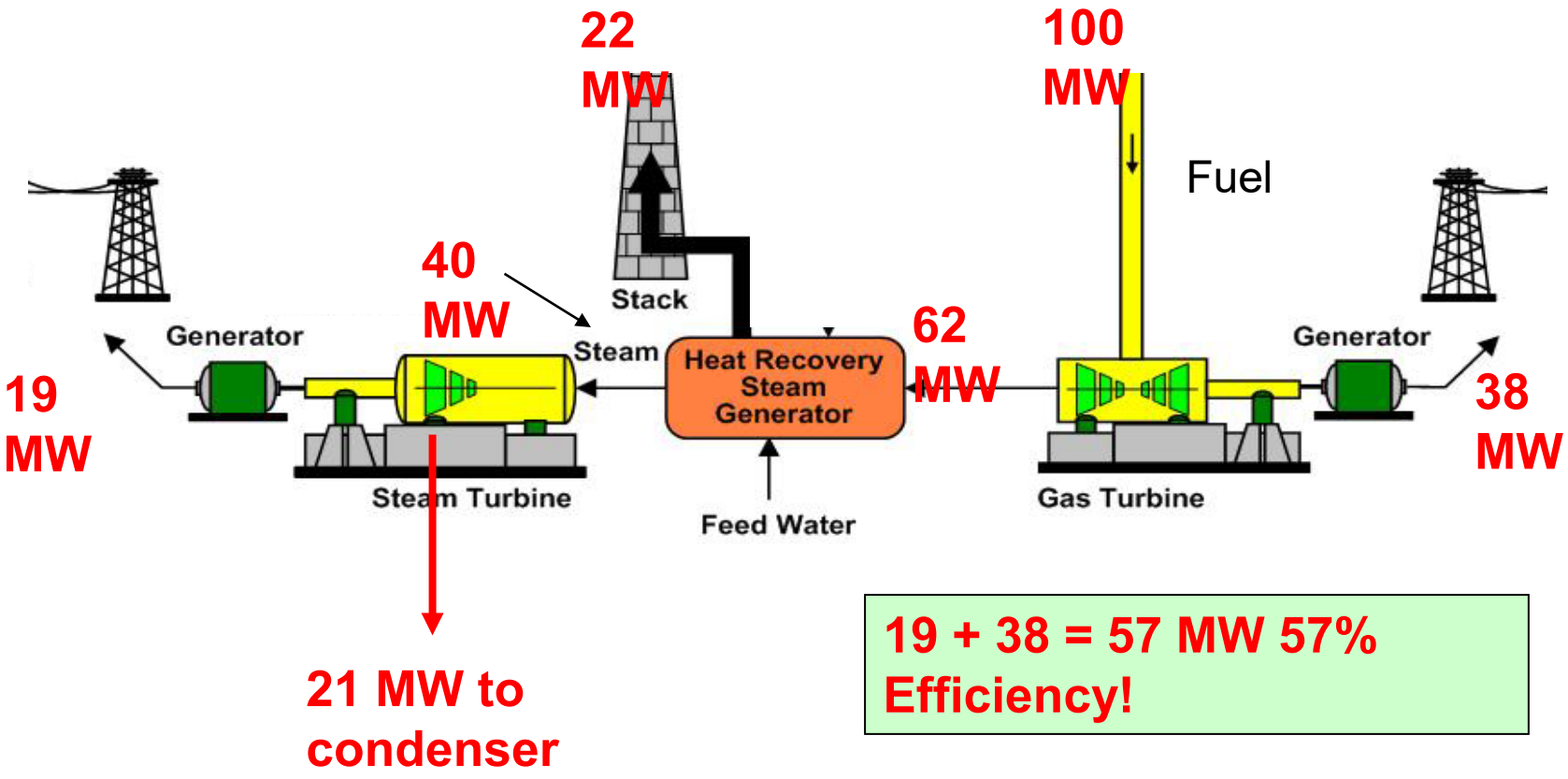
Comparison of Air Emission Controls: PC vs. IGCC

	SO_2	NOx	PM	Mercury
PC	FGD system	Low-NOx burners and SCR	ESP or baghouse	Inject activated carbon
IGCC	Amine system removes H_2S from syngas	Syngas saturation and N_2 diluent	Wet scrubber, high temperature cyclone, ceramic filter	Pre-sulfided activated carbon bed

Conventional Coal Plant
(Illustration only)



Natural Gas Combined Cycle (Illustration only)



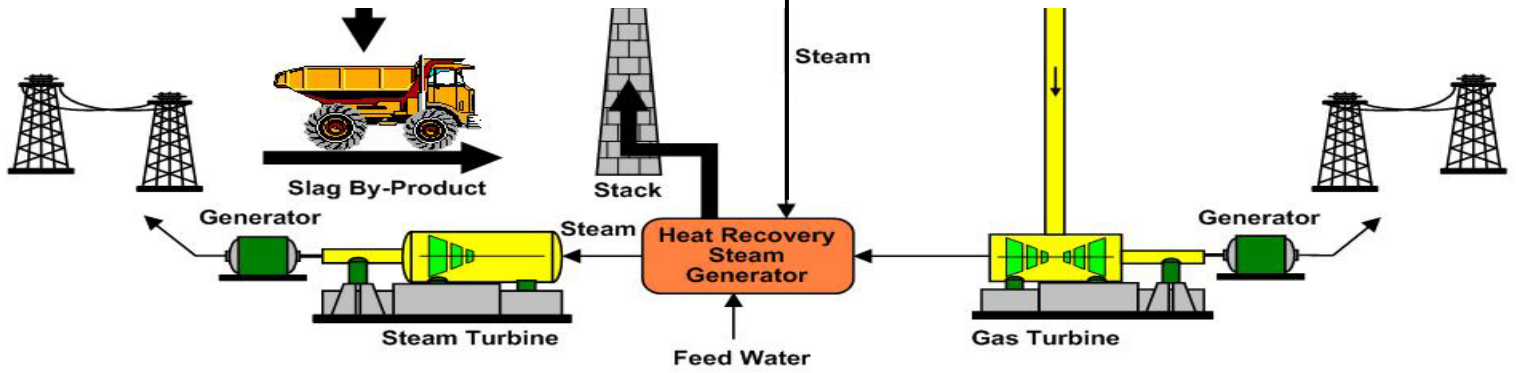
19 + 38 = 57 MW 57% Efficiency!

Coal-Based IGCC Power Plant

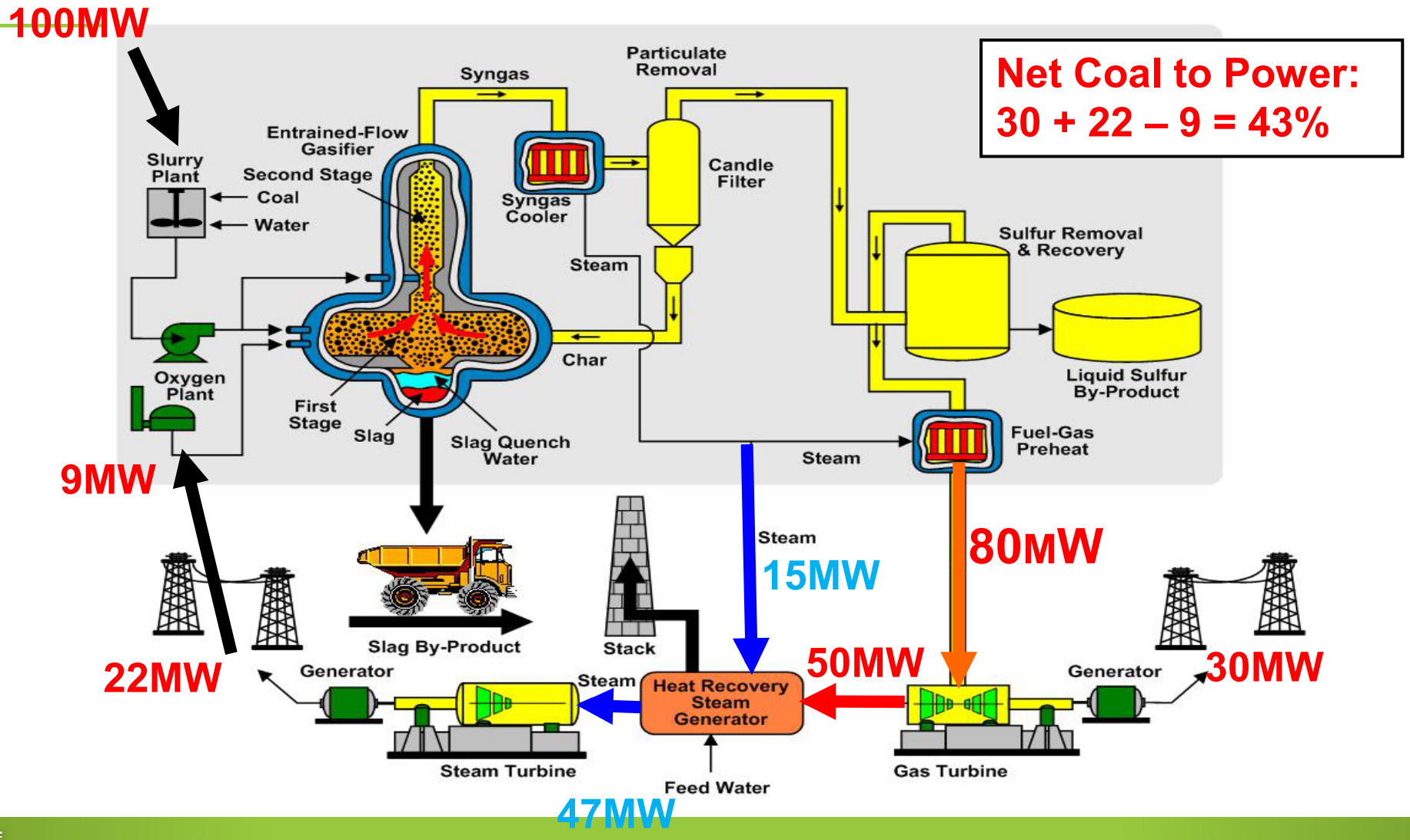
Gasification Island

- Converts coal to synthesis gas
- Synthesis gas cleaned and conditioned

Natural gas is replaced by coal-based fuel gas



Coal-Based IGCC Power Plant (Illustration only)



Gasifier Types

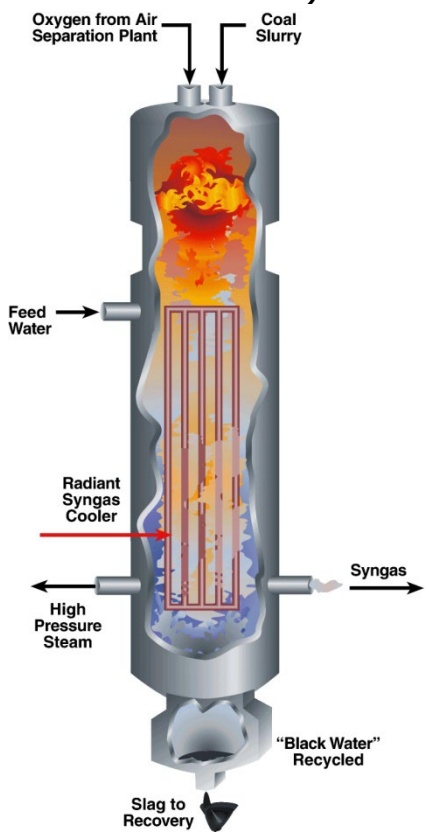
Flow Regime	Moving (or "Fixed") Bed	Fluidized	Entrained Flow	Transport
Combustion Analogy	grate fired combustors	fluidized bed combustors	pulverized coal combustors	Circulating fluidized bed combustors
Fuel Type	solids only	solids only	solids or liquids	solids only
Fuel Size	5 - 50 mm	0.5 - 5 mm	< 500 microns	0.5 - 5 mm
Residence Time	15 - 30 minutes	5 - 50 seconds	1 - 10 seconds	2 to 10 seconds
Oxidant	air- or oxygen-blown	air- or oxygen-blown	almost always oxygen-blown	air- or oxygen-blown
Gas Outlet Temp.	400 - 500 ºC	700 – 900 ºC	900 – 1400 ºC	700 – 900 ºC
Ash Handling	slagging and non-slagging	non-slagging	always slagging	non-slagging
Commercial Examples	Lurgi dry-ash (non-slagging), BGL (slagging)	IGT U-Gas, HT Winkler, KRW	GE (Texaco), Shell, Prenflo, E-Gas, Noell	KBR
Comments	"moving" beds are mechanically stirred, fixed beds are not	bed temperature below ash fusion point to prevent agglomeration	not preferred for high-ash fuels due to energy penalty of ash-melting	bed temperature below ash fusion point to prevent agglomeration
	gas and solid flows are always countercurrent in moving bed gasifiers	preferred for high-ash feedstocks and waste fuels	unsuitable for fuels that are hard to atomize or pulverize	preferred for low rank feedstocks and waste fuels

Gasifiers

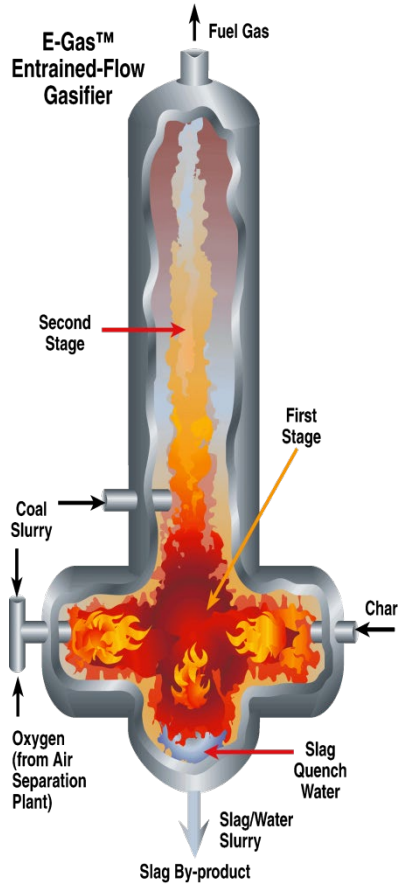
Air Products

(GE Energy &

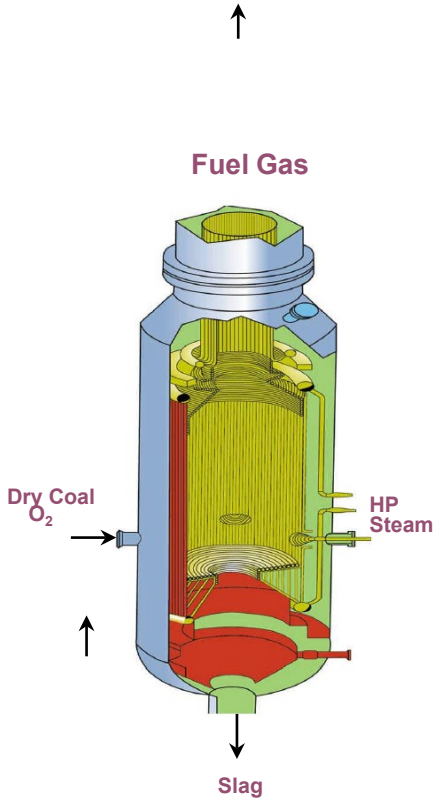
Chevron-Texaco)



ConocoPhillips E-Gas

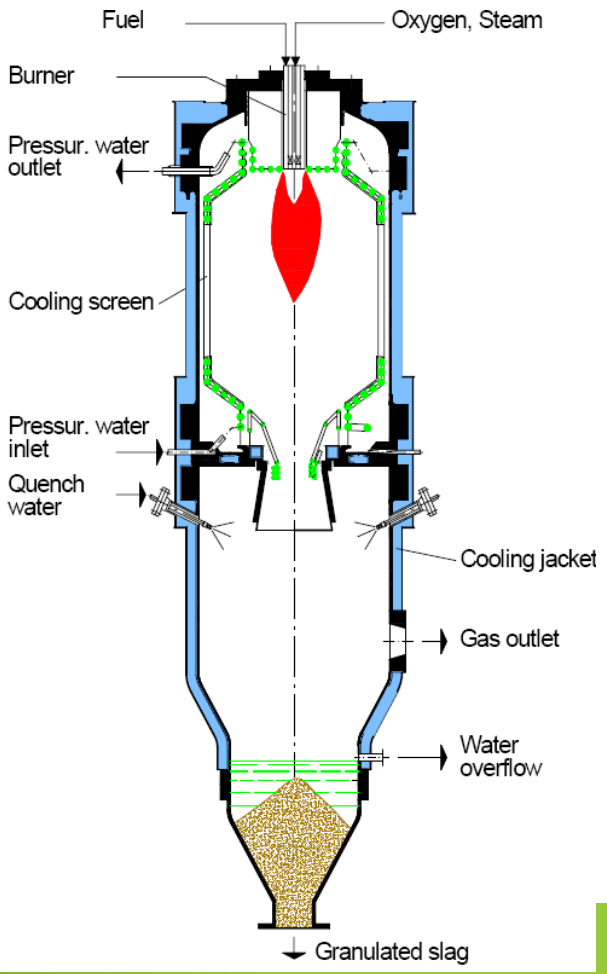


Shell SCGP

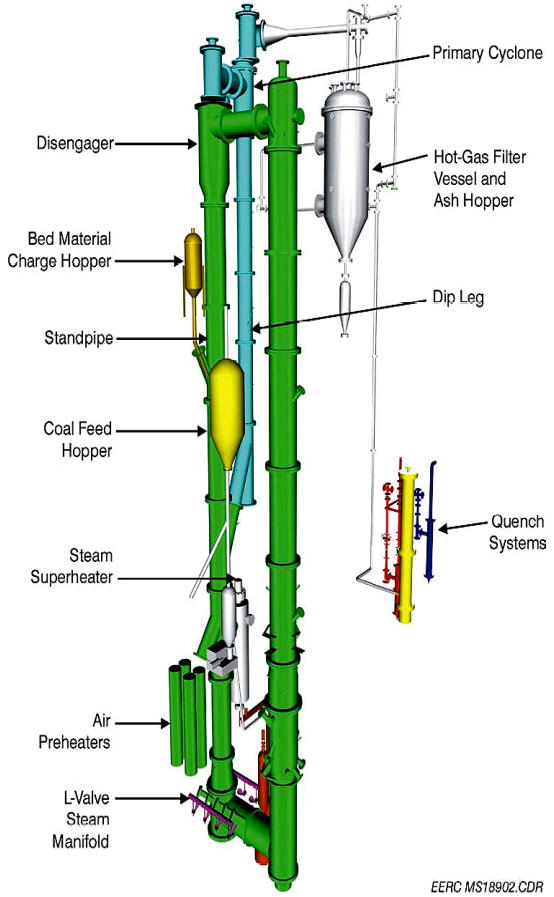


Gasifiers (continued)

Siemens *(GSP/Noell)*

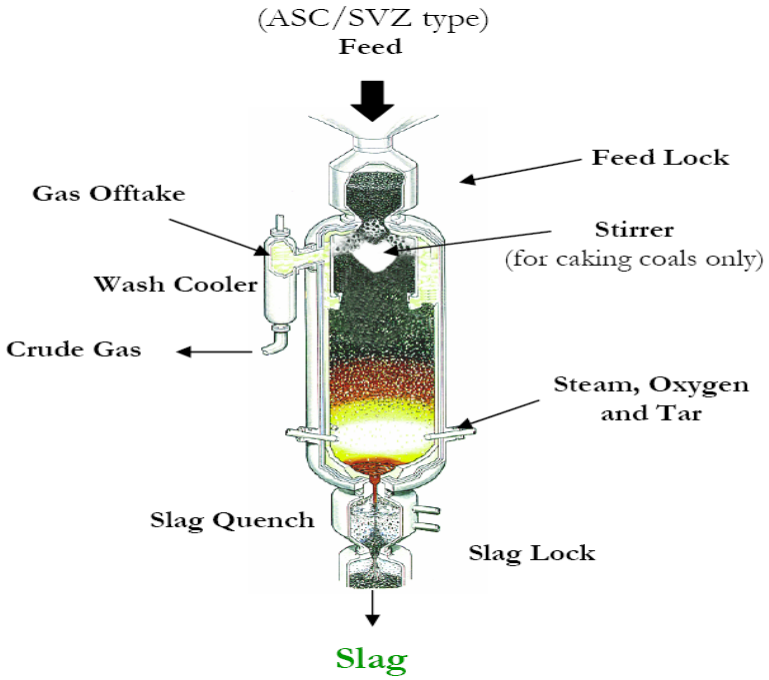


KBR Transport

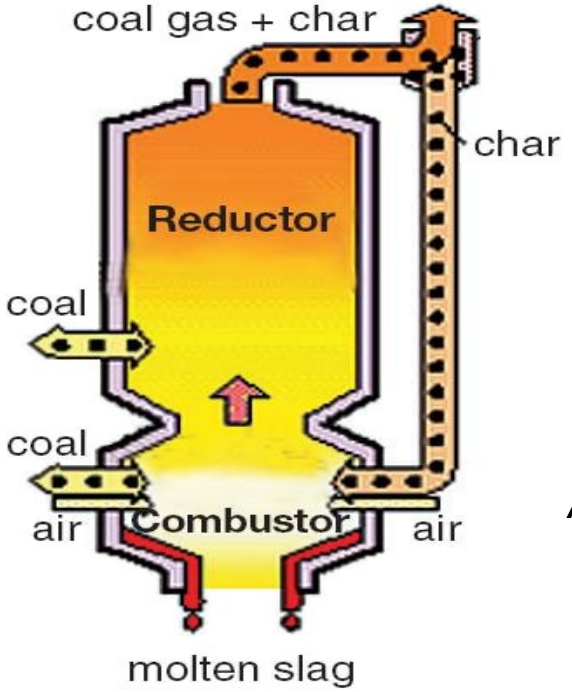


Gasifiers (continued)

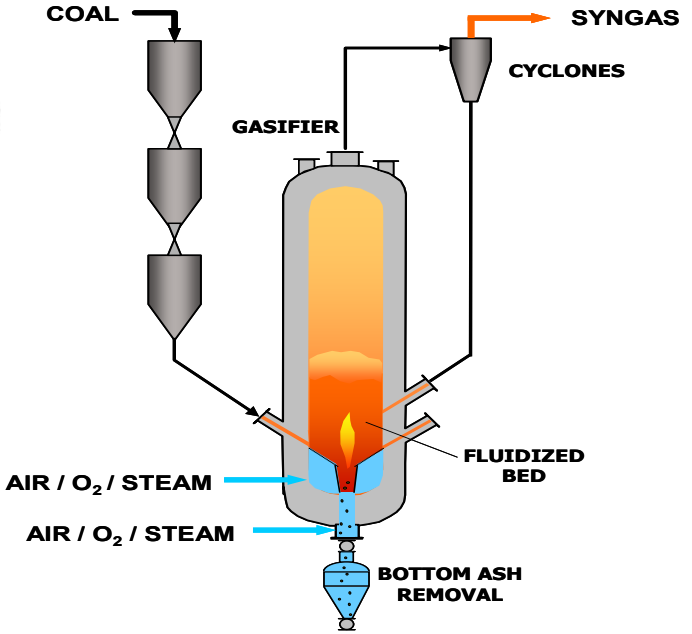
BGL



MHI

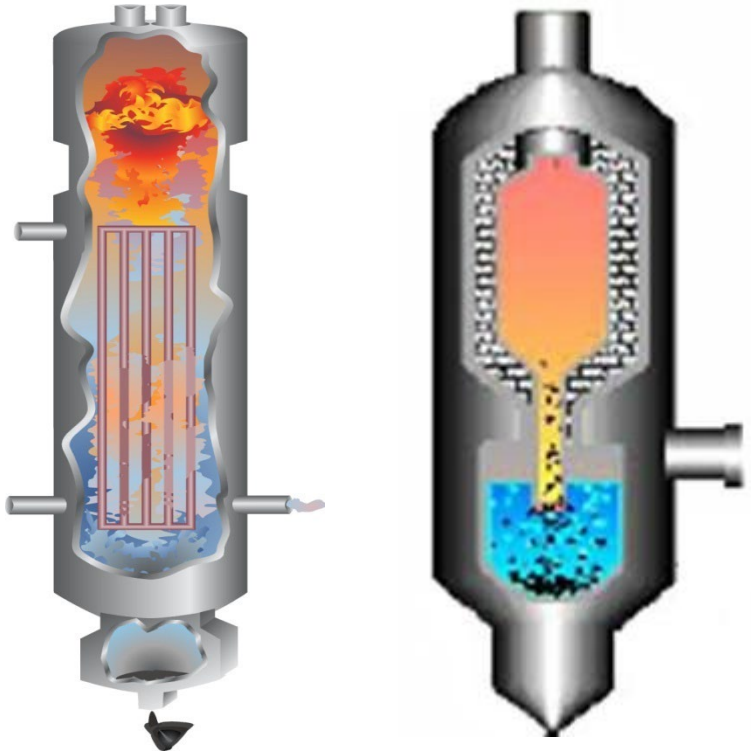


U-Gas



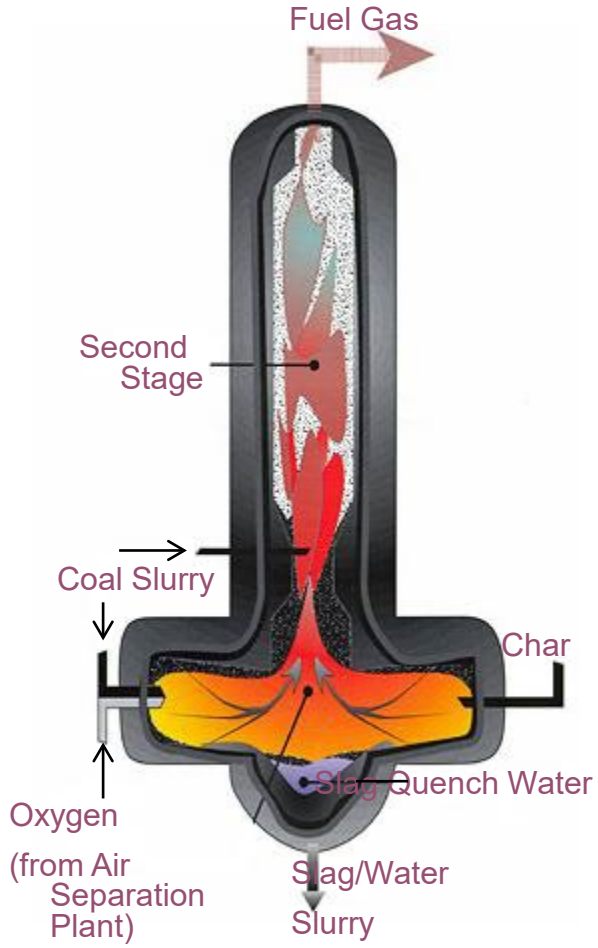
Air Products Gasifier (Formerly: GE, Chevron, Texaco)

- Coal-water slurry feed
- Entrained-flow
- Oxygen-blown
- Refractory-lined gasifier
- Two versions offered
  - Gasifier with radiant cooler
  - Quench gasifier
- Slagging
- Good for bituminous coal, pet coke, or blends of pet coke/low-rank coals
- 64 Plants operating – 15,000 MWth Syngas (2010)



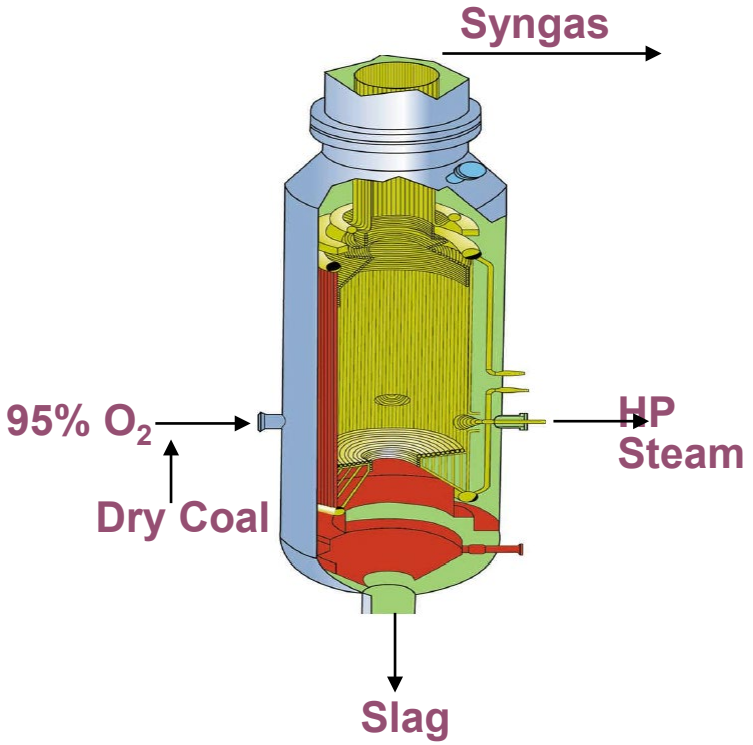
ConocoPhillips (E-Gas) Gasifier

- Two-stage gasifier
  - 80% of feed to first stage (lower)
  - Advanced E-STR gasifier feeds 100% to second stage (upper)
- Coal-water slurry feed
- Oxygen-blown
- Refractory-lined gasifier
- Continuous slag removal system, dry particulate removal
- Good for a wide range of coals, from pet coke to PRB to Bituminous and blends



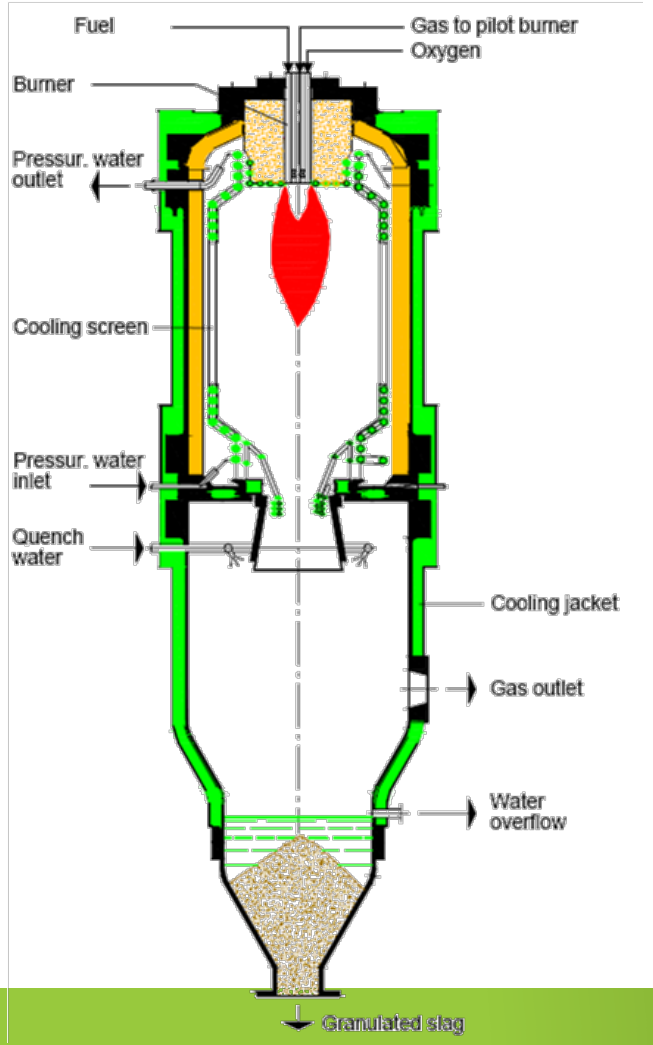
Shell Gasifier

- Dry feed (coal is crushed and dried and then fed into gasifier)
- Oxygen-blown
- Waterwall in gasifier
- Good for wide variety of feedstocks, from pet coke to low-rank coals
- Shell provides gasification technology
- 26 (2012) Plants operating – 8,500 MWth Syngas



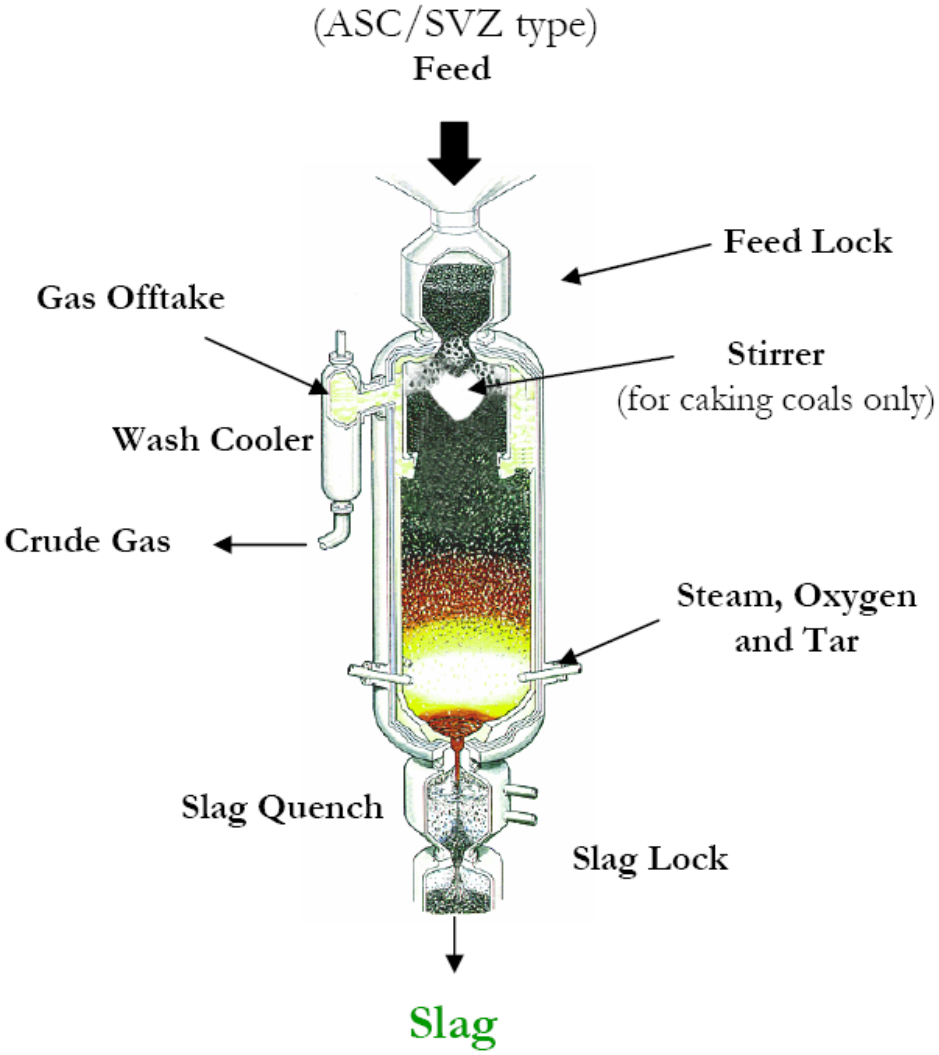
Siemens (FutureEnergy) Gasifier

- Dry feed
- Oxygen-blown
- Top fired reactor
- Waterwall screen in gasifier
- Good for a wide variety of feedstocks, from bituminous to low-rank coals



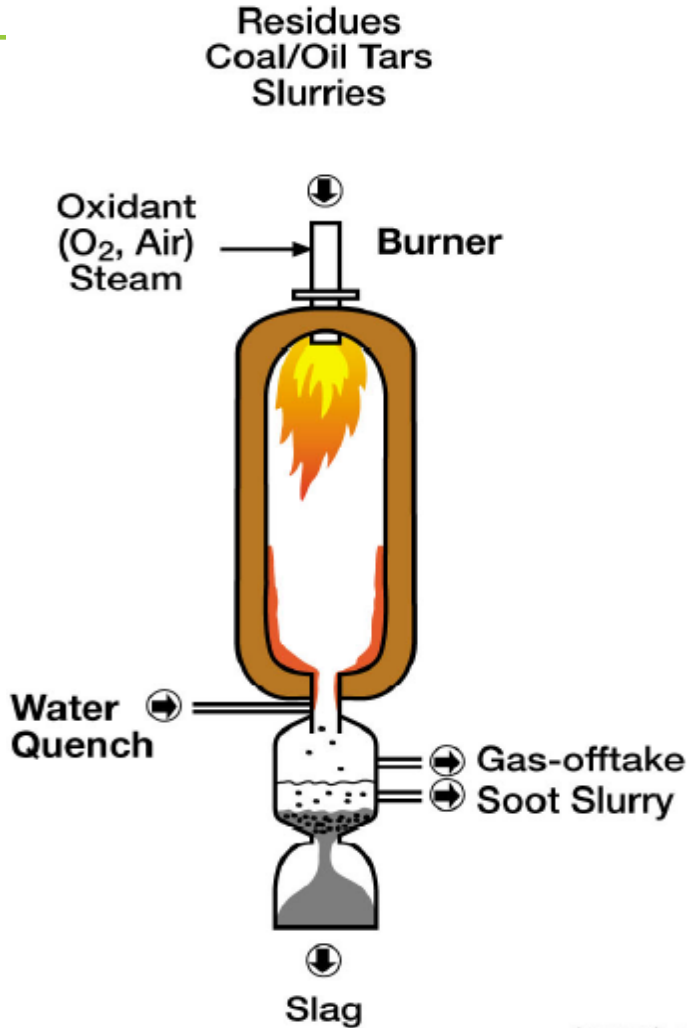
British Gas/ Lurgi (BGL) Gasifier

- "Slagging" version of Lurgi
- Dry feed
- Oxygen-blown
- Refractory-lined gasifier
- Good for wide range of coals
- Opportunity fuel blends
  - RDF, tires, wood waste
- Modular design
- Allied Syngas build, own and operate in North American
- Demonstration plant
  - Westfield 1986 – 1990
  - 500 TPD
- 1st Commercial plant Schwarze Pumpe
  - operated 2000 -2005
  - BGL-1000



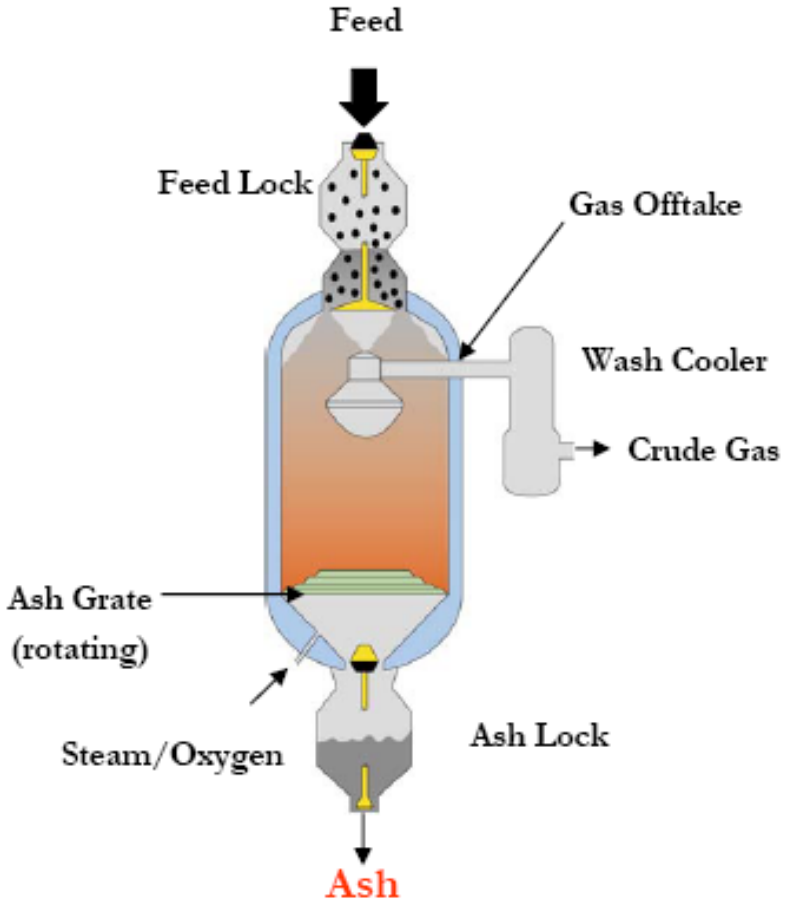
Multi Purpose (MPG) Gasifier

- Oxygen-blown
- Good for wide range of feedstocks
  - Petcoke/ coal slurries and waste
- Quench configuration for coal/petcoke feedstock
- MPG technology developed from Lurgi's fixed-bed gasification process
- "Reference plant"
  - Schwarze Pumpe in operation since 1968



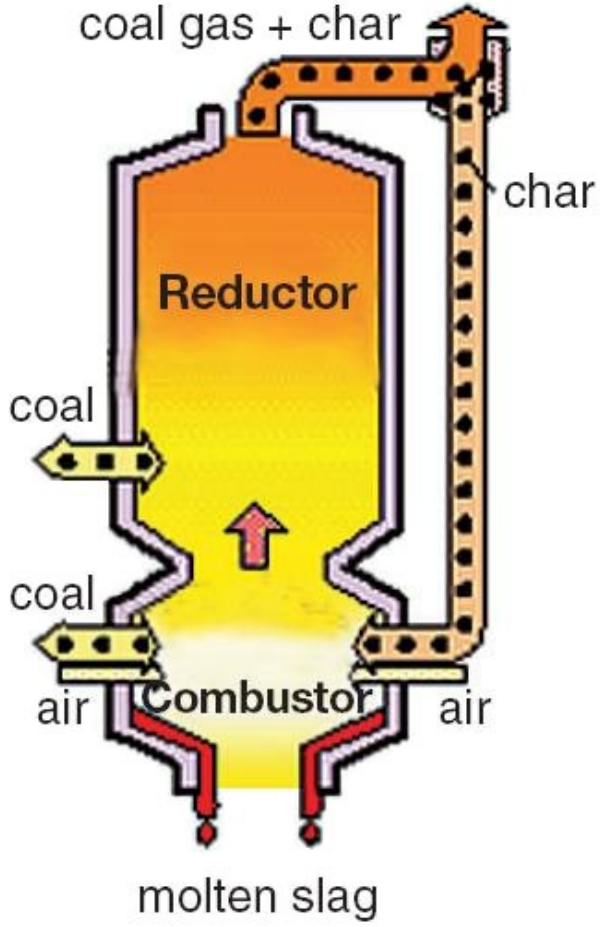
Lurgi Mark IV Gasifier

- Extension of the proven Lurgi gasifier
  - Lock hoppers
  - Quench cooler
- Dry feed system
  - Distributor
- Dry bottom ash
- Extensive experience with low rank coals
- North Dakota/Sasol type
- 8 Plants operating – 18,600 MWth Syngas



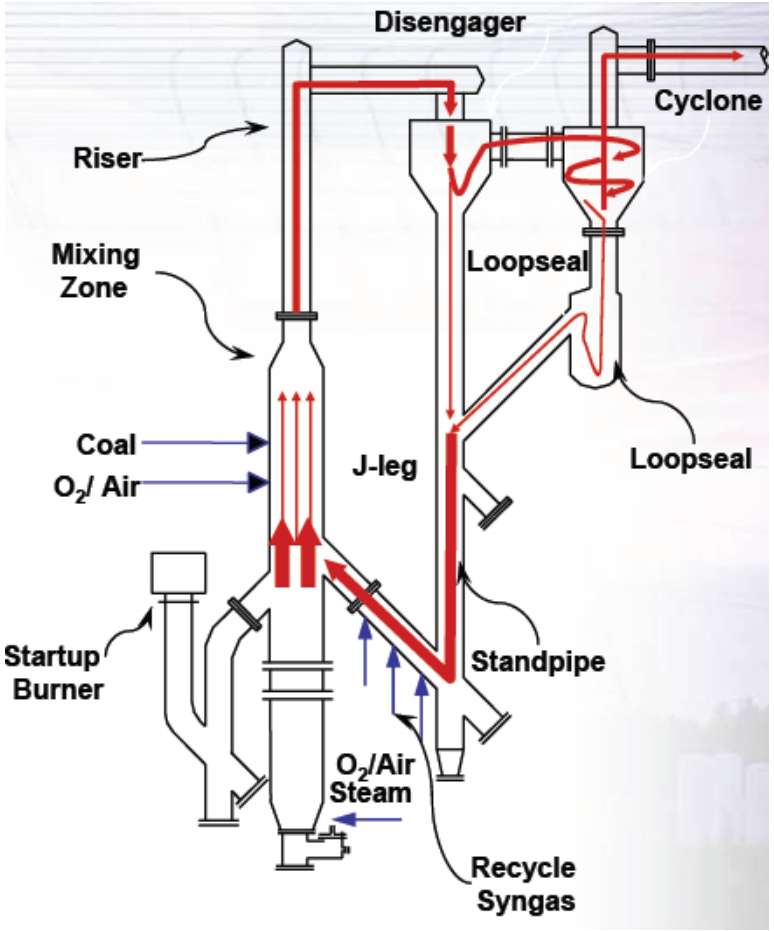
Mitsubishi Gasifier

- Dry feed system, suitable for low rank coal with high moisture content
- Two-Stage feeding
- Entrained bed
- Air Blown
- Membrane Waterwall
- Slagging
- Developed by CE (ALSTOM) under DOE Funding



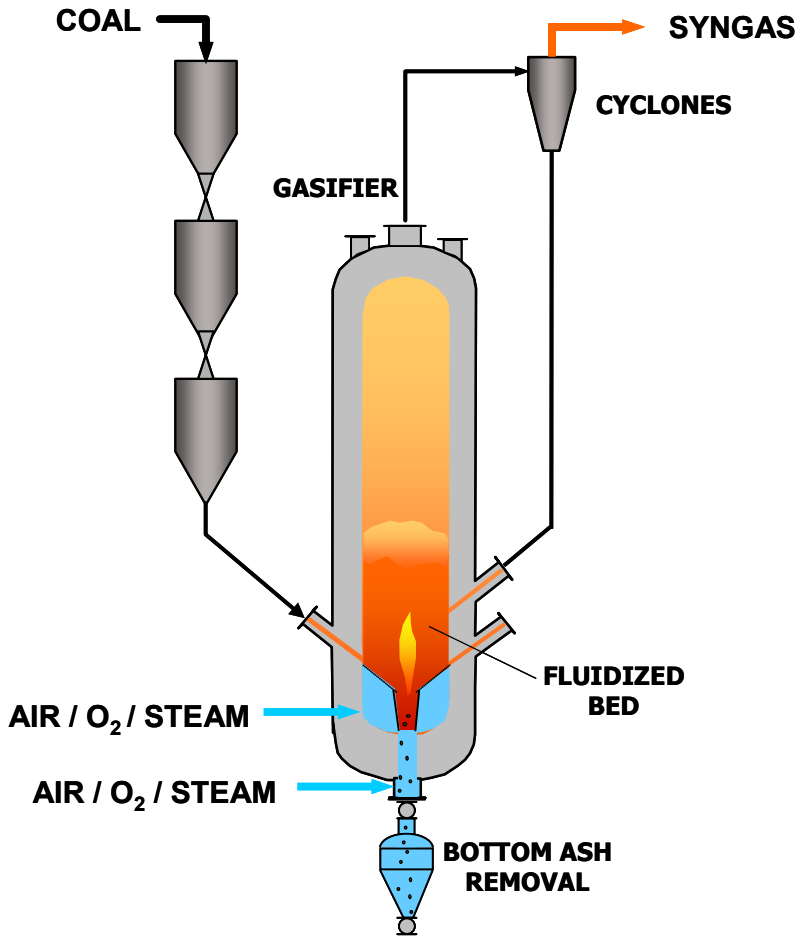
Kellogg Brown & Root (KBR) Gasifier
Transport Gasifier

- Oxygen or air-blown
  - Air blown for power generation
  - Oxygen for liquid fuels and chemicals
- High reliability design
  - Non-slagging
  - No burners
  - Coarse, dry coal feed



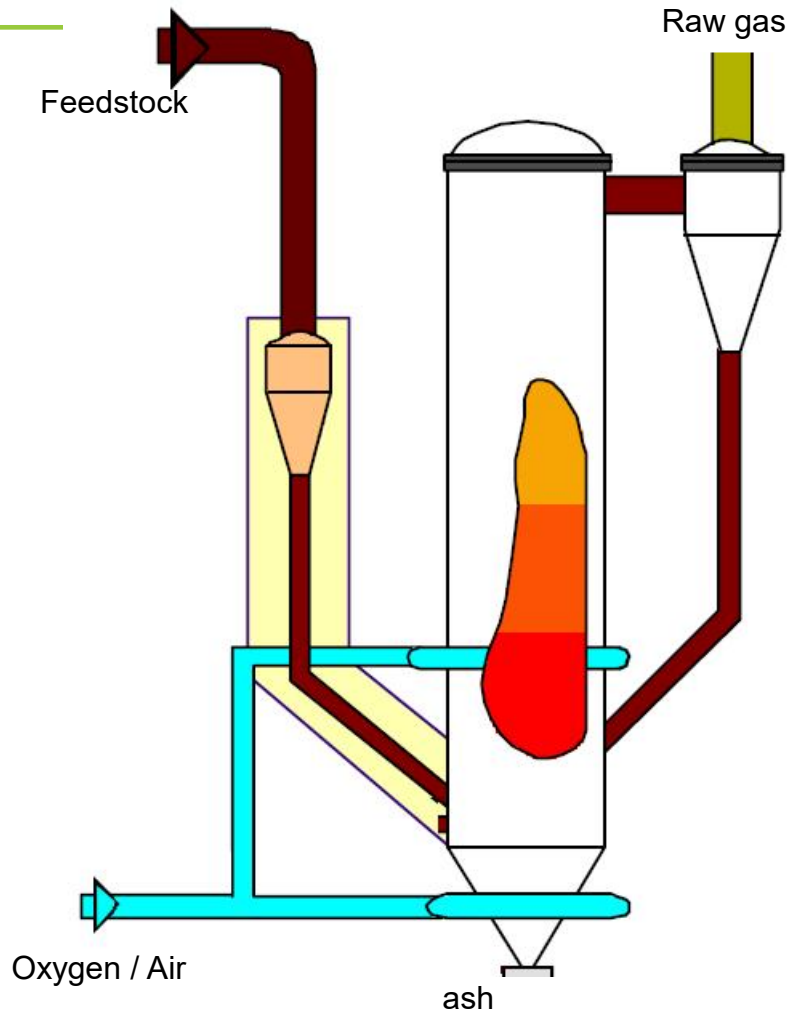
GTI (U-Gas) Gasifier

- Fluidized bed gasifier
- Dry feed system
- Coals and coal / biomass blends
- Highly efficient
- Air or oxygen blown
- Non-slagging/bottom ash
- 30 year license agreement w/ Synthesis Energy Systems (SES)
- 20+ years experience including plants in Shanghai, Finland & Hawaii
- 2 Plants (2012) in operation
  - 520 MWth Syngas



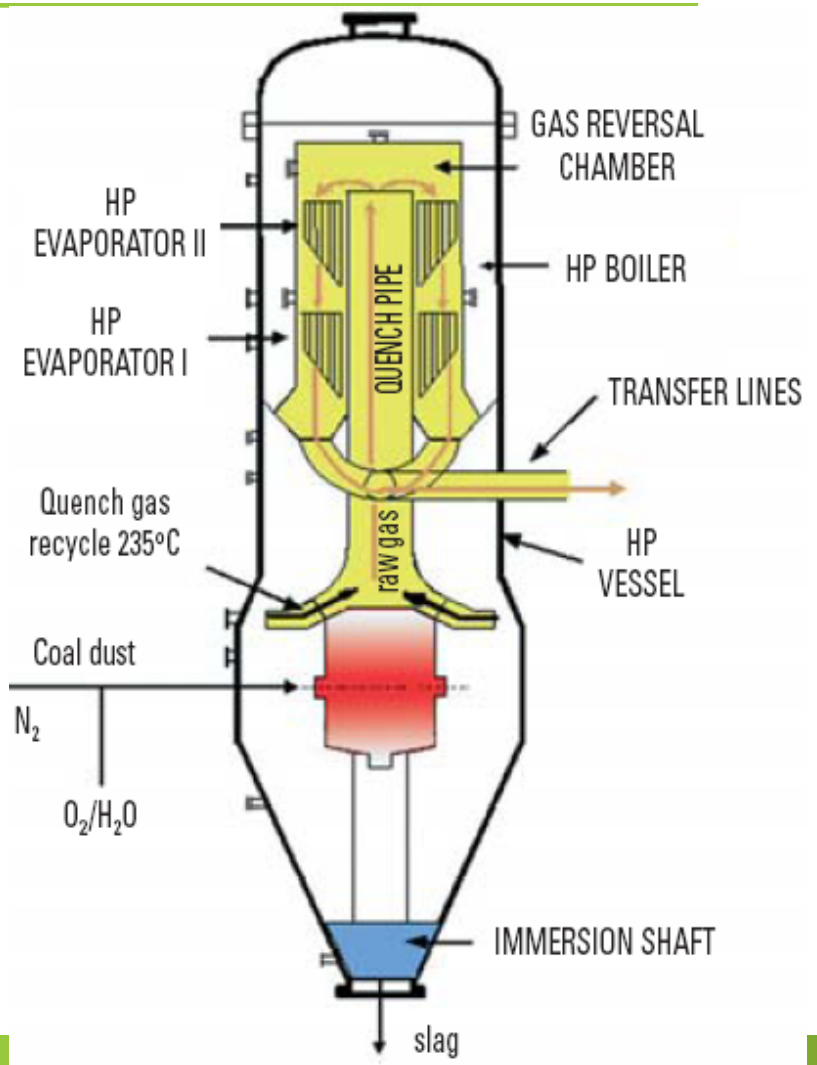
High Temperature Winkler Gasifier

- Fluidized bed gasifier
- Dry feed
- Oxygen or air-blown
- Dry bottom ash
- Developed to utilize lignite coal
- Capable of efficiently gasifying a broad range of feedstock
- R&D complete



PRENFLO™ Gasifier/Boiler (PSG)

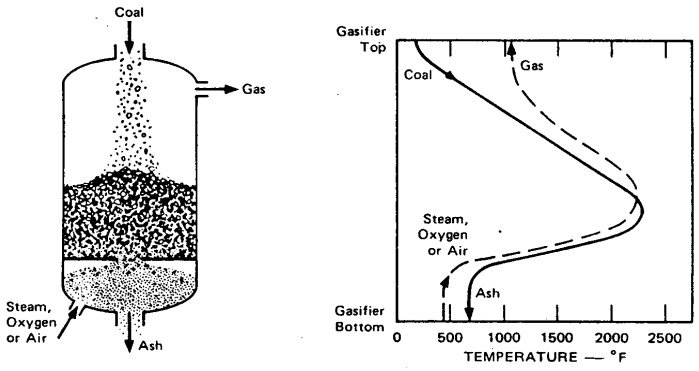
- Pressurized entrained flow gasifier with steam generation
- Uhde
- Oxygen blown
- Dry feed system
- Membrane wall
- Waste heat boiler
- Able to gasify a wide variety of solid fuels
  - hard coal, lignite, anthracite, refinery residues, etc.
- Demonstration plant Fürstenhausen, Germany
  - 48 TPD
- Used in world's largest solid-feedstock-based IGCC plant in Puertollano, Spain



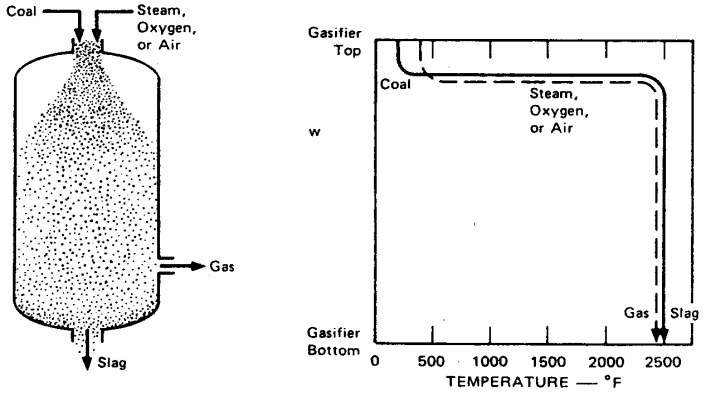
"Integrated Gasification Combined Cycle Technology: IGCC It's Actual Application in Spain: ELCOGAS, Puertollano. Manuel Treviño Coca

Summary Gasifier Configurations

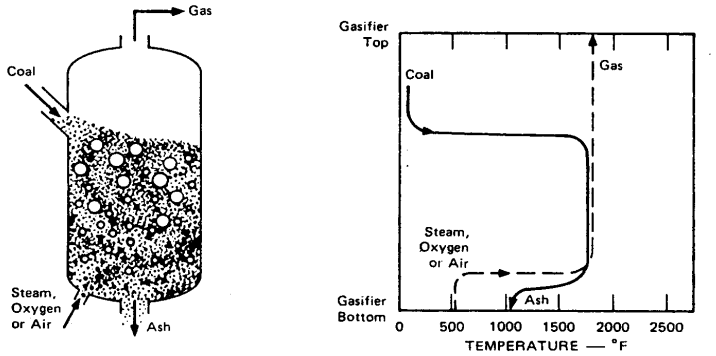
Moving Bed



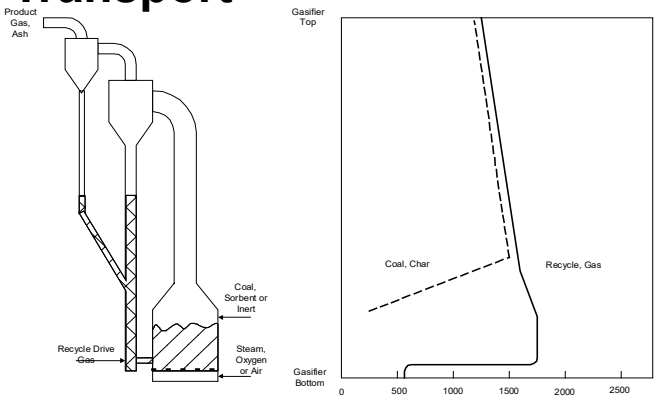
Entrained Flow



Fluidized Bed



Transport



Comparison of Gasifier Characteristics

	Moving Bed		Fluidized Bed		Entrained Flow	Transport Flow
Ash Cond.	Dry	Slagging	Dry	Agglomerate	Slagging	Dry
Coal Feed	~2in	~2in	~1/4 in	~1/4 in	~ 100 Mesh	~1/16in
Fines	Limited	Better than dry ash	Good	Better	Unlimited	Better
Coal Rank	Low	High	Low	Any	Any	Any
Gas Temp. (°F)	800-1,200	800-1,200	1,700-1,900	1,700-1,900	>2,300	1,500-1,900
Oxidant Req.	Low	Low	Moderate	Moderate	High	Moderate
Steam Req.	High	Low	Moderate	Moderate	Low	Moderate
Issues	Fines and Hydrocarbon liquids		Carbon Conversion		Raw gas cooling	Control carbon inventory and carryover

BIOMASS AND MUNICIPAL SOLID WASTE (MSW) GASIFICATION

- **The gasification of biomass and municipal solid waste (MSW) differ in many ways from the gasification of coal, petcoke, or conversion of natural gas to syngas.**
- **These next few slides will discuss these differences, the technology used to gasify biomass and MSW, and give a brief overview of some operating plants.**
- **Characteristics of Biomass and MSW**
  - While the gasification technologies used with biomass or MSW are straightforward, performance depends greatly on the unique characteristics of the biomass or MSW feedstock.
  - These feedstocks have much higher moisture content and less heating value by volume than coal.
  - In addition, the non-uniformity of the feedstocks and the variability of the specific compositions over time require flexible and robust gasifiers.

Gasifiers for Biomass

- **A 2002 NETL study on biomass and MSW gasifiers analyzed published information about demonstration and operating biomass gasifiers. Operating conditions, syngas composition, other required systems, and other parameters were compared to the optimum conditions for electricity, fuel, chemicals, and hydrogen production to determine which gasifier technologies best fit a certain product application. The work identified potential gasifier types:**
  - ***Bubbling Fluidized-Bed (BFB) gasifiers*,**
  - ***Circulating Fluidized-Bed (CFB) gasifiers*,**
  - ***Fixed-Bed (FB) gasifiers***
  - ***Indirectly Heated gasifiers*, which can be entrained, fluidized, or circulating fluidized bed gasifiers,**

- **Example of Biomass and MSW Gasification Facilities**
  - **Burlington, VT –In August 2000, a 12-MW, low-pressure wood gasifier was added to the existing McNeil Generating Station. The gasifier uses 200 tons per day (tpd) of wood chips, producing syngas that is fed into the plant's existing boiler (EIA article on the EIA Biomass for Electricity Generation Web Page).**

BFB Gasifier for Biomass

- A type of **fluidized bed gasifier** generally characterized by larger cross-section, shorter height, lower fluidization velocities and denser beds, are the most demonstrated of the biomass gasification technologies reviewed.
- The BFB technology has been operated over a wide range of temperatures, pressures, throughput, and a variety of biomass types.
- Fuel, chemicals, and hydrogen production benefits from high temperatures, like those seen in coal gasification, because at temperatures over 1,200-1,300°C little or no tar, methane, or higher hydrocarbons are formed, while syngas (hydrogen [H_2] and carbon monoxide [CO]) production is maximized.
- Several BFB gasifiers have been operated at the high pressures (>20 bar) that would be advantageous for fuel and chemical synthesis.
- While this eliminates the need for a compressor following the gasifier, it does necessitate a more complex feed system.
- BFBs may require the feed to be chopped, pulverized, or otherwise reduced in size, and would most likely need to be dried or torrefied to allow for the higher operating temperatures.
- The choice of oxidant—some combination of air, oxygen, and/or steam—has a substantial effect on the output syngas composition.
    - Air introduces nitrogen, which dilutes the product gas and is detrimental to synthesis processes.
    - For this reason, an oxygen plant is usually required. Varying steam to oxygen ratio input is a way to adjust the H2/CO ratio in order to match synthesis requirements.
        - For example, Fischer-Tropsch transportation fuel synthesis using iron catalysts requires an H2/CO ratio of around 0.6, optimally, while for cobalt catalyst a ratio of 2 would be preferred.
        - Methanol production would be favored with an H2/CO ratio of around 2 and for hydrogen production it should be as high as possible.
        - If higher temperatures cannot be achieved inside the BFB gasifier, tar cracking might be required. Typically, though, this is not the case and therefore gas cleanup is somewhat minimal for synthesis applications.
        - The study finds that BFB gasifiers are among the lowest capital cost options for biomass gasification and, all things considered, BFB gasifiers are quite suitable for fuels, chemicals, and hydrogen production.

CFB Gasifier for Biomass

- *Circulating Fluidized-Bed (CFB) gasifiers*, generally characterized by smaller cross-section, taller height, and higher fluidization velocities, have not been demonstrated with biomass to the extent of BFB.
- In fact, the literature surveyed showed very few tests at elevated pressure and all with temperatures below 1000°C.
- While Bubbling Fluidized-Bed gasifiers have been tested (at the time of the article) up to 35 bar, CFBs have only been tested up to 19 bar.
- Like BFB gasification, particle sizes would need to be reduced and feedstock dried.
- Probably the biggest issue with CFB is the lack of demonstrations with pure oxygen and/or steam, which greatly limits the confidence in the technology for synthesis applications.
- From the information available, carbon dioxide (CO_2) levels in the syngas are low, as are H_2/CO ratios, because the lack of steam means the water-gas-shift reaction is suppressed.

Fixed Bed Gasifiers for Biomass

- ***Fixed-Bed (FB) gasifiers*** **have not been demonstrated over a large range with biomass.**
- **This gasifier design tends to produce large quantities of either tar or unconverted char and therefore have not been extensively pursued.**
- **However, they are able to handle heterogeneous feedstock like MSW and so have a use for waste-to-fuel or waste-to-power.**

Indirectly Heated Gasifiers for Biomass

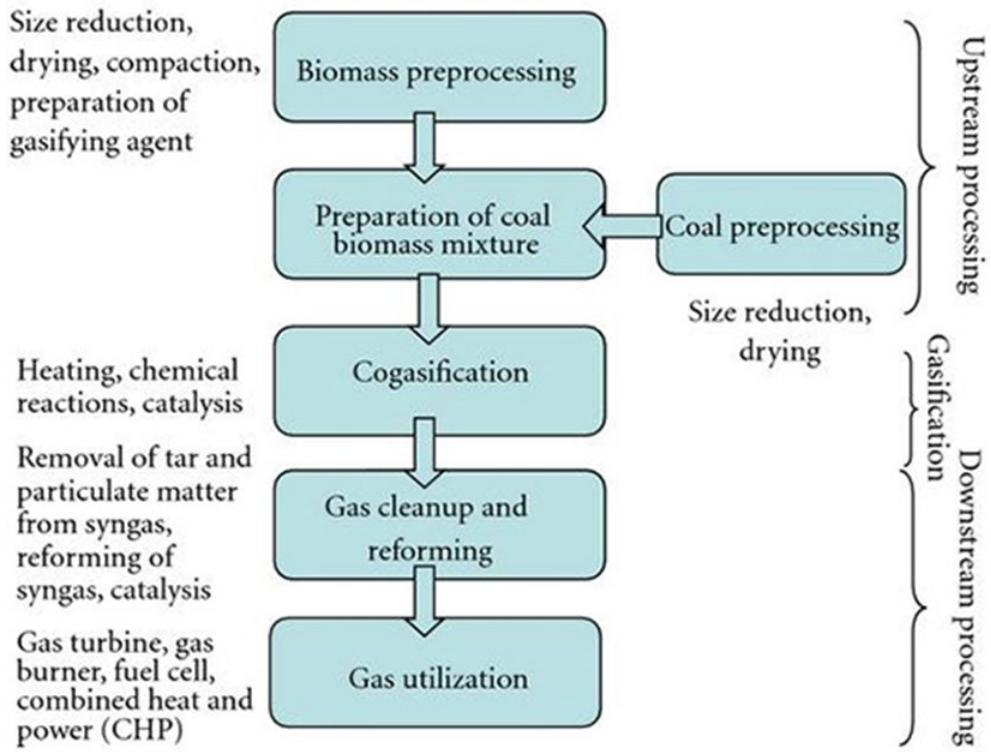
- *Indirectly Heated gasifiers*, which can be entrained, fluidized, or circulating fluidized bed gasifiers, are at an early stage of development and have not been tested over a wide range for application suitability.
- These units have only been tested at atmospheric pressure.
- They are more complicated (and have higher capital costs), owing to a separate combustion chamber, but are capable of producing a syngas with a very high heating value, which is important for power/heat applications.
- One advantage is that they do not require oxygen or air for gasification, which means no oxygen plant is needed (lower capital cost and efficiency losses) and no nitrogen dilution.
- These units tend to have higher methane and other hydrocarbon yields, which would be a problem for synthesis applications, but beneficial for heat/power generation.
- For fuels or chemicals synthesis, the hydrocarbons can be steam reformed or partially oxidized, usually through high steam addition rates which promote water-gas-shift activity.
- Primarily, though, these systems need to be studied further.

Gasifiers for Municipal Solid Waste

- **FB gasifiers are able to handle heterogeneous feedstock like MSW.**
  - This is important because , MSW can vary widely in composition (imagine the contents of a dumpster, with many varying shapes, sizes, densities, and composition) and requires a flexible gasifier.
  - Atmospheric pressure gasification reduces complexity compared to feeding a highly non-uniform feed at pressure. If possible, avoiding costly feed preparation systems like pulverization results is advantageous.
- **Plasma gasification**
  - Uses an extremely hot electrical plasma arc to break down MSW into simple gases and leftover solids, is currently being considered for many large MSW gasification facilities.
  - High voltage and current electricity produces a plasma arc between two electrodes.
  - While this requires a substantial amount of energy, the syngas product can be used in a turbine to potentially generate more electrical power than required.
  - The plasma arc can reach temperatures as high as 13,900°C which can break down difficult feedstocks into simple constituent gas molecules and a solid slag byproduct.
- **Difficulties**
  - Biomass and municipal solid waste can pose problems to gasification system designers.
  - Both present issues for feed systems as these feedstocks are largely heterogeneous in their delivered state.
  - Some biomass, such as sawdust from lumber mills, can be in a condition suitable for many existing feed systems, while others, like most MSW, would require extensive preparation or feed system customization.
  - Biomass and MSW also may have characteristics like higher moisture content which may necessitate pre-gasification drying.
  - Ash contents can also vary widely, meaning the gasifier must be able to handle potentially high levels of ash.
  - Essentially, biomass and MSW gasification requires flexibility in design to handle non-uniform feeds.

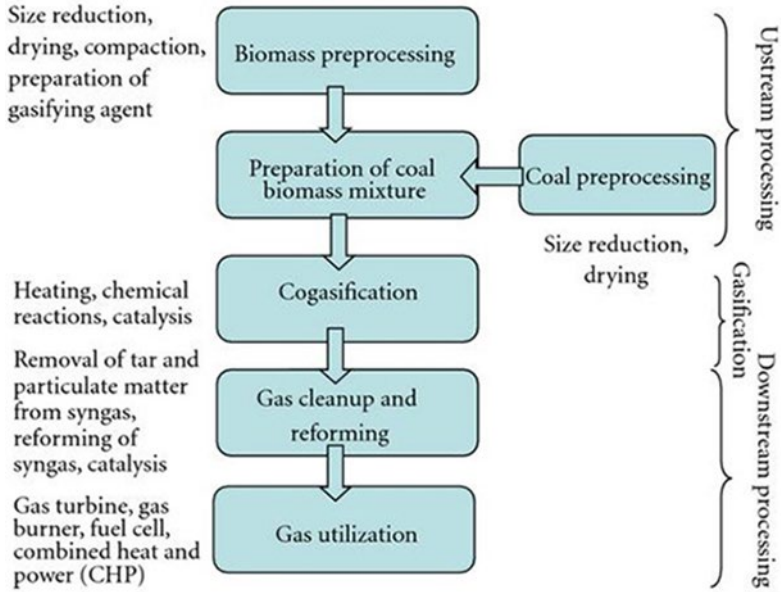
Co-gasification of Coal & Biomass

- Co-gasification of coal and biomass blends is of considerable current interest, stemming from a number of benefits that can result from the approach relative to conventional gasification of straight coal:
- The low or zero carbon emissions characteristics of biomass proportionally lowers the carbon footprint of the overall gasification process on the environment.
- Addition of biomass to the feed mix improves the H_2/CO ratio in the produced gas, which is usually desirable for liquid fuel synthesis.
- Inorganic matter present in biomass catalyzes the gasification of coal.
- Co-gasification also works to advantage by reducing the typical high tar content resulting from biomass gasification of straight biomass



Co-gasification of Coal & Biomass (Continued)

- **Some of the complications arising from co-gasification are apparent from this figure.**
  - First, instead of a single feedstock preparation scheme, it is usually necessary to have separate preprocessing operations for coal and biomass.
  - The typically high moisture-content biomass is usually not just dried, but also torrefied (which involves heating to temperatures typically ranging between 200 and 320°C in absence of oxygen, at which point the biomass undergoes a mild form of pyrolysis) and possibly compacted, which greatly improves the quality as a feedstock for either fuel use or gasification.
  - Also, size reduction of both the coal and biomass to uniformly-sized particles is required for optimum gasification.
- **Co-gasification reactions and transformations share aspects of those for coal gasification and biomass gasification, but also include some synergistic effects that are not definitively described.**
  - If the syngas is to be used for electricity generation, a downdraft **fixed-bed gasifier** is a good choice because it releases gas at high temperature with low impurities.
  - Fluidized-bed gasifiers may not be the best choice for some co-gasification applications, because defluidization of the fluidized bed can occur due to agglomeration of low melting point ash present in the biomass, along with clogging of the downstream pipes due to excessive tar accumulation.
- **It has been observed that entrained flow gasifiers should be investigated for the co-gasification of coal and biomass, given**
  - their capacity to accept different types of feedstock,
  - the uniform temperature profile inside the reaction zone,
  - short reactor residence time, and high carbon conversions,
  - all of which are of increased importance to addressing the issues associated with co-gasification.



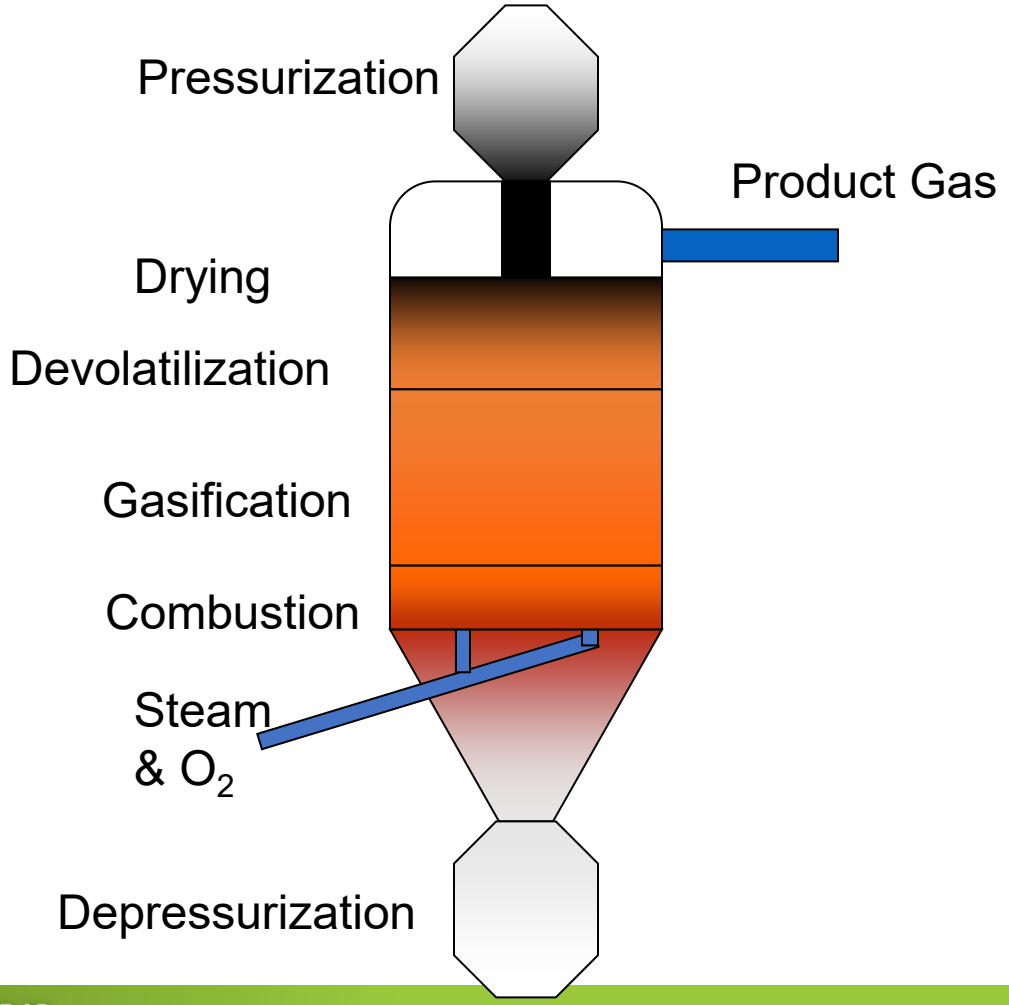
NATIONAL ENERGY TECHNOLOGY LABORATORY

Thank you and have a good conference

Additional Slides

- Hydrodynamics and Kinetics
- Typical Gas compositions
- Acid Gas

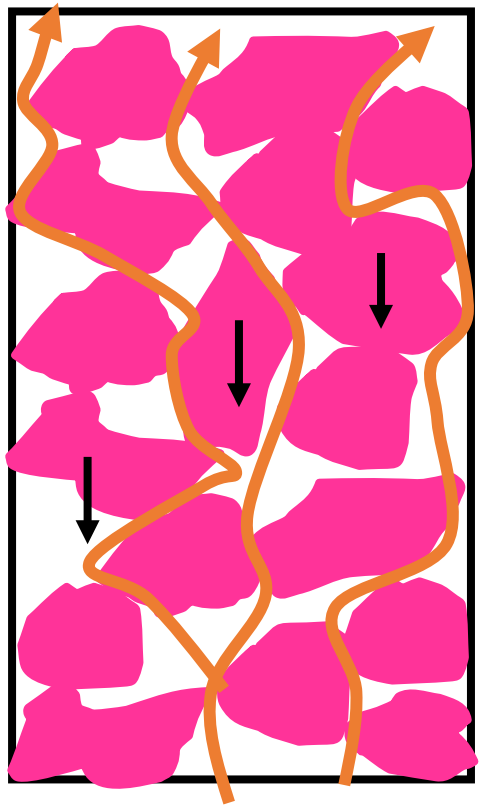
Fixed/Moving Bed



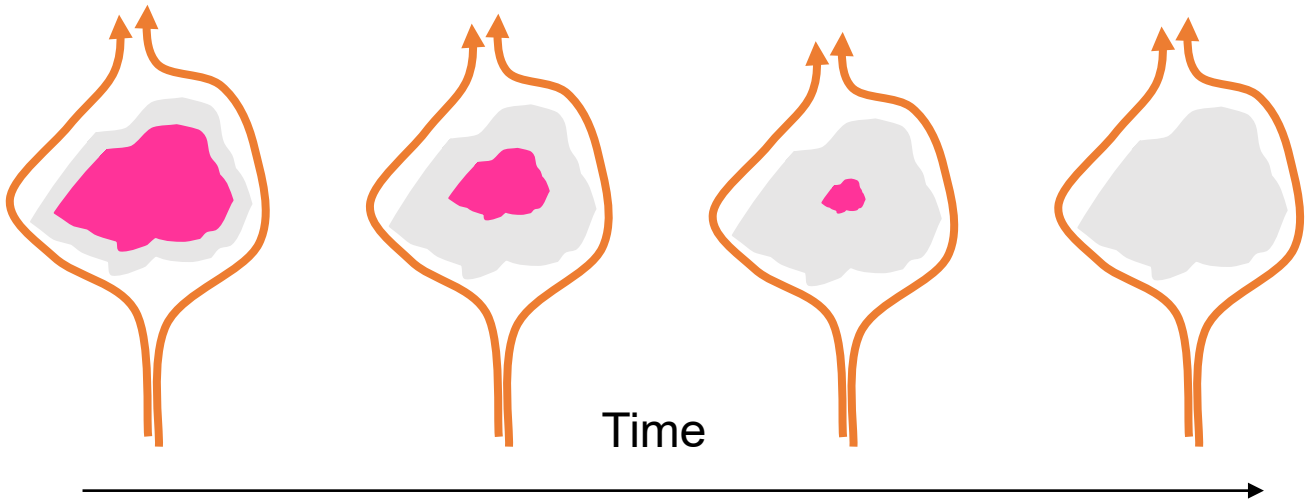
- Lurgi & British Gas Lugri
- Counter Current Flow
- Ash Removal
  - Lurgi – Dry Ash
  - BGSL – Slagging
- Issues: Obtaining uniform flow of Gas and Solids
- Design: Bottom temperature determines H_2O/O_2 ratio
- Product gas contains HCs and tar
- High cold gas efficiency
- Low O_2 requirement

Hydrodynamics

- Flow through porous media
- Counter Current – Solids move down while gas moves up
- Non-uniform flow
  - Poor Inter-phase mixing
  - Unreacted carbon
  - Hot spots
  - Lower Conversion



Kinetics for Fixed/Moving Bed



Low Temperature – Kinetic Controlled Shrinking particle Reaction

$$\tau = \frac{2\rho_B R}{kC_{O_2}}$$

Where: τ is the time for complete conversion

ρ_B is the Coal particle density

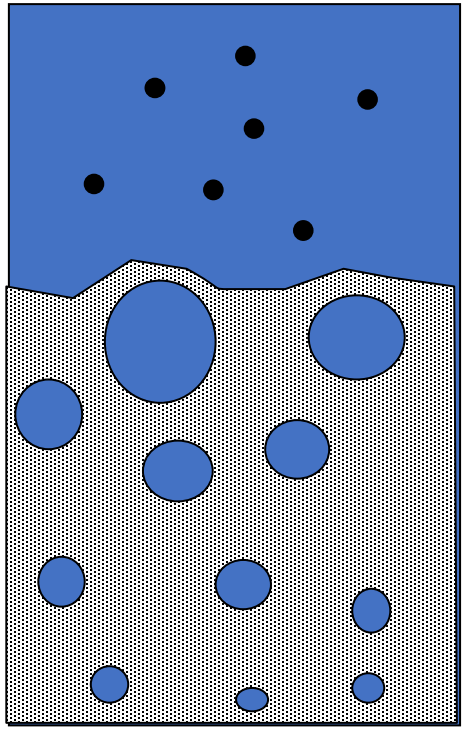
2 is 1/stoichiometri coefficient for O_2

k is the rate constant

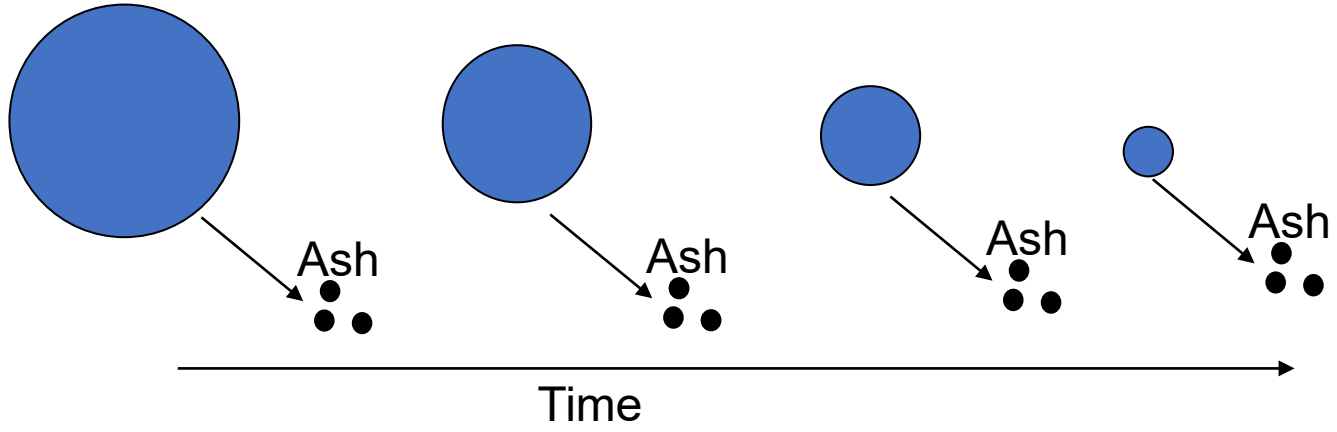
C is the concentration of O_2

Fluid Bed Gasification Hydrodynamics

- More complicated hydrodynamics
- Bubble induced mixing
- Better mixing of gas and solids
- Better inter-phase transport
- Ash “scrubbed” from particles



Kinetics for Fluid Bed Gasification



Kinetic controlled shrinking particle

$$\tau = \frac{2\rho_B R}{kC_{O_2}}$$

Where: τ is the time for complete conversion

ρ_B is the Coal particle density

2 is 1/stoichiometri coefficient for O_2

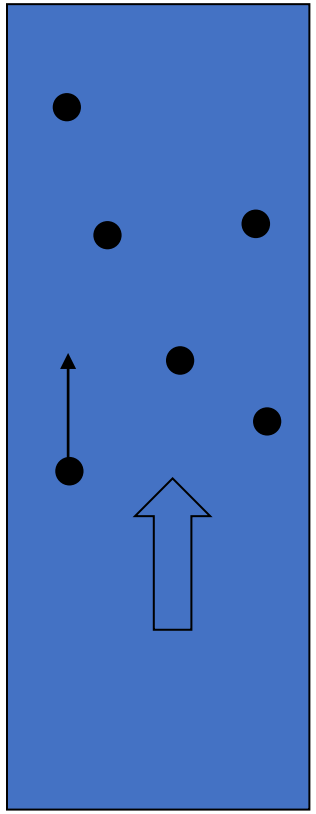
k is the rate constant

C is the concentration of O_2

Entrained Flow Gasifiers

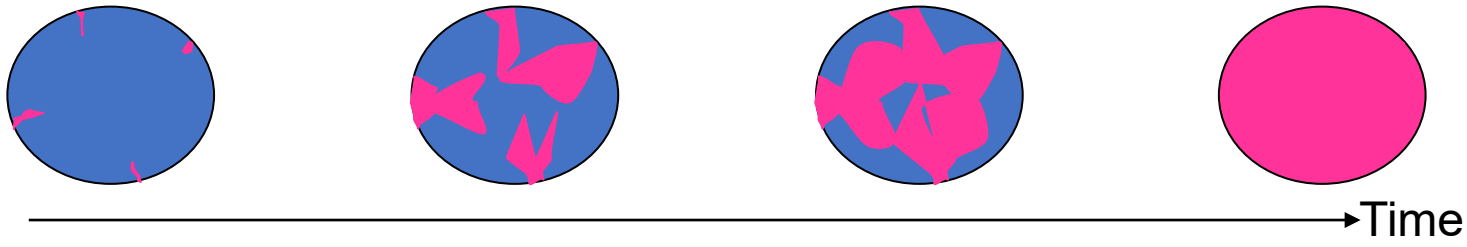
- Examples: Conoco Phillips, GE (formerly Texaco) and Shell
- Widely dispersed small particles, radiantly heated
- High temperature for slagging & rapid gasification
- Issues: Obtaining uniform feed, slurry drying, separation of gas from ash, heat recovery
- Volume determined from conversion time for average particle
- Low cold gas efficiency and high O_2 demand

Hydrodynamics



- Simple hydrodynamics
  - Co-current
  - Up flow or down flow
- Non-uniform flow
  - Poor bulk mixing mixing
  - Unreacted carbon
  - Hot spots
- Better inter-phase transport – controls reaction rate

Kinetics for Entrained Flow Gasifiers



Bulk Diffusion controlled fixed diameter particle

$$\tau = \frac{2\rho_B R}{3k_g C_{O_2}}$$

Where: τ is the time for complete conversion

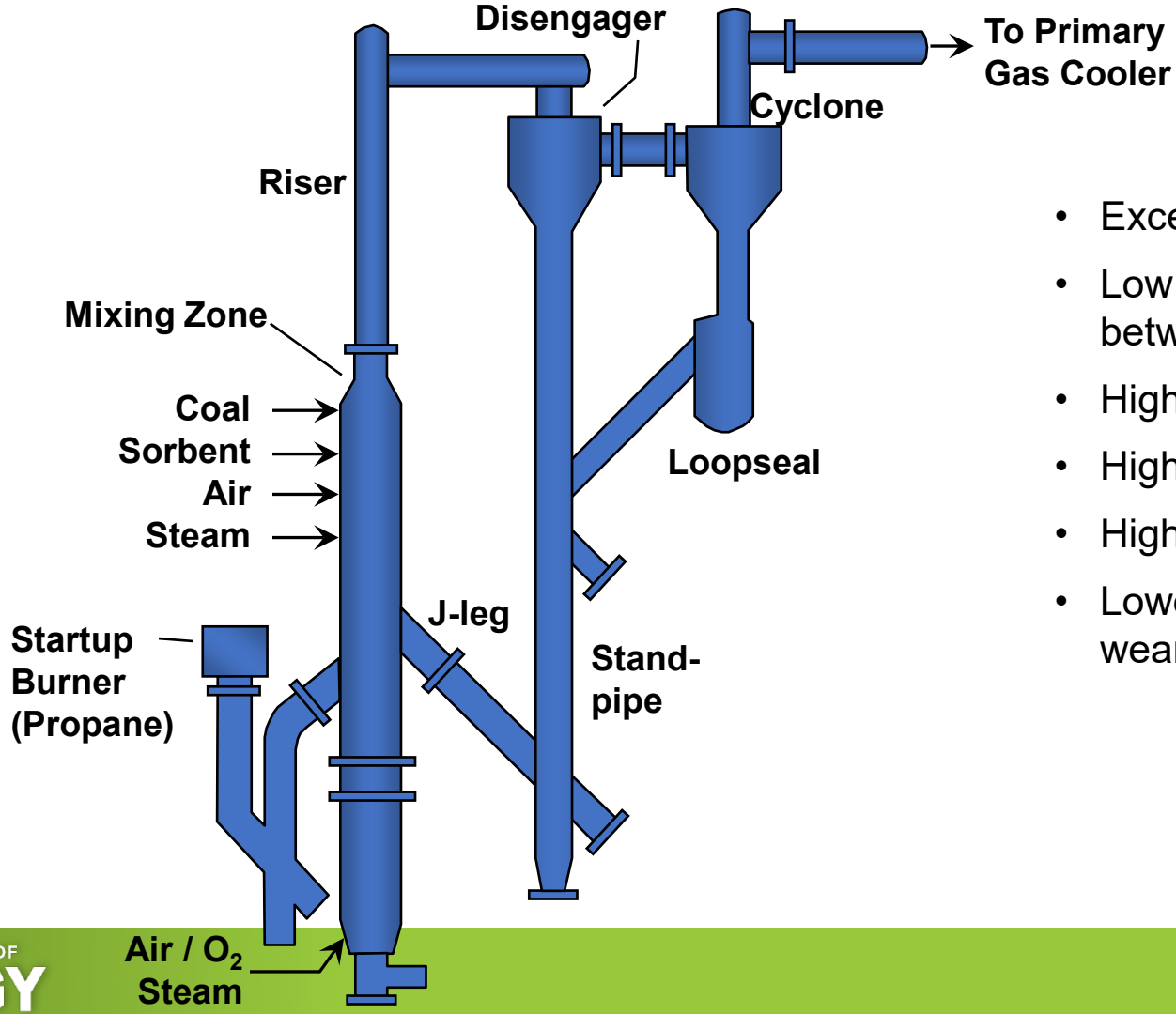
ρ_B is the Coal particle density

2 is 1/stoichiometri coefficient for O_2

k_g is the mass transfer rate constant

C is the concentration of O_2

Transport and Circulating Fluidized Beds

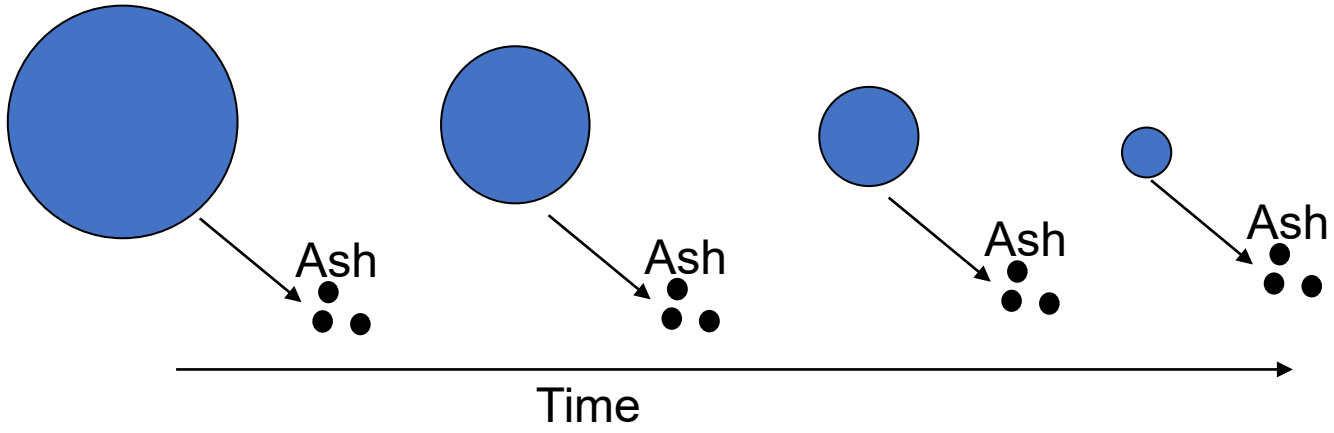


- Excellent gas-solids contact
- Low mass transfer resistance between gas and solids
- Highly turbulent atmosphere
- High coal throughput
- High heat release rate
- Lower temperature – less refractory wear, no slag

Hydrodynamics

- Particles form clusters
- Clusters act as “big particles” and fall
- Stresses break up clusters into separate particles which from new clusters

Kinetics in Transport Reactor



Kinetic controlled shrinking particle

$$\tau = \frac{2\rho_B R}{kC_{O_2}}$$

Where: τ is the time for complete conversion

ρ_B is the Coal particle density

2 is 1/stoichiometri coefficient for O_2

k is the rate constant

C is the concentration of O_2

Product compositions for oxygen blown moving bed gasifiers

Oxygen Blown											
	Dry Bottom Moving Bed							Slagging Moving Bed			
Coal type	Brown/Lignite		Sub-Bit	Bit			Anth	Bit			
Pressure atm	up	to 92	25	24	to	100	~	21.0	to	32.0	
Gas Composition (Dry)											
CO	17.4	to 19.7	15.1	15.2	to	19.5	22.1	55.0	to	61.2	
CO2	30.4	to 32.2	30.4	28.9	to	32.4	30.8	2.4	to	3.5	
H2	37.2	to 37.2	41.1	38.3	to	42.3	40.7	28.1	to	31.5	
N2	0.5	to 0.5	1.2	0.5	to	1.6	0.4	3.3	to	3.3	
CH4	11.8	to 12.1	11.7	8.6	to	10.1	5.6	5.0	to	8.3	
H2S	0.1		0.5	0.8	to	1.1	~	1.3	to	1.3	

Product compositions moving bed gasifiers

Air Blown						
Dry Bottom Moving Bed						
Coal type	Sub-Bit			Bit		
Pressure atm	20			1		
Gas Composition (Dry)						
CO	17.1	to	17.4	22.7	to	27.8
CO2	14.8		14.8	5.9	to	6.3
H2	23.3		23.3	16.2	to	16.6
N2	38.5		38.5	48	to	50.5
CH4	5.1		5.8	1.7	to	3.6
H2S	0.2		0.2	0	to	0

Gas composition fluidized bed gasifiers

Oxygen Blown						
Gasifier	Fluidized Bed					
Coal type	Lignite			Bit		
Pressure atm	1.0	to	30.0	9.0	to	30.0
Gas Composition (Dry)						
CO	31.0	to	53.0	19.2	to	52.0
CO2	6.7	to	19.5	5.3	to	9.3
H2	32.8	to	40.0	14.4	to	37.3
N2	0.3	to	1.7	0.3	to	54.3
CH4	0.3	to	3.1	2.7	to	3.5
H2S		0.4			~	

Gas composition for fluidized bed gasifiers

Air Blown				
Gasifier	Fluidized Bed			
Coal type	Lignite	Bit		
Pressure atm	1	5.0	to	30.0
Gas Composition (Dry)				
CO	22.5	12.5	to	30.7
CO2	7.7	1.9	to	15.9
H2	12.6	14.7	to	28.6
N2	55.7	0.2	to	52.7
CH4	0.8	0.7	to	47.0
H2S	~		~	

Typical gas composition for entrained flow gasifiers

Oxygen Blown							
Gasifier	Dry-entrained						Slurry-entrained
Coal type	Brown/Lignite	Sub-Bit	Bit				Bit
Pressure atm	30	30	25 to 30				42
Gas Composition (Dry)							
CO	62.01	64.48	61.53	to	64.97		49.46
CO2	6.88	1.33	0.81	to	1.63		12.30
H2	30.42	33.37	30.61	to	32.08		35.95
N2	0.34	0.51	0.51	to	4.80		0.97
CH4	0.00	0.00	0.00	to	0.00		0.36
H2S	0.23	0.31	1.33	to	1.42		1.33

Typical gas analysis from the Transport Gasifier Pilot Plant

Coal Type	Subbituminous		Lignite		Bituminous	
Mode	Air	Oxygen	Air	Oxygen	Air	Oxygen
Pressure, atm	30	30	30	30	30	30
Gas Composition (Dry)						
CO	23.7	39.1	18.8	37.9	13.3	25.5
CO_2	7.6	19.9	11.7	21.8	13.4	28.6
H_2	11.8	36.2	14.8	37.4	15.7	41.9
N_2	54.3	0.1	53.2	0.1	55.6	0.1
CH_4	2.6	4.8	1.6	2.9	2.0	3.9

Acid Gas Removal

Commercial Technologies

- Physical Sorbents
  - Rectisol
  - Selexol
  - Purisol
  - Morphysorb
- Chemical Sorbents
  - MDEA
  - Other amines
- Single Species Processes
  - CrystaSulf - Sulfur
  - Fluor Solvent – CO_2
- Advanced Technologies in Development

Physical Sorbents

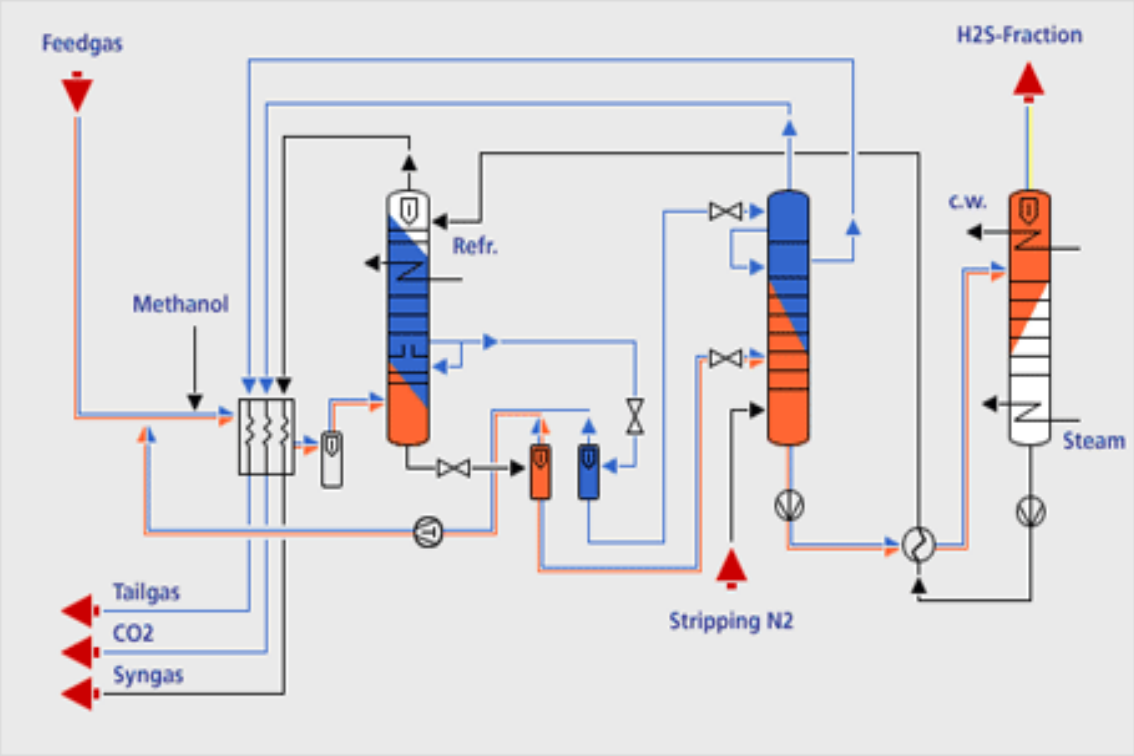
- Rectisol
- Selexol
- Purisol
- Morphysorb

Rectisol

- Rectisol is a physical acid gas removal process using an organic solvent (typically methanol) at subzero temperatures.
- Rectisol can purify synthesis gas down to 0.1 vppm total sulphur (including COS) and CO_2 in ppm range.
- The main advantages of the process are the rather low utility consumption figures, the use of a cheap and easily available solvent and the flexibility in process configuration.
- Performance
  - Total Sulfur (H_2S + COS) – 0.1 to 1 ppm
  - CO_2 – 10 to 50 ppm
  - H_2S in CO_2 by-product – 5 ppm

Basic Flow Diagram/Process Scheme for Rectisol

- CO_2 and sulfur compounds are removed in separate fractions;
  - a pure
  - an H_2S
- Spiral w



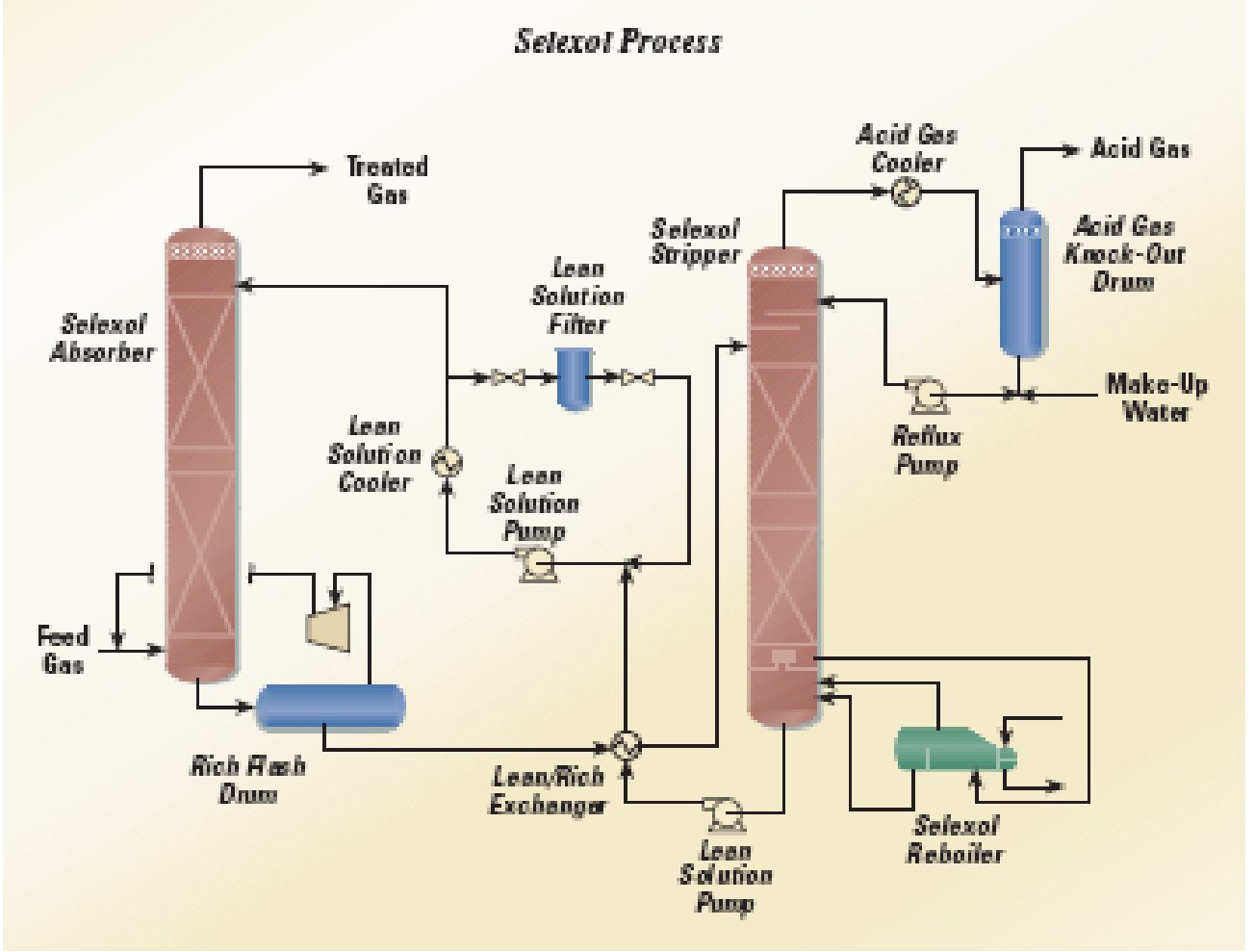
CO_2 Capture via Rectisol Scrubbing

- Based on low-temperature (refrigerated methanol ~ -40° F or C)
- Capable of deep total sulfur removal as well as CO_2 removal
- Most expensive AGR process – deepest cleaning
- Predominantly used in chemical synthesis gas applications
  - As low as < 0.1 ppmv total sulfur requirements
- Proposed for use in IGCC for CO_2 removal but no published cost studies

RECTISOL unit for a coal gasification plant in Japan



UOP's Selexol



APPLICATIONS

- The Selexol process can be tailored for either bulk or trace acid gas removal. It is primarily used in the following applications and markets:
  - Selective removal of H_2S and COS in integrated gasification combined cycle (IGCC), with high CO_2 rejection to product gas (85% +) and high sulfur (25% to 80%) feed to the Claus unit
  - Selective removal of H_2S/COS plus bulk removal of CO_2 in gasification for high purity H_2 generation for refinery or fertilizer use
  - Natural gas treating to achieve either LNG or pipeline specification with dew-point reduction

Selexol Process

- The Selexol process uses a physical solvent to remove acid gas from streams of synthetic or natural gas.
- The process may be regenerated either thermally, by flashing, or by stripping gas.
- The Selexol process is ideally suited for the selective removal of H_2S and other sulfur compounds, or for the bulk removal of CO_2.
- The Selexol process uses Union Carbide's Selexol solvent, a physical solvent made of a dimethyl ether of polyethylene glycol (DPG or DEPG).
- The Selexol solvent is chemically inert and is not subject to degradation.
- The Selexol process also removes COS, mercaptans, ammonia, HCN and metal carbonyls.
- The Selexol process allows for construction of mostly carbon steel due to its non-aqueous nature and inert chemical characteristics.

PRODUCTS AND FEEDSTOCKS

Acid gas partial pressure is the key driving force for the Selexol process.

- **Typical feed conditions range between 300 and 2000 psia with acid gas composition (CO_2 + H_2S) from 5% to more than 60% by volume.**
- **The product specifications achievable depend on the application and can be anywhere from the ppmv level up to percent levels of acid gas.**

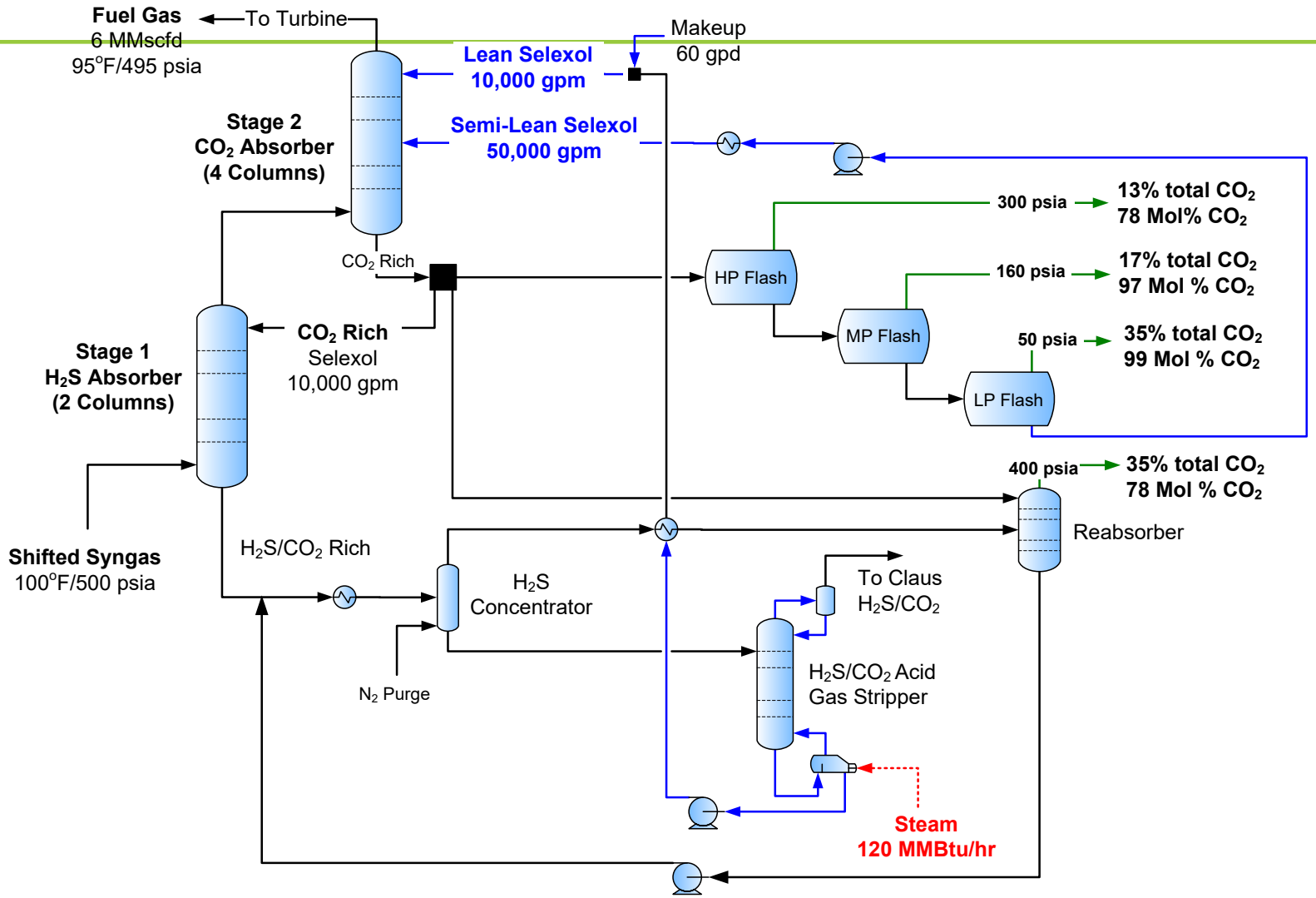
Selexol Experience

- The Selexol process was introduced over 30 years ago.
- The Selexol process continues to be used in a wide variety of applications;
  - natural gas
  - has been the dominant acid-gas removal system selection in gasification project awards within the past three years.





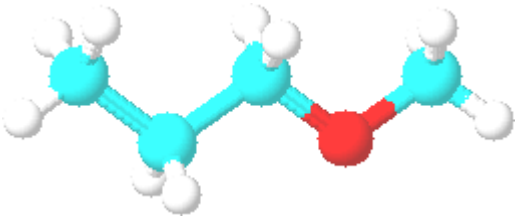
Selexol™ Scrubbing for CO_2 Capture



CO_2 Capture via Selexol Scrubbing

Advantages

- Physical Liquid Sorbent → High loadings at high CO2 partial pressure
- Highly selective for H2S and CO2 → No need for separate sulfur capture system
- No heat of reaction (DHrxn), small heat of solution
- Chemically and thermally stable, low vapor pressure
- 30+ years of commercial operation (55 worldwide plants)



Disadvantages

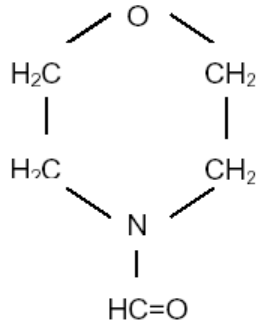
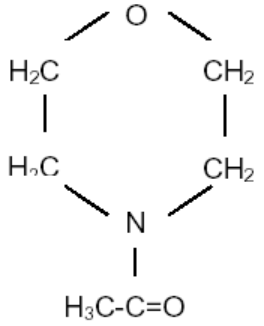
- Requires Gas Cooling (to ~100^{o}F)
- CO_2 regeneration by flashing (requires considerable heat)

Morphysorb Process

> What is it?

- Proprietary solvent/process
  (GTI and Uhde own the technology)

- N- formyl morpholine/
  N-acetyl morpholine mixtures

NFM	NAM
N-formyl-morpholine	N-acetyl-morpholine
	

> What is the application?

- Bulk or trace removal of acid gas components
- Subquality natural gas upgrading to either pipeline or LNG specification
- Selective removal of H_2S from natural/synthesis gas for generation of acid gas stream suitable for Claus plant feed
- Selective removal of H_2S, CO_2, COS, CS_2, mercaptans and other components from coal/oil gasification syngas at IGCC facilities

Morphysorb Process

> Benefits

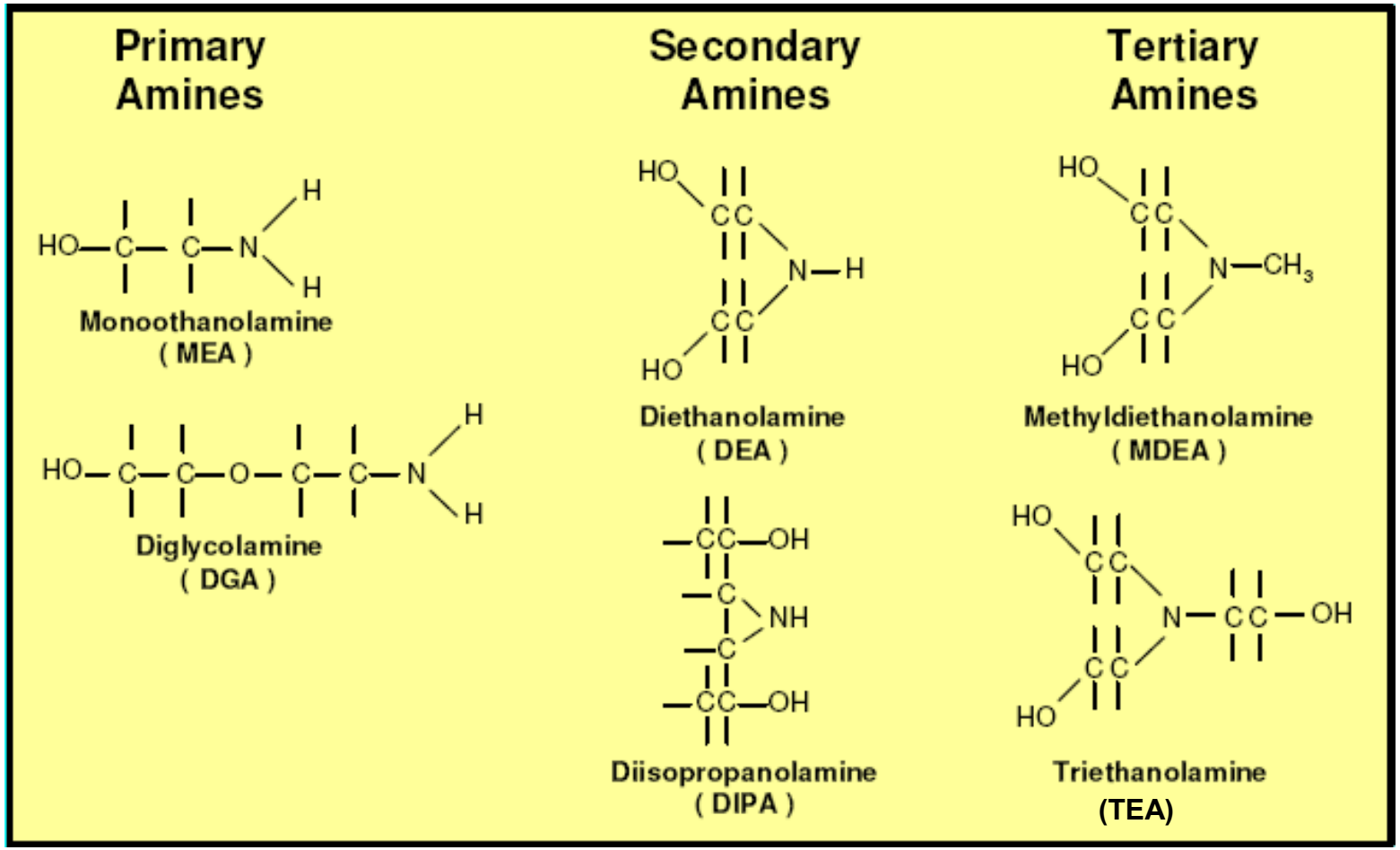
- Higher solvent loading = lower circulation or higher throughput
- Lower co-absorption of hydrocarbons (less losses)-less recycle gas flow
- Lower CO and H_2 absorption
- In situ, partial COS Hydrolysis
- Low corrosion, low environmental hazard
- Low capital and operating costs

Natural Gas Commercial Application

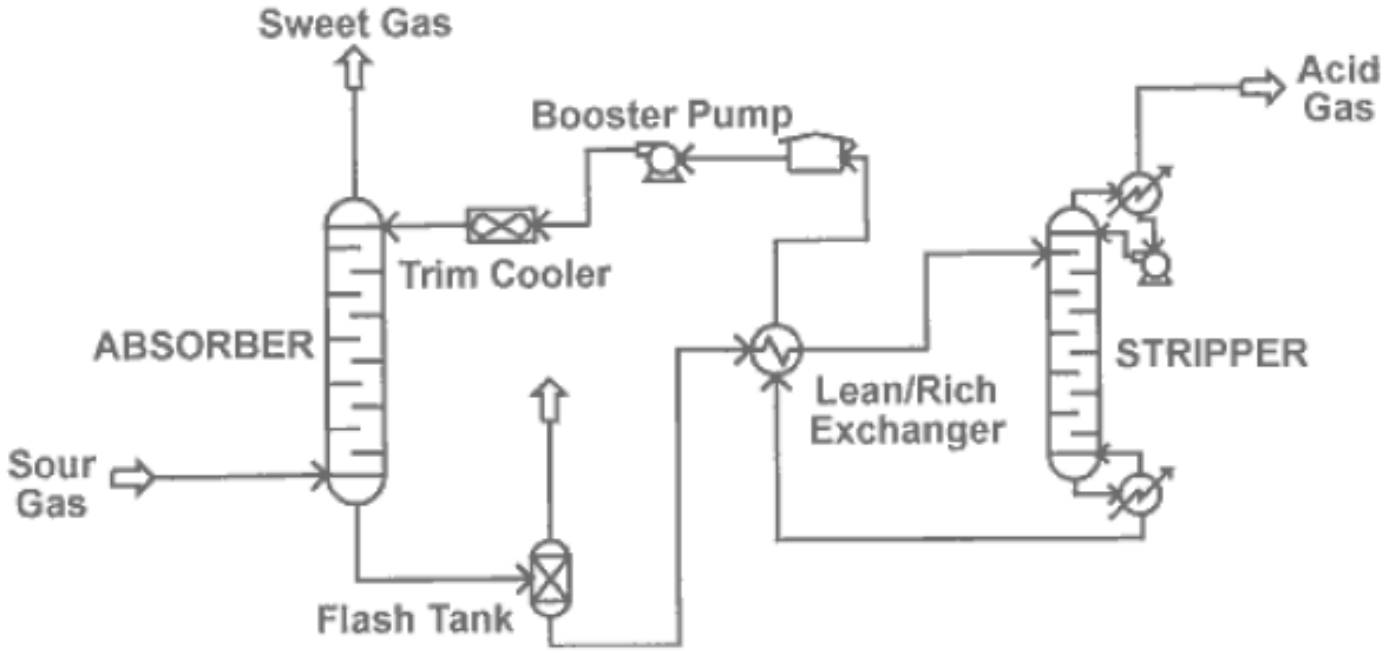
- Plant started in late 2002
- Owned by Spectra Energy℠ Transmission
- 300 MMscfd orig., 450 MMscfd expansion
- ~4500 gpm circulation
- ~2000 psia liquefied acid gas to injection
- Bulk removal of 25+% acid gas concentration stream

Chemical Sorbents

Chemical Sorbents
(MDEA and Other amines)



Typical Amine based Process



Process flow diagram of a typical amine treating process used in industrial plants

MEA/DEA/MDEA

- The absorption of acid gases (H2S, SO2, CO2) in amine solution is conducted with a two column operation: the first column is used to absorb the acid gas into the absorbent amine, the second column is used to regenerate the amine.
- The process relies on counter current flow to achieve optimum mixing. A lean solution (low acid gas) enters the top of the absorber and flows to the bottom; acid gas enters the bottom of the absorber tower and bubbles to the top.
- The rich amine (high acid gas) enters the stripper were the acid gases are released and the "clean" amine is returned to the absorber. The acid gases exit from the top of the stripper.
- The MEA/DEA/MDEA is regenerated in the stripper column. It is beneficial to be sure the amine concentration is at proper level in order to optimize the H2S, SO2 and CO2 removal. The final amine concentration can be controlled by the amine make-up ratio.

Advanced DOE Sponsored/Developed Technologies

- Warm Gas Cleanup Progress for H2S control
- Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents

Warm Gas Cleanup Progress

RTI Process Development Testing at Eastman Chemical

Field Test Objective:

First integrated evaluation of warm-gas contaminant cleanup technologies wi commercial gasification



Preliminary Test Resul

- 3,017 hours of operatio hours)
- H_2S reduced to < 5 ppn ppm
- Stable operation with c 300 – 600 psig
- 2,541 bypassing guard bed
  - no observed chemica
- Attrition loss < design v

Future Plans:

- **Slipstream testing of 50 MWe unit at a commercial power station (2010)**
- **Deployment in IGCC – post 2010**

Warm Gas Desulfurization Operations Summary

September 2006 to November 2007

- Reached Steady State Regeneration within 10 hours of startup on 9/5/06
- 3017 hours of Syngas Operations
  - 346 hr longest continuous run
  - 61% - 81% On-Stream
  - Most downtime caused by support equipment
- 116 hours of DSRP operation with >90% sulfur removal
- Guard Bed
  - 2541 hr bypassing Guard Bed
  - 476 hr using Guard Bed
  - No detectable difference in WGDS performance

RTI Desulfurization Unit / DSRP at Eastman Plant

