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Gasification Technology Options for SOFC Applications

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Presentation Outline

- SOFC Syngas Purity Requirements
- Gasification Technologies and Characteristics
- Gas clean up options
  - Currently available
  - In Development
  - R&D Status

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Contaminants in Coal

- Your average lump of coal contains a lot more than just Carbon, Hydrogen, Oxygen, Nitrogen and Sulfur (with a touch of Chlorine)

Typical Metal Contaminants in Coal

Coal Type	Hg (ppm)	As (ppm)	Se (ppm)	Cd (ppm)
Pittsburg	0.11	4.1	0.6	0.06
Elkhorn/Hazard	0.13	4.0	3.1	0.31
Illinois No.6	0.22	2.7	2.2	0.15
Wyodak	0.19	1.3	1.6	0.30

Bool et al., 1997

- In addition to these metal contaminants, coal ash contains the following:
  – Si, Al, Fe, Ti, P, Ca, Mg, Na, K, S, and more

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Coal Gasification Chemistry & Reactions

Important reactions in coal gasification:

Coal Devolatilization = CH_4 + CO + CO_2 + Oils + Tars + C (Char)	
C + O_2 = CO_2	(exothermic – rapid)
C + 1/2O_2 = CO	(exothermic – rapid)
C + H_2O = CO + H_2	(endothermic – slower than oxidation)
C + CO_2 = 2CO	(endothermic – slower than oxidation)
CO + H_2O = CO_2 + H_2	**Shift Reaction (slightly exothermic)**
CO + 3H_2 = CH_4 + H_2O	Methanation (exothermic)
C + 2H_2 = CH_4	Direct Methanation (exothermic)

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Typical O_2-Blown Gasifier Produced Syngas

- H_2 30 - 50%
- CO 40 - 60%
- *CO_2* 4 - 20%
- *H_2S* 0.5 - 2%
- *COS* ~500$^+$ ppmv

Acid Gases

- Ar 0.5 - 1%
- N_2 0.7 - 6%
- NH_3 ~50-100 ppmv
- Ni & Fe* Carbonyls 1 to 4 ppmv
- *HCN* ~50-100 ppmv
- HCOOH* ~50 ppmv

Trace Components Include: As, P, Hg, Cd, Zn, Bi, Sb, Pb, Na, K, Fe, Ni

+ H_2S:COS is typically about 95%:5% of total sulfur

**** Carbonyls and Formic Acid (HCOOH) formed downstream of Gasifier***

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Estimated Thermodynamic Equilibrium State of Trace Components

Element	>1000°C	400° to 800°C	100° to 400°C	<100°C
As	AsO, As_2	AsO, As_4	As_2,	AsH3,
Be	$Be(OH)_2$	Condensed Species	Condensed Species	Condensed Species
Hg	Hg	Hg	Hg, $HgCl_2$	Hg, $HgCl_2$
B	HBO	HBO	HBO	-
V	VO_2	Condensed Species	Condensed Species	Condensed Species
Se	H_2Se, Se, SeO	H_2Se	H_2Se	H_2Se
Ni	NiCl, $NiCl_2$	Condensed Species	$Ni(CO)_4$	$Ni(CO)_4$
Co	$CoCl_2$, CoCl	Condensed Species	Condensed Species	Condensed Species
Sb	SbO, Sb_2	SbO, Sb_2	Sb_4	Condensed Species
Cd	Cd	Cd	$CdCl_2$	Condensed Species
Pb	Pb, $PbCl_2$	PbS, Pb, $PbCl_2$	Condensed Species	Condensed Species
Zn	Zn	Zn, $ZnCl_2$	Condensed Species	Condensed Species

Gasifier operating range

Source: SRI International presentation from 2006 SECA Review Meeting

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Known Issue: Nickel Carbonyls

- Nickel in feedstock ash can react with CO in the syngas if at high partial pressure and form Nickel carbonyl
  - $Ni + 4CO \leftrightarrows Ni(CO)_4$
  - $NiS + 4CO + H_2 \leftrightarrows Ni(CO)_4 + H_2S$
- Both ISAB and Puertollano have reported that Ni carbonyl has passed through all the gas clean-up steps and reached the CT where it has plated out on the hot section parts
- Direct water quench should remove some carbonyls
- Some AGR processes will remove carbonyls
  - Rectisol, yes
  - Selexol, expected to remove carbonyls but no verified experience
  - MDEA solvents do not remove carbonyls
- Activated carbon beds should remove iron and nickel carbonyls

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SOFC Gas Purity Requirements

- No chlorides (reduced H_2/CO adsorption on Ni)
- <5 ppm H_2S (reduced steam reforming activity)
- Very low (Zero?) Aromatic Hydrocarbons (Benzene, Naphthalene etc)
- No Cl, P, As (<1 ppm), Hg
- CO, H_2, CH_4 are the main fuel components but the SOFC must be designed to handle the appropriate heat balance for the actual composition
- CO_2 and H_2O can be tolerated but take up space and are preferably minimized

- Contaminant impacts require further study

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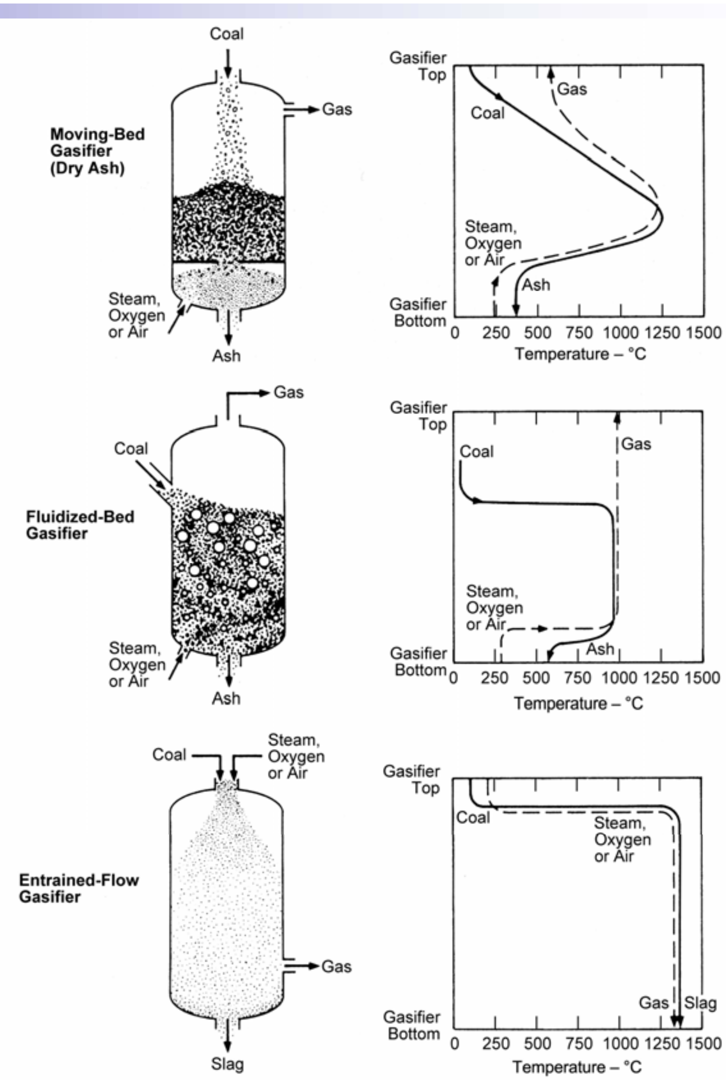
The 3 Major Types of Gasification Processes

1. Moving-Bed Gasifier (Dry Ash)

2. Fluidized-Bed Gasifier

3. Entrained-Flow Gasifier



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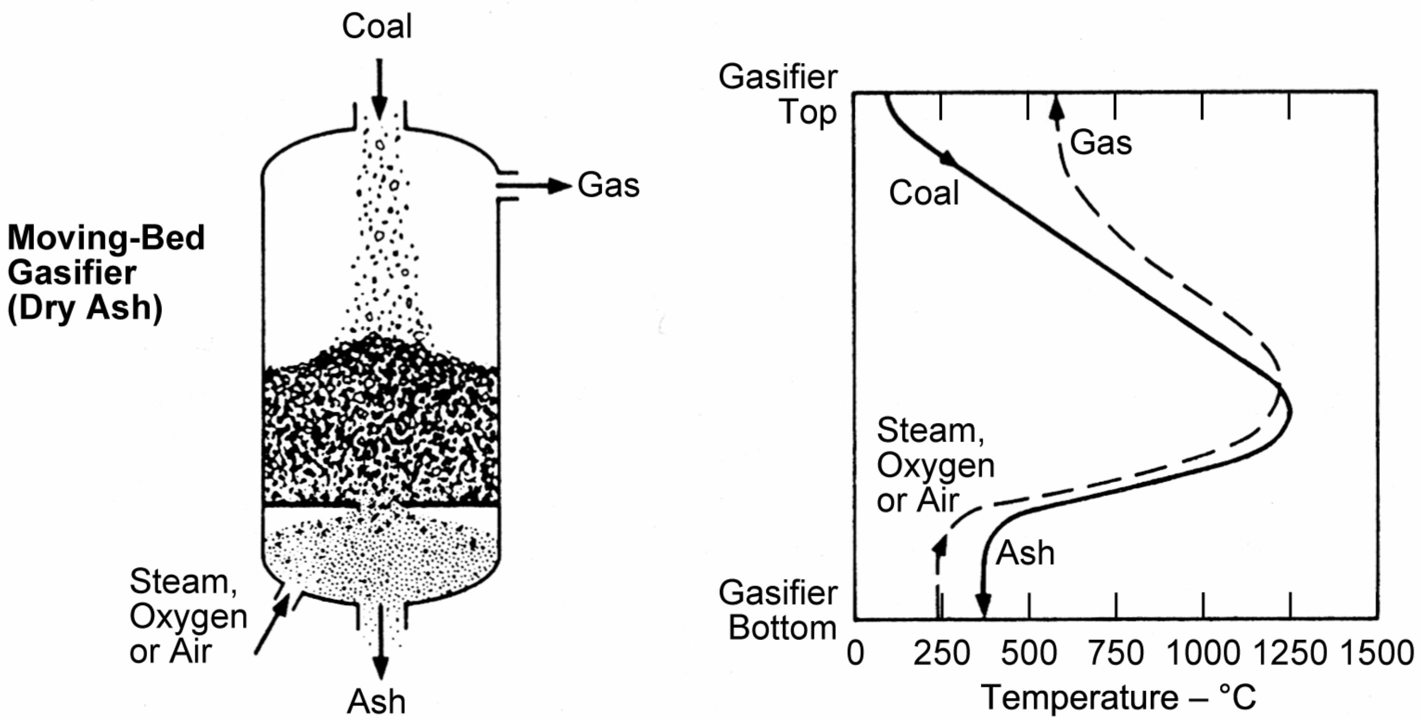
1. Moving-Bed Gasifier (Dry Ash)



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Moving Bed Gasifiers – Main Features (Lurgi dry ash, BGL etc)

- Lock Hopper top feed. Sized coal 2” x ¼” required
- Countercurrent operation
- Low outlet temperature 600-1000 F
- Tars, oils and phenolic byproducts
- Syngas 9-10% CH_4 or ~ 15-18% of Carbon in coal. Syngas not well suited for synthesis of Hydrogen, Ammonia, Methanol, DME, but OK for SNG.
- Lurgi dry ash units in operation worldwide (Sasol F-T, BEPC SNG)
- Steam added to keep coal below ash softening point in dry ash version. Results in high H_2 to CO ratio
- Most experience with lignites and lower rank coals. Bituminous coals need mechanical stirrer
- Atmospheric pressure units (Wellman etc) once widely used are not suitable for most current gasification applications
- BGL slagging version has some improvements over dry ash but limited commercial experience (one unit at Schwarze Pumpe)

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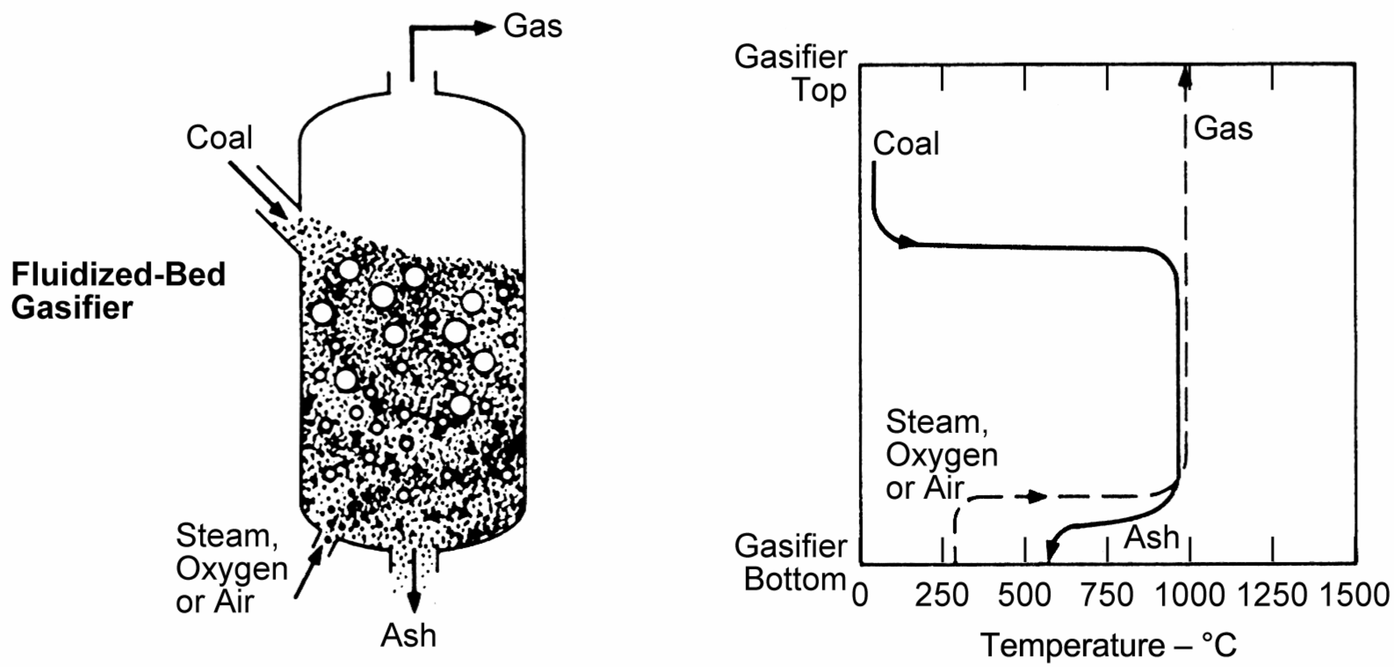
2. Fluidized-Bed Gasifier



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Fluid Bed Gasifiers – Main Features (KBR, HT Winkler, U Gas etc)

- Dry coal feed 1/8” minus
- Steam added to control temperature below ash softening , however GTI U Gas and KRW piloted ash agglomerating mode
- Should operate at temperature sufficient to destroy tars yet not slag.
- Lower carbon conversion than entrained dependent on coal reactivity
- Main experience low rank coals. Poor carbon conversion with bituminous coal and pet coke
- Syngas contains CH_4 so not well suited for synthesis of Hydrogen, Ammonia, Methanol or DME but OK for SNG.
- Can be either air blown or Oxygen blown
- Need scale up in pressure and to commercial size
- Three velocity modes : Bubbling bed <3 fps (GTI U Gas, KRW), Circulating 8-16 fps (HT Winkler, GRI U Gas) and Fast or Transport (KBR) 20-45 fps.

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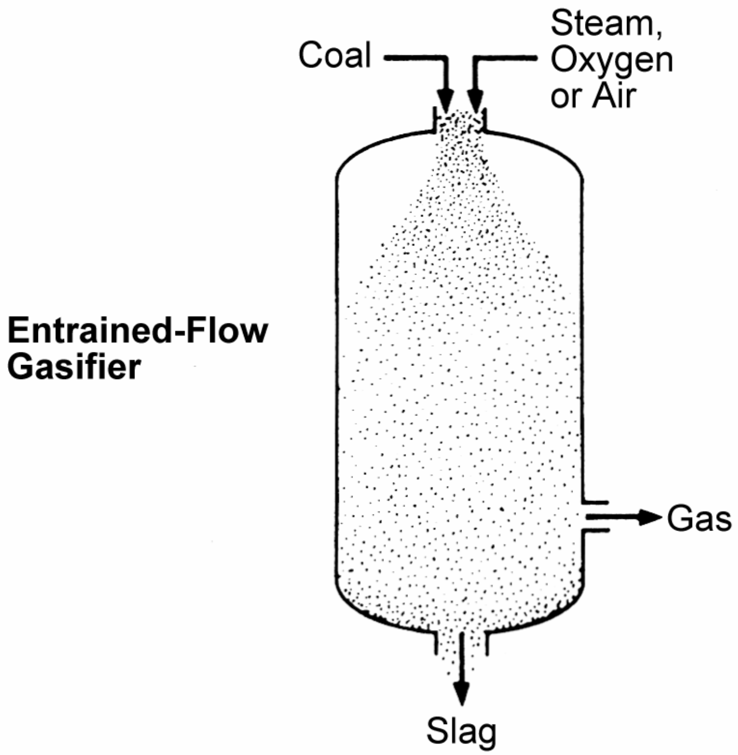
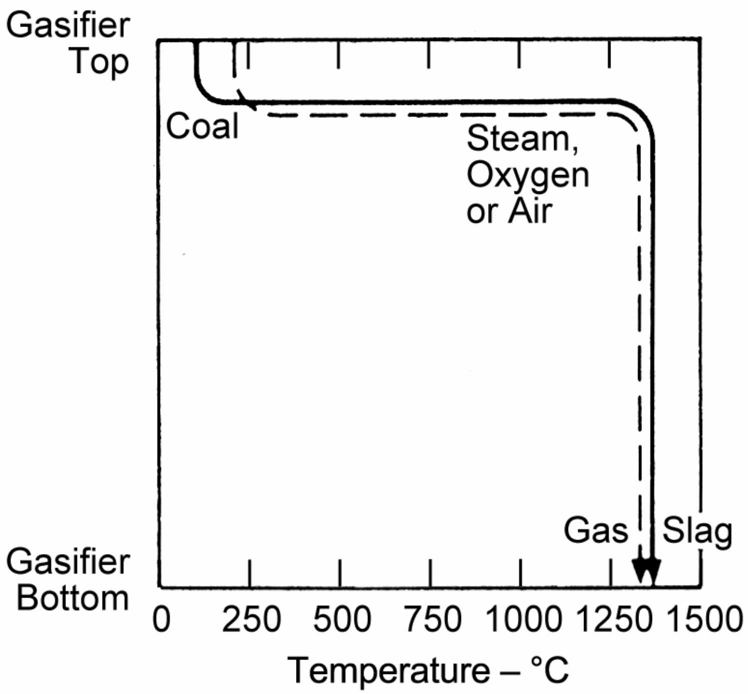
3. Entrained-Flow Gasifier (GE, COP, Shell, Siemens, MHI etc)





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Entrained Flow Gasification - Main Features

- Operates in the slagging region 2400-3000F. Inert slag produced.
- No troublesome tars and very low CH_4 in single stage gasifiers
- Single stage gasifiers (GE, Shell) very suitable for Hydrogen, Ammonia, Methanol and F-T production
- In two stage gasifiers outlet temperature decreases and CH_4 content increases as more coal is fed to the second stage (COP, MHI).
- Slurry fed gasifiers can be run at up to 1000 psig (Eastman)
- Slurry fed gasifier (GE, COP) efficiency deteriorates and oxygen usage increases with high moisture and high ash coals
- Dry coal fed gasifiers (Shell, Siemens/FutureEnergy, Eagle, MHI) need pre drying of high moisture coals for reliable feed control but can handle a wide range of coals.
- GE, COP and Shell all proven at commercial size in IGCC plants.

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Gasification Process Selection

- Selection depends upon:
- Product/Application – Hydrogen, Synthesis (Ammonia, Methanol, Fischer-Tropsch liquids), SNG, Power only, Co-production or Polygeneration
- Coal types or range
- Overall Plant/Project Objectives
  - Lowest Cost-of-Electricity (COE) ?
  - Highest Efficiency? Lowest dispatch cost?
  - Maximum CO_2 capture?
  - Near Zero (Minimal) Emissions?
  - Lowest cost of product ?

No Single "Best" Gasifier – "Best" Depends on Project Requirements

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IGCC/Gasification Status for CO_2 Capture

- GE gasifiers with full or partial water quench provide best CO_2 capture economics for bituminous coals
- COP partial slurry quench (PSQ) design (ala Wabash) includes some water quench and lower CH_4 production
- Shell gasifiers offer high efficiency over wide range of feed stocks. Water quench design is in development.
- Siemens gasifiers include partial water quench and handle wide range of feedstocks
- Selexol and Rectisol processes for CO_2 capture are commercial and proven
- Gas Turbine vendors currently offering gas turbines that are enabled for Hydrogen firing

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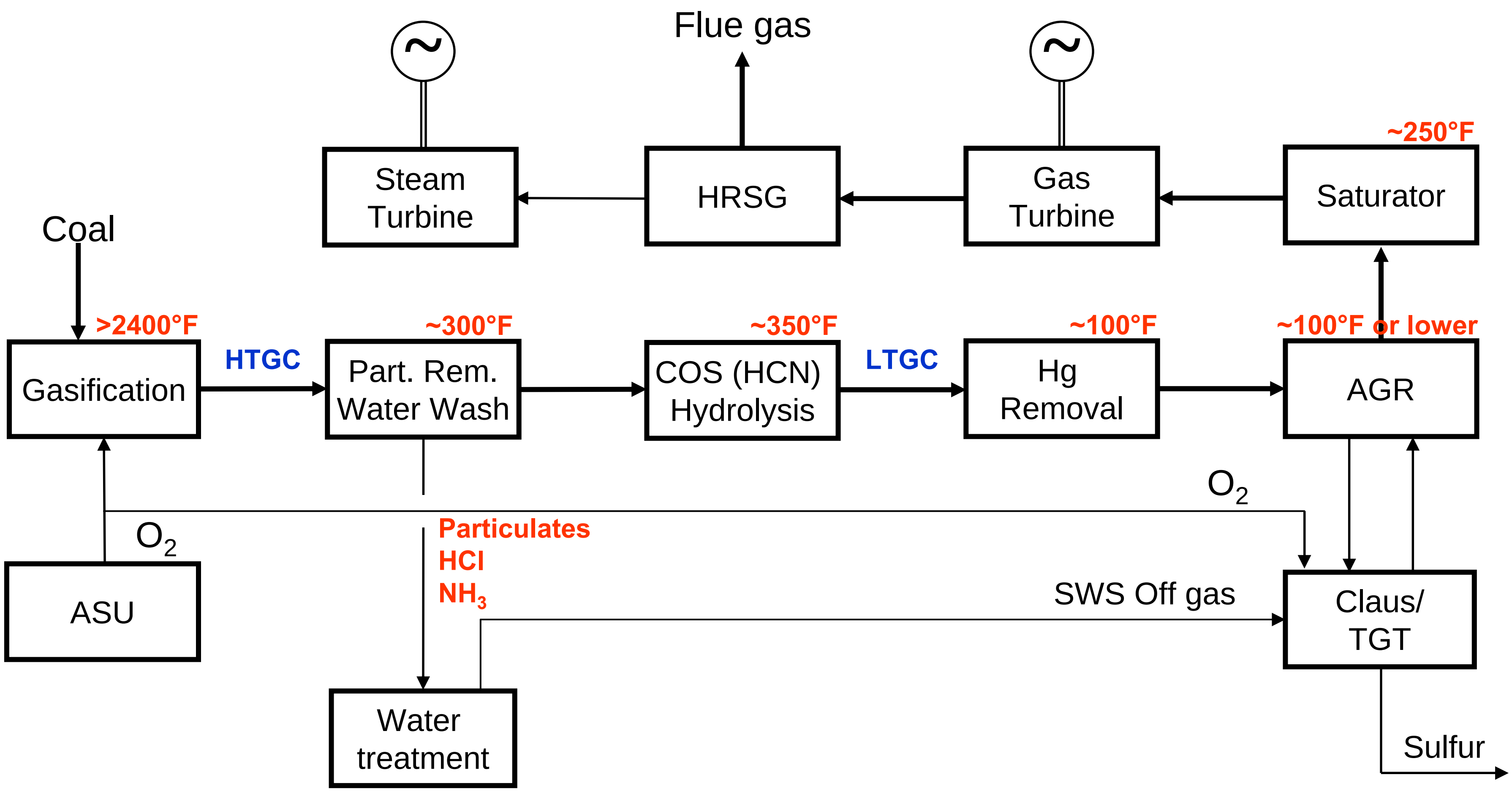
Simplified IGCC Block Flow Diagram



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IGCC Environmental Attributes

- Sulfur is removed (99.5-99.99%) from syngas
- NOx emissions are controlled by removal of nitrogen-containing species from the syngas and by flame temperature moderation in the gas turbine with a downstream SCR possible
- Particulates are removed from the syngas by filters and water wash prior to combustion so emissions are negligible
- Current IGCC design studies with SCR plan ~3ppmv each of SOx, NOx and CO
- Mercury and other HAP's removed from the syngas by adsorption on activated carbon bed
- Water use is lower than conventional coal
- Byproduct slag is vitreous and inert and often salable
- CO_2 under pressure takes less energy to remove than from PC flue gas at atmospheric pressure

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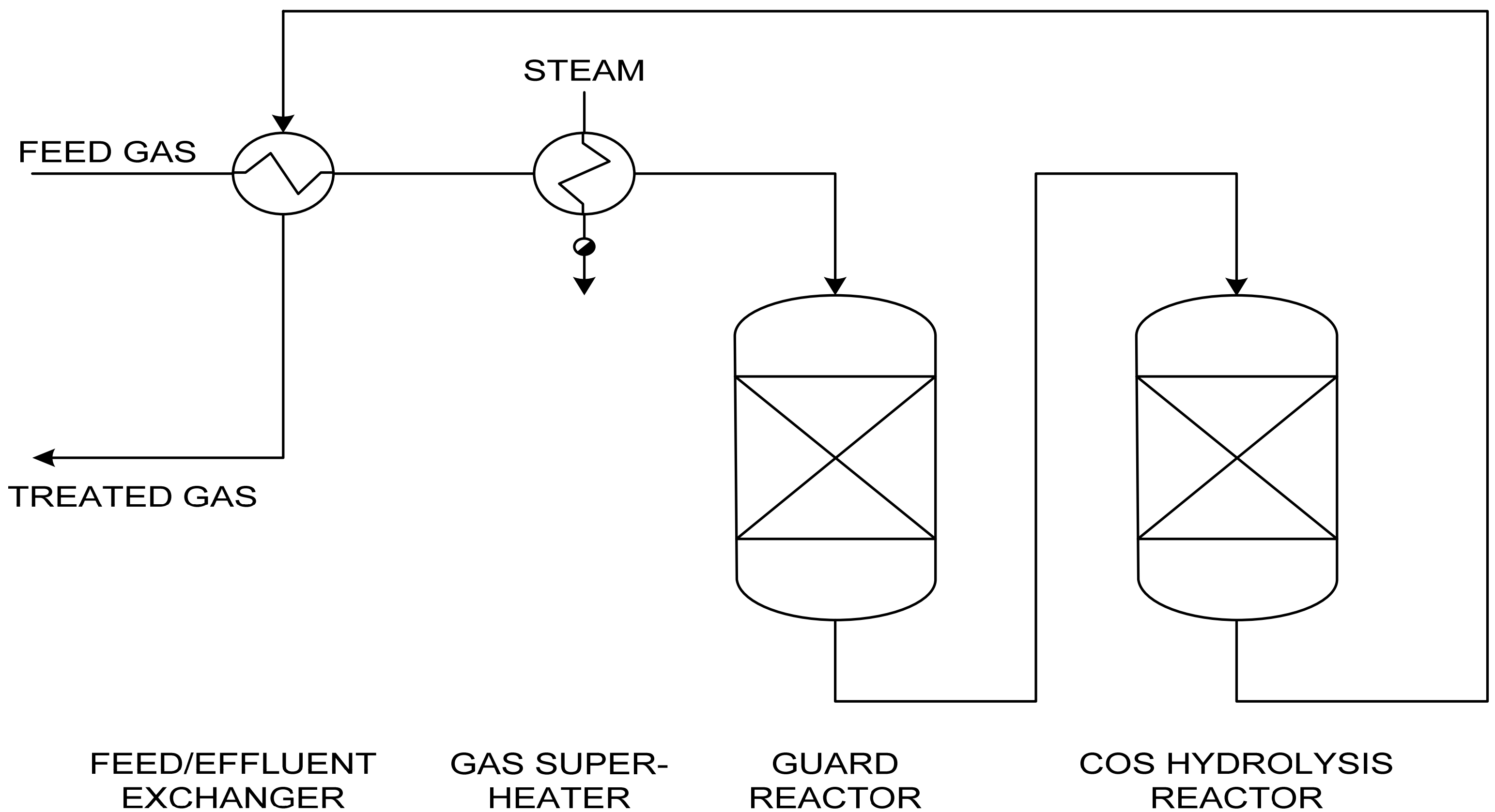
COS Hydrolysis / Simplified PFD

Process Schematic



Source: EPRI UDBS-2007

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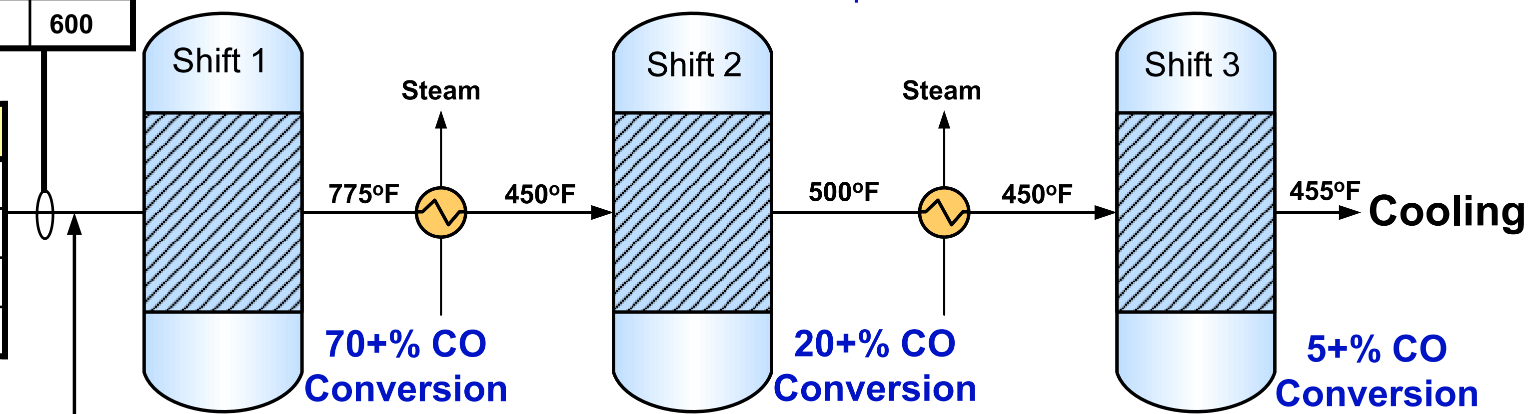
Water-Gas Shift Reactors

Pressure (psig)	
GE RQ	800
GE Q	1000
E-Gas FSQ	600
Shell GQ	600

H_2O/CO Ratio	
GE RQ	1.3
GE Q	≥3.0
E-Gas FSQ	0.4
Shell GQ	0.1

★ Shell WQ ~1.5

Design:
- Haldor Topsoe SSK Sulfur Tolerant Catalyst
- Up to 99% CO Conversion
- H_2O/CO = 2.3 (Project Assumption)
- Overall ΔP = ~30 psia



	Relative HP* Steam Flow
GE RQ	1.0
GE Q	0.0
E-Gas FSQ	2.0
Shell GQ	2.8

*High Pressure Steam

$$H_2O + CO \longleftrightarrow CO_2 + H_2 + Heat$$

Water-Gas Shift Reaction

★ Shell Water Quench design can substantially reduce HP Steam Flow

Steam injection requirements have significant impact on plant performance

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Mercury Capture in IGCC

- Capture on sulfur impregnated activated carbon
- Standard natural gas application for LNG plants
- In syngas service at Eastman Chemical Co. since 1984
- Capture rate ~94% of vapour phase mercury
- Bed life ~ 2 years
- Spent carbon to hazardous landfill

Source: Trapp, 2002

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IGCC CO_2 Capture Technologies
Current & Developmental Systems

Currently Available Technologies

- **MDEA**
- UOP **Selexol**
- Linde **Rectisol**

Developmental Physical Solvent Absorption

- GTI & Uhde – **Morphysorb** Solvent Absorption

Developmental Membrane CO_2/H_2 Separation

- NETL & Eltron **H_2 Transport Membranes (HTM)**
- RTI & Air Liquide **Reverse Selective Polymeric Membranes**

Other Developmental Technologies (NETL + Other Research Organizations)

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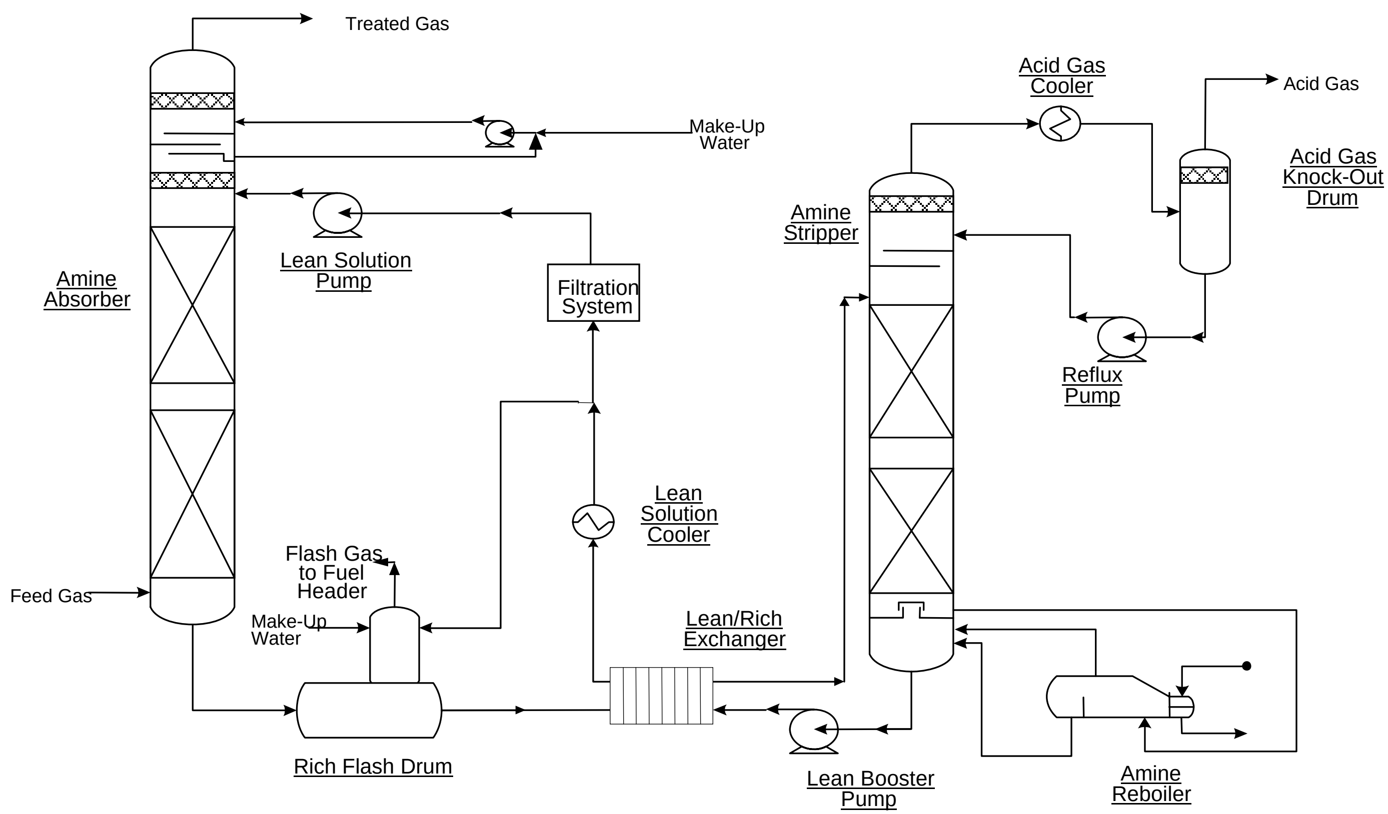
MDEA Process for IGCC

Process Flow Diagram: H_2S Capture Only



AMINE-H2S PROCESS FLOW DIAGRAM

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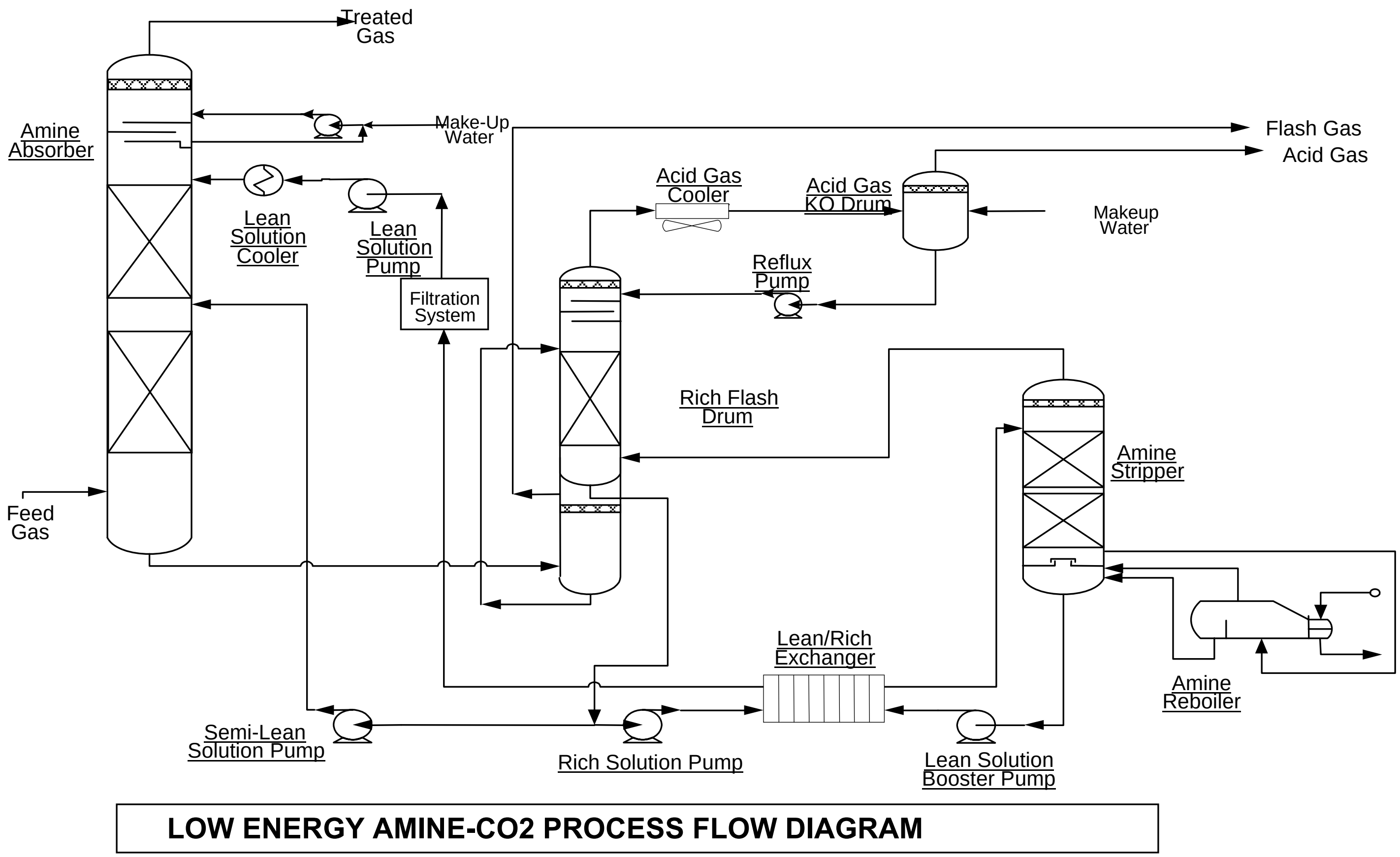
MDEA Process for IGCC

Process Flow Diagram: H_2S and CO_2 Capture (Low energy design)



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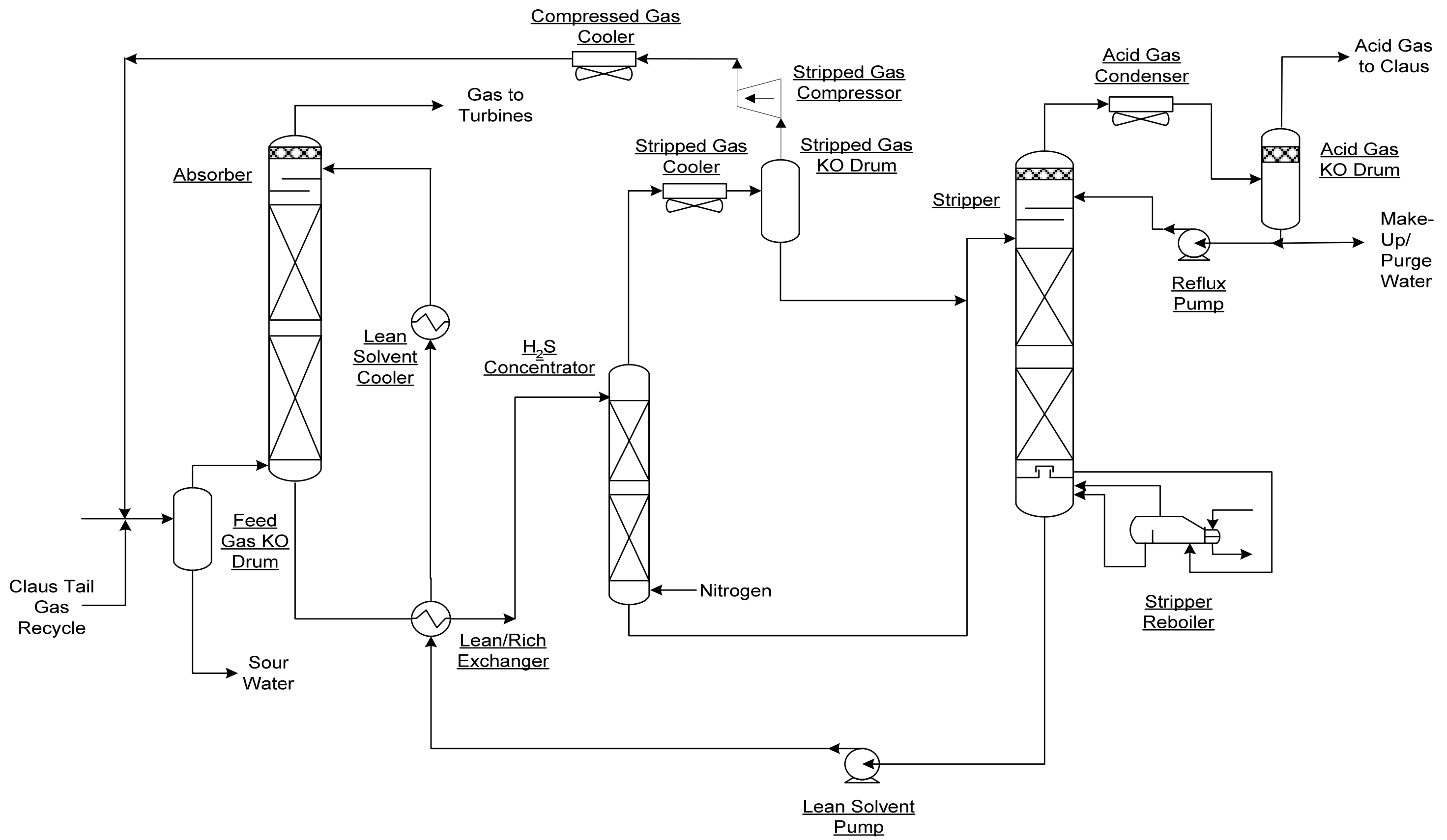
UOP Selexol Process for IGCC

Process Flow Diagram: H_2S Capture Only



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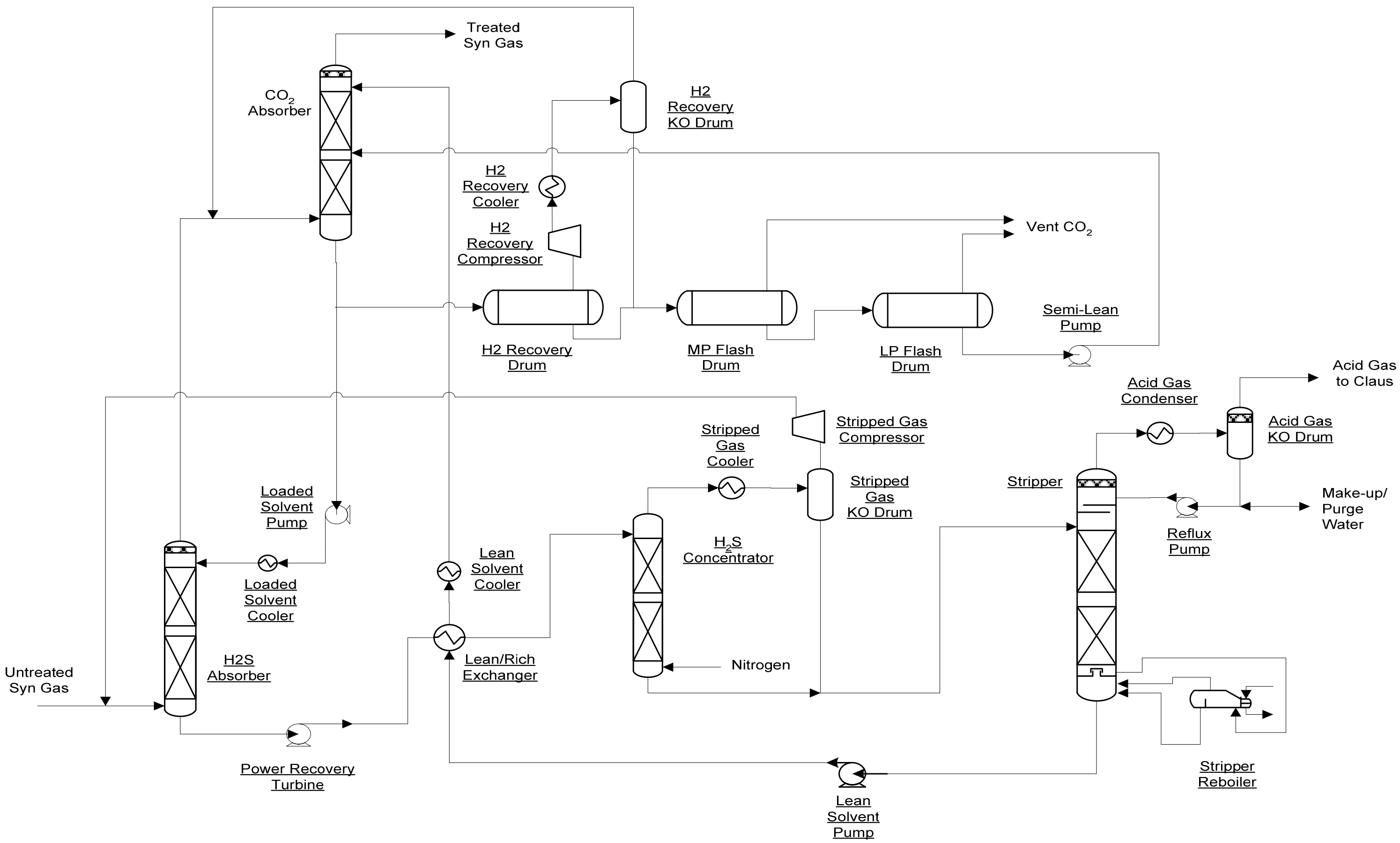
UOP Selexol Process for IGCC

Process Flow Diagram: H_2S and CO_2 Capture (4 tower design)



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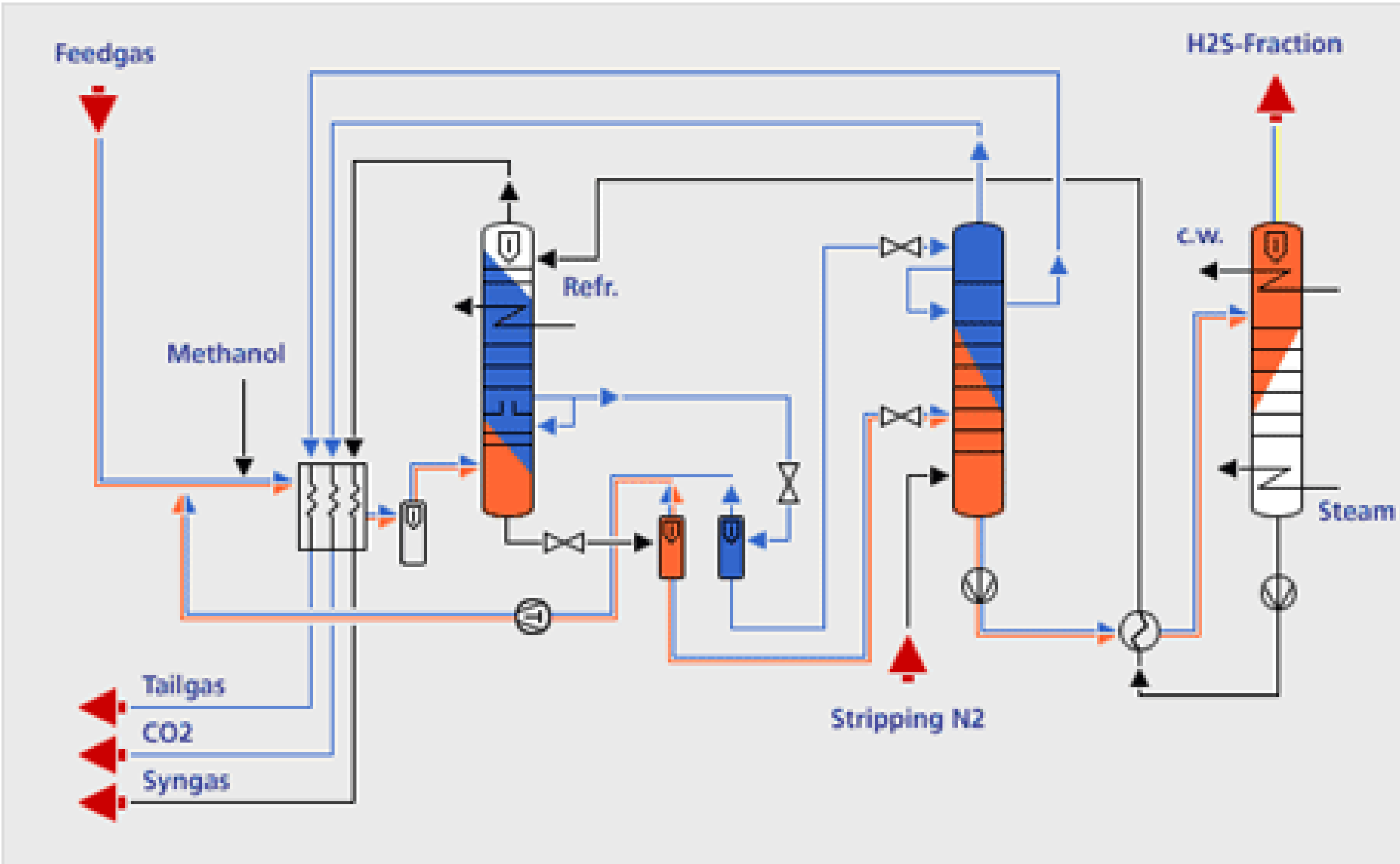
Linde Rectisol for IGCC

Process Flow Diagram: H_2S and CO_2 Capture (3 tower design)



Source: www.linde-anlagenbau.de/process_plants/hydrogen_syngas_plants/gas_processing/rectisol_wash.php

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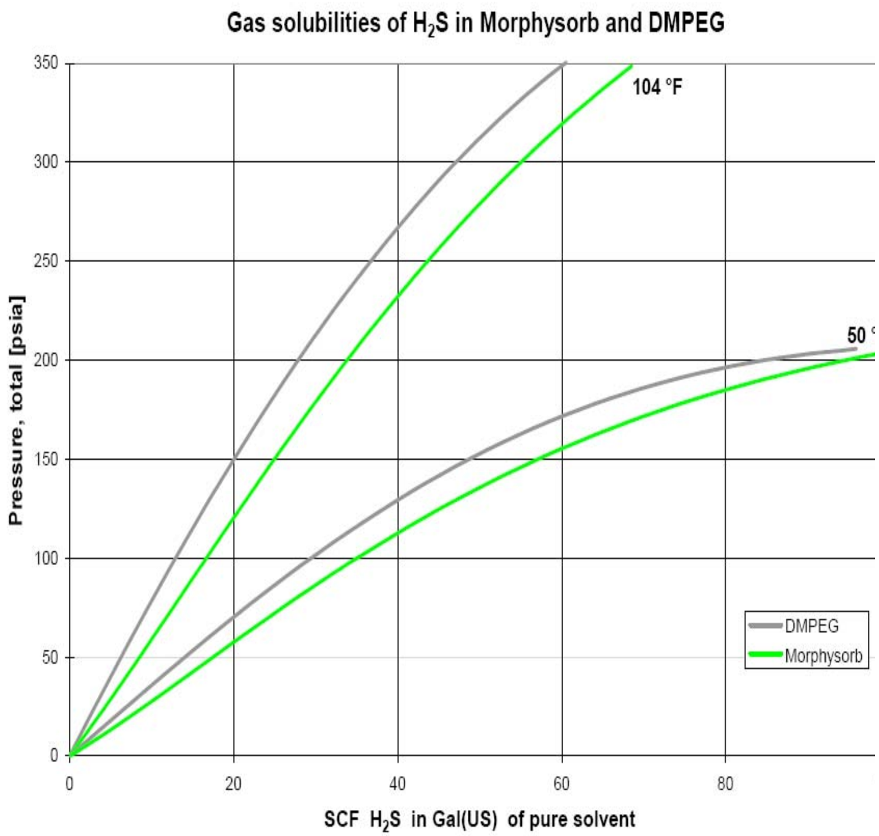
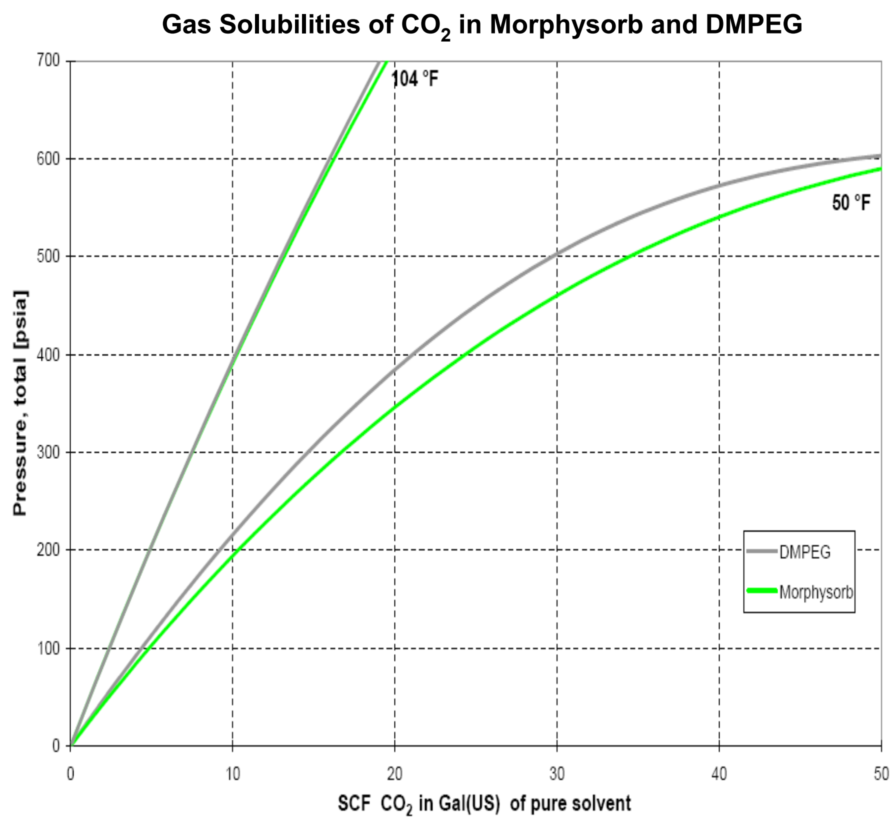
Morphysorb Solvent Process

H_2S & CO_2 Solubility – Morphysorb vs. Selexol (DMPEG)





Source: GTI 2002

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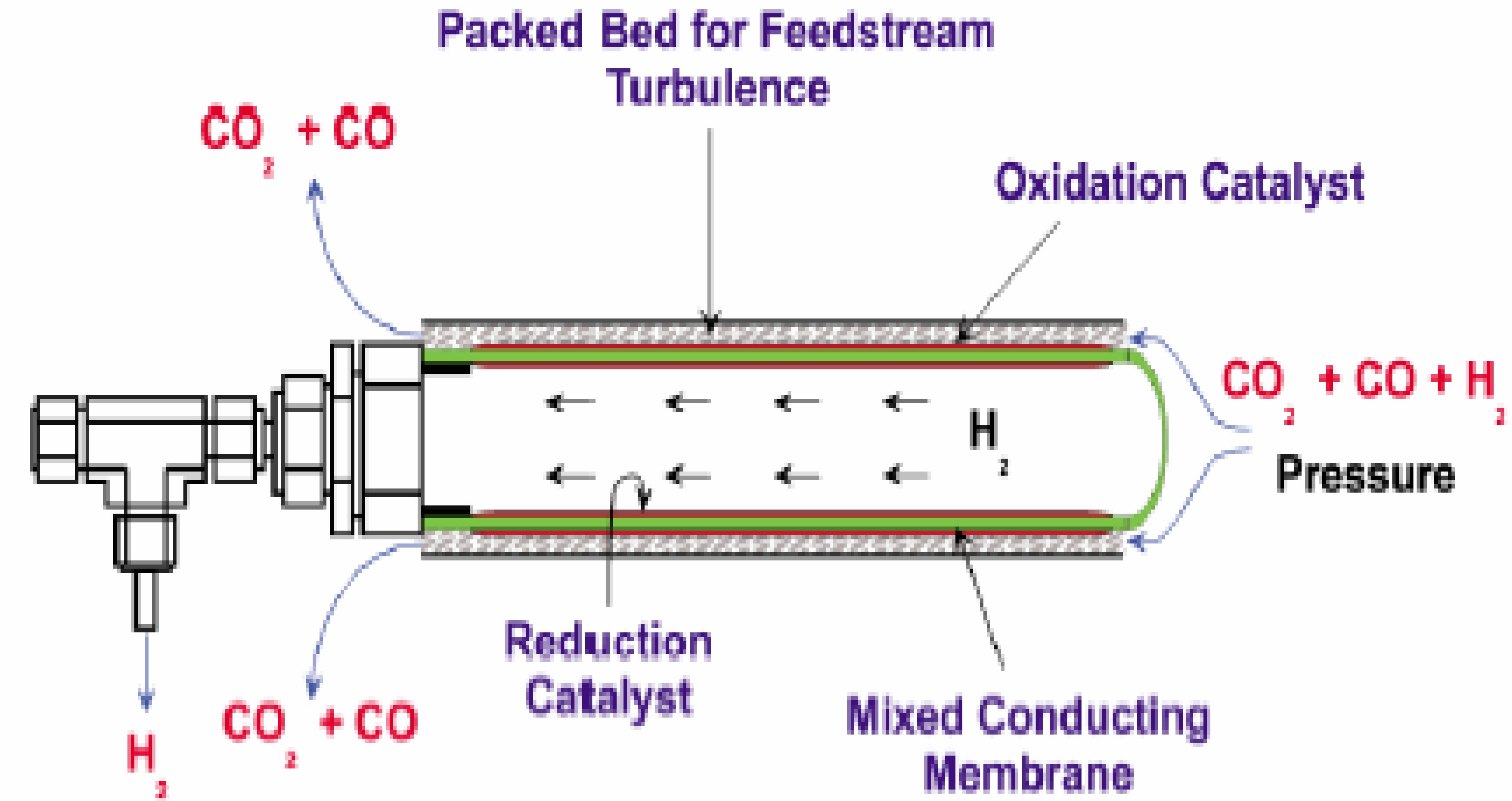
Hydrogen Ion-Transport Membranes
Process Drawing



Source: Eltron 2005

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Reverse Selective Polymer Membranes
Technology Description

<u>Opportunity</u>

Hydrogen production

- Steam reforming or gasification of hydrocarbon fuels, followed by water gas shift reaction

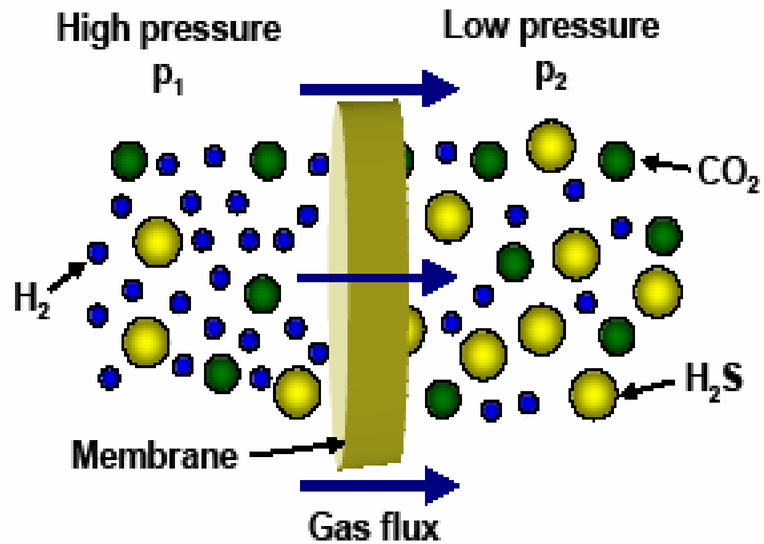
<u>Problem</u>

H_2 product contaminated with CO_2 byproduct and other polar, acid gases (H_2S, COS, etc.)

<u>Technical approach</u>

Reverse-selective membranes for H_2 purification

- Bulk removal of acid gases (CO_2, H_2S)
- Selective permeation of larger acid gases over smaller H_2



<u>Project Team</u>

- RTI International
- The University of Texas at Austin (Academic partner)
- MEDAL, L.P./Air Liquide (Industry partner)
- DOE/NETL (Federal government support)

Source: RTI 2006

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Development Activity for IGCC
Key Long-Term Research Projects

- Stamet pump for dry coal feed
- AP ITM Oxygen process (note: single point failure, no other ASU improvements being funded, need more processes)
- Advanced sulfur removal processes (high temperature or low energy)
- Advanced H_2 and CO_2 separation processes (Solvents or Membranes)
- Advanced H_2-fired combustion turbines (GE and Siemens are current contractors for DOE work)
  - Results need to be extended to H-class CTs
- RamJet CO_2 Compressor (heat recovery improvement)
- Fuel Cell development
- FutureGen
  - Should provide first opportunity to test many of the items above at reasonable scale and realistic conditions

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R&D Work Underway

- SRI International, RTI, & NETL working to quantify the impact of contaminants on fuel cell operation
- TDA Research is researching a catalyst that can remove Arsenic at high temperatures that may also remove some Selenium
  - Testing of system at PSDF with Southern Company should be underway
  - Removal of As and Se would be beneficial for GT and WWT
- Others…?

EPRI may be able to provide support: Contact us with your ideas

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Questions and Discussion

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