

**SYSTEMS ANALYSES OF ADVANCED BRAYTON CYCLES
FOR
HIGH EFFICIENCY ZERO EMISSION PLANTS**

Task 1.2: Identify Overall Baseline Cycle Configuration

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SUMMARY

This document discusses the various process options available or under development for an IGCC facility and a qualitative technology evaluation is conducted in order to identify those options that may be suitable for incorporation in the Baseline Case design.

The selected plant scheme consists of cryogenic air separation unit (ASU) supplying 95% purity O₂ to GE type HP total quench gasifiers. The raw gas after scrubbing is treated in a sour shift unit to react the CO with H₂O to form H₂ and CO₂. The gas is further treated to remove Hg in a sulfided activated carbon bed. The syngas is desulfurized and decarbonized in a Selexol acid gas removal unit and the decarbonized syngas after humidification and preheat is fired in GE 7H type steam cooled gas turbines. HP N₂ from the ASU is also supplied to the combustors of the gas turbines as additional diluent for NO_x control. A portion of the air required by the ASU is extracted from the gas turbines.

An ultra low NO_x (< 2 ppmvd, 15% O₂ basis) sensitivity case is developed by the inclusion of an SCR in each of the heat recovery steam generators (HRSGs). Gas turbine inlet air fogging is also evaluated as a sensitivity case.

Gasifier Technology

Current-state-of-the-art (commercially proven) and near-term gasification technologies are listed below:

- 1) Advanced Transport Reactor
- 2) General Electric (GE)
- 3) Shell
- 4) ConocoPhillips (E-Gas)

The four gasifier types are depicted in Figures 1 through 4 and their major attributes and their suitability are discussed below:

Advanced Transport Reactor

This type of gasifier is depicted in Figure 1 and its main features along with its status are summarized below:

- Bottom-mounted Injectors
- Dry Solid Feeds and Low Operating Temperature
 - Potential for High Cold Gas Efficiency if High Carbon Conversion can be Maintained
 - O₂ Consumption Similar to Previous Gasifier
 - Dried Solids Conveyed by N₂ or Syngas
- Convective Waste Heat Boilers

- ~ 50 tonne/d Process Demonstration Unit (PDU) Operated
- Company & Orlando Utilities Commission to build 285 MW IGCC in Florida.

This gasifier is very suitable for low rank reactive coals where high carbon conversion may be achieved while maintaining a relatively low gasifier operating temperature, i.e., less than 1000°C. The cold gas efficiency can thus be increased while the specific O₂ or air consumption can be kept low. However, in the case of bituminous coals (such as Pittsburgh No. 8 chosen for this study) which tend to be less reactive as compared to the lower rank coals, the PDU experience has shown that the carbon conversion is limited to about 90% while operating in the neighborhood of 1000°C. Based on current operating experience, the carbon conversion is expected to be limited to about 95% by increasing the operating temperature of the gasifier by as much as 50°C.

In light of the above, this gasifier is not chosen for use in the Baseline Case.

GE Gasifier

This type of gasifier is depicted in Figure 2 and its main features and its status are summarized below:

- Top-mounted feed injector
- Solid feeds fed as water slurry
- Syngas with high H₂/CO ratio
- Total Quench (TQ) design
 - Lower capital cost
 - Suitable for sour shift (H₂ production/CO₂ Capture)
- Syngas cooler available for higher efficiency (more suitable in power only applications)
- Commercially proven up to ~ 80 bar operating pressure on oil feed.

The two main characteristics of this type of gasifier which are slurry feed and high operating temperature (in the neighborhood of 1300°C) give it the flexibility to operate at very high pressures and gasify relatively unreactive feedstocks while achieving high carbon conversion especially when recycle of the unconverted carbon is included in the design. On the other hand, these same attributes limit the cold gas efficiency of the gasifier (defined as the ratio of the HHV of the net syngas produced by the gasifier to the HHV of the feedstock) while increasing the specific O₂ consumption.

Three options are available for heat recovery from the raw syngas leaving the gasifier and before it is scrubbed with water: (1) a radiant cooler followed by a convective cooler, (2) only the radiant cooler, and (3) quenching the gas with water by direct contact while eliminating the costly syngas coolers as depicted in Figure 2. For applications involving a high degree of shifting of the syngas to convert most of the CO into CO₂ for capture, the following steps are utilized: (1) shift the raw gas leaving the particulate scrubber utilizing a sour shift catalyst after preheating to the required temperature and (2) remove the CO₂ in the acid gas removal unit used for desulfurization of the syngas, after syngas cleanup / heat recovery. This sour shift

configuration integrates especially well with the GE gasifier incorporating the direct contact cooling of the gasifier effluent (“total quench” design). Steam injection into the raw gas upstream of the shift unit is not required, since the moisture present in the scrubber outlet gas is sufficient. It also simplifies the design of a physical solvent-based acid gas removal unit (required to remove the sulfur compounds and the CO₂) as explained later. This type of gasifier is highly suitable for zero emission IGCC plants but for IGCC plants without CO₂ recovery where high efficiency is a primary goal, this type of gasifier may not be the optimum choice.

In light of the above, this gasifier is chosen for use in the Baseline Case.

Shell Gasifier

This type of gasifier is depicted in Figure 3 and its main features are summarized below:

- Horizontally opposed injectors near bottom for solid feeds
- Dry solid feeds
 - Potential for higher cold gas efficiency
 - Lower O₂ consumption
 - Dry solids conveyed by N₂
 - Convective waste heat boilers
- Membrane wall gasifier for solid feeds
- Reduction of waste heat boiler inlet temperature by gas recycle
- Candle filters remove dry solids from syngas
- Pressure limited to ~ 40 bar.

The Shell gasifier is offered with syngas coolers as depicted in Figure 3 which tends to maximize the heat recovery. The Shell gasifier with its dry feed system has a lower O₂ demand, typically about 5 to 6% lower than the GE gasifier. The lower O₂ demand does reduce the cost of the air separation unit but the cost savings are typically largely off-set by the higher cost of the gasifier and its high temperature syngas coolers as compared to the GE gasifier system with the total quench design. Also, the dry feed system with its drier and other special equipment, has greater power consumption, higher costs and limits the operating pressure of the gasifier as compared to a gasification system using a slurry feed. The Baseline Case as well as the more advanced Brayton cycles to be investigated under Task 2 of this program as explained later, will require the gasifier to operate at a pressure in excess of 40 bar in order to supply the syngas at a pressure consistent with the requirement of the high pressure ratio advanced gas turbines.

In light of the above, this gasifier is not chosen for use in the Baseline Case.

E-Gas Gasifier

This type of gasifier is depicted in Figure 4 and its main features are summarized below:

- Horizontally opposed bottom injectors with upward flow of syngas
- Feed injected in top section (2nd stage) also but without O₂
 - Evaporation of slurry water and endothermic reactions help cool syngas to limit temperature in syngas cooler
 - Increases cold gas efficiency
- Reduction of syngas cooler inlet temperature by gas recycle
- Candle filters for recovery of entrained ash and unconverted carbon for recycle directly to gasifier (i.e., without slurring)
- Commercially proven at ~ 30 bar operating pressure but higher operating pressure conceptualized.

The E-Gas gasifier with its two stages has a lower O₂ demand, typically about 5% lower than the GE gasifier. The lower O₂ demand reduces the cost of the air separation unit. The lower O₂ demand results in increasing the cold gas efficiency of the E-Gas gasifier over the GE gasifier. The CO/H₂ ratio and the CH₄ content in the syngas both tend to be higher than those for the GE gasifier which are disadvantages for a plant incorporating CO₂ capture. The higher CO/H₂ ratio increases the load on the downstream shift unit while the higher CH₄ content limits the amount of CO₂ capture.

The overall efficiency of the IGCC utilizing this type of gasifier has been shown to be similar to that of a Shell gasifier based plant but a proposed design improvement consisting of increasing the amount of slurry fed to the E-Gas gasifier 2nd stage would increase its cold gas efficiency significantly. When a greater fraction of the slurry is fed to the 2nd stage however, the temperature within the gasifier in this 2nd stage is reduced which may result in a lower destruction of the tars and oils and CH₄ formed during the pyrolysis step within the 2nd stage. The presence of tars and oils in the raw syngas will pose special challenges to their gas cleanup process while the higher concentration of CH₄ will further limit the amount of carbon capture.

In light of the above, this gasifier is not chosen for use in the Baseline Case.

Air Separation Technology

The largest consumer of parasitic power in an IGCC is the ASU. ASU power consumption constitutes more than half of the total power consumed by the plant or 10 to 20 percent of the total power produced by the plant. Thus, technologies are being developed as well as various studies have been performed with the intent to minimize this parasitic power consumption of the plant.

High Temperature Membrane Technology

Praxair as well as Air Products are developing membranes (semi-conductor materials) that operate at temperatures in the neighborhood of 800°C to 900°C (1500°F to 1600°F) for air separation. This technology promises reduction in both power consumption and capital cost by

about 30%. Praxair, however, points out that for this technology to be economical, it will require the integration of the membrane unit with a gas turbine capable of roughly 50% of the total gas turbine inlet air (i.e., air entering the gas turbine compressor) being available for extraction. The integrated system consists of providing hot pressurized air extracted from the gas turbine compressor to the membrane unit which separates a portion of the O₂ by transferring the O₂ as ions through the membrane wall while the depleted air is returned to the gas turbine. Thus the gas turbine must also be capable of receiving the depleted air from the membrane unit which is typically at 800°C to 900°C (around 1500°F to 1600°F), the operating temperature of the membrane unit. Note that the air supplied to the membrane unit is preheated to the operating temperature of the membrane unit by directly firing syngas into the air stream. The depleted air exiting the membrane unit consists of a stream that has an O₂ content that is lower than that of fresh air; a portion of the O₂ being separated from the air stream by the membrane.

Air Products has stated at the Gasification Technologies Council Annual Meeting [Armstrong, 2006] that a large scale ITM unit with a capacity of 2,000 ST/D (1800 MT/D) will be available for demonstration in 2012. The challenge still remains that a gas turbine with the above stated 50% extraction rate is required and such gas turbines are not expected to be available in the near-term.

In light of the above, this technology is not chosen for use in the Baseline Case but may be considered for the Advanced Brayton Cycles to be investigated under Task 2 of this program.

Cryogenic Technology

O₂ Purity

The optimum O₂ purity for IGCC applications with low pressure (LP) or HP cryogenic ASUs is 95% based on internal studies made by both Praxair and Air Products for the Demkolec IGCC plant. The number of distillation stages decreases steeply as the purity is reduced from 99.5% to 95%, but remains quite insensitive as the purity is further reduced. The O₂ compression costs (both capital and operating) continue to increase as purity is decreased below 95%. Note that the size of equipment downstream of the ASU also increases (slightly) while the efficiency of the gasification unit decreases as the purity is reduced.

A paper published by Linde [Baker, 1981] supports the above stated relationship between the number of stages and the O₂ purity although the results are for an LP ASU. The separation energy according to the Linde paper also tends to flatten off at purity levels below 95%.

Thus 95% purity O₂ will be utilized for all the cases incorporating a Cryogenic ASU, i.e., including the Baseline case.

HP versus LP ASU and Gas Turbine Air Extraction

For IGCC applications, HP ASUs are preferred over LP ASUs since the oxygen and nitrogen product can be used at elevated pressures, and air extraction from the gas turbine for the ASU is

possible. The operating pressure of the ASU distillation operation affects the bubble point of the liquid being distilled in the cold box. The higher the pressure, the less severe the cold box temperature is, which results in a reduced pressure ratio of the incoming air to that of the outgoing streams (O₂ and N₂). If the O₂ and the N₂ leaving the cold box can be utilized within the gasification plant at the product supply pressure or higher, then a net increase in the overall IGCC plant efficiency is realized. The HP N₂ produced by the cold box is further compressed and fed to the gas turbine for increased power output and NO_x reduction.

Results from previous studies have indicated that about 2% reduction in both the plant heat rate and plant cost may be realized by installing the HP ASU over the LP ASU. Both the Demkolec IGCC and the Polk County IGCC utilize an HP ASU (with 95% purity O₂).

The feed air pressure for an LP ASU is in the range of 350 to 600 kPag (50 to 90 psig) while the feed air pressure for an HP ASU is typically set based on the pressure of the air extracted from the gas turbine which corresponds to the discharge pressure of the gas turbine compressor. Note that extraction of air from the gas turbine compressor discharge increases the commonality for the gas turbine design for both IGCC and natural gas applications. When the feed air pressure is very high, a partial expansion step may be required in order to limit the operating pressure of the cold box such that the relative volatility between O₂ and N₂ is not too close to unity in order to limit the number of stages required in the distillation operation. The advanced Brayton cycle as explained later is expected to have a high pressure ratio (in excess of 30) and thus a partial expansion step is foreseen. The other option consisting of mid-compressor air extraction may not be practical from a gas turbine design standpoint since such a design would limit the versatility and fuel flexibility of the gas turbine.

Based on the above considerations, an HP ASU will be utilized with partial air and full N₂ integration with the gas turbine in the Baseline case.

Acid Gas Removal Technology

The various impurities that may be present in raw syngas are listed in Table 1. Conventional (proven) technology for cleanup consists of “Cold Gas Cleanup,” i.e., cleanup of the syngas near ambient temperatures. “Warm Gas Cleanup” technology is being developed to treat syngas in the temperature range of 300° to 400°C with the potential for increasing the thermal efficiency of the plant while minimizing the generation of a waste water stream (condensate stream formed during cooling of the raw syngas below its water dew point). The two types of technologies are described in the following along with the justification for recommending the Cold Gas Cleanup technology for the Baseline Case.

Warm Gas Cleanup

The first required step in this process is the removal of particulates from the syngas. Barrier filters are required with the requirement to remove over 99.99% of the particulates entrained in

the syngas to protect the downstream cleanup units. The syngas may then be treated in a nahcolite bed to remove chlorides as well as the other halides. This will have to be followed by another barrier filter after which it may be treated with ZnO. This treatment process with the ZnO may be accomplished in a transport desulfurizer in order to make the process continuous since the ZnO is converted to ZnS which has to be regenerated. The regeneration may be accomplished using air extracted from the gas turbine to release the sulfur as SO₂ from which the saleable product H₂SO₄ may be made.

Warm gas mercury removal processes are also being developed and one such process is that being developed by ADA technologies (funded by the EPA and the DOE) that operates around 300° to 400°C [Butz 2003] and uses a fixed bed reactor containing an Amended Silicates™ sorbent where the mercury is chemisorbed from the syngas.

Most (~90%) of the nitrogen containing compounds such as NH₃ and HCN if present in the syngas fed to the gas turbine will form NO_x and thus removal of these components is essential for a “Clean Coal” plant. Technologies are being investigated for this cleanup step but are at a very preliminary stage of development.

Warm gas cleanup technologies to capture components such as the metal carbonyls as well as the very fine particulates formed by the condensation of the volatile alkali salts are also required to meet the very stringent specifications expected for the advanced Brayton cycle gas turbine operating at elevated temperatures. Based on the current status of this technology, it will not be used in the baseline Baseline Case but will be considered for application in the Advanced Cases to be investigated under Task 2 of the project.

Cold Gas Cleanup

The selection of the acid gas removal process for desulfurization and decarbonization of the syngas is described next followed by a description of the processes recommended for the removal of metal carbonyls and mercury (as well as arsenic, cadmium and selenium).

Acid Gas Removal

The proposed scheme for controlling the carbon emissions consists of the following steps: (1) shifting of the raw syngas leaving the particulate scrubber utilizing a sour shift catalyst after preheating to the required temperature, (2) heat recovery and gas cleanup to remove trace components, and (3) capture of the CO₂ in the acid gas removal unit used for desulfurization of the syngas.

The following five acid gas removal technologies are considered:

1. Amine Scrubbing
2. Rectisol
3. Benfield (licensed by UOP)
4. Morphysorb (licensed by Thyssen Krupp)
5. Selexol™ (licensed by UOP)

The amine scrubbing process with additives to improve the selectivity between H₂S and CO₂ absorption does not produce an acid gas suitable for even a Selectox sulfur recovery unit, as a minimum of 5% H₂S concentration is required in its feed gas for stable operation. An acid enrichment unit is required and in addition to this enrichment step, another amine unit to remove additional CO₂ that slips through the primary amine unit is required. The equivalent power consumption (net electric power + thermal energy of low pressure steam converted to electric power using an appropriate conversion efficiency) of the amine-based unit is significantly higher than the Selexol-based unit.

With respect to the Benfield process, it is found that it is unable to meet the sulfur specifications in the product gases, and cannot demonstrate selectivity between H₂S and CO₂, which is critical to this application. The modest incremental back pressure of the Regenerator does not overcome its serious deficiencies for this application.

Since the sulfur specification for the fuel gas is not too stringent, it is not necessary to install a Rectisol unit, the Rectisol unit tends to be relatively expensive, and its use is typically justified when the treated gas suitable for chemical synthesis is required (< 0.1 ppmV sulfur).

The Morphysorb process which utilizes a physical solvent is a potential candidate especially suitable to IGCC applications where large amounts of sour gas components have to be removed. The solvent has already been used for the sour gas removal from natural gas in a plant located in Kwoon, British Columbia, Canada and has proven to be a safe and reliable process for more than two years. However, little experience if any exists with treating of coal derived syngas in the Morphysorb process, the first application to syngas was to be tested at the FlexFuel facility in Des Plaines by the Gas Technologies Institute. The licensor of this process is not willing to provide any performance information at the current time and wants to wait till they have obtained significant data from field testing. This technology will be considered for application in the Advanced Cases to be investigated under Task 2 of the project contingent upon the availability of licensor data, while for the Baseline case, the Selexol™ process will be utilized since it does not suffer from the disadvantages pointed out for the first three processes listed above.

Metal Carbonyls

Metal carbonyls that may be present in the raw gas, such as those of nickel and iron, deposit as nickel sulfide at elevated temperatures (such as those in the shift reactors) in the presence of a catalyst in the top layers of the first-stage shift reactor catalyst bed. It has been found that the top 0.5 meters (1 to 2 ft) of the shift catalyst needs to be replaced approximately every two years due to increased pressure drop caused by the sulfide deposition. The impact on the annual operating cost of replacing the top section of the bed at a greater frequency (2 years instead of the normal 3 years) is not expected to have a very significant effect on the overall economics of the plant.

Mercury, Arsenic, Cadmium and Selenium

These metals typically volatilize within the gasifier and leave the gasifier along with the raw syngas. Sulfided activated carbon has been used to remove mercury and arsenic from coal

derived syngas at the Tennessee Eastman gasification plant. Calgon offers this type of activated carbon for removal of mercury, reducing its concentration to as low as 0.01 to 0.1 $\mu\text{g}/\text{Nm}^3$ Hg in the syngas depending on the operating temperature and moisture content. Mercury is captured predominantly as a sulfide, but some of it is captured in its elemental form. The spent carbon has to be disposed off as a hazardous waste although attempts are being made to recover elemental Mercury. Mercury capture by sulfided carbon beds is unaffected by pressure of the syngas. The capture efficiency is reduced, however, as the operating temperature is increased and as the relative humidity of the syngas is increased.

Experience at the Tennessee Eastman plant indicates that activated carbon is even more effective in capturing the arsenic. Calgon's experience has shown that arsenic if present in the form of an arsine, is captured by this sulfided carbon. SudChemie offers the activated carbons for removal of arsenic and its compounds. A copper impregnated carbon is offered to capture arsenic if present as an organic compound.

Other volatile metal compounds that may be present in coal derived syngas are those of cadmium and selenium. Capture of these species by the activated carbon is yet to be ascertained. Any metal (Ni and Fe) carbonyls that may remain in the syngas may be expected to be captured by the sulfided activated carbon bed.

Power Generation Technology

Fuel Cell Hybrids

Higher conversion efficiencies are achievable with a fuel cell when compared to heat engines; the chemical energy is directly converted into electricity, the intermediate step of conversion into heat as in a heat engine is eliminated, and thus without being constrained by temperature limitations of the materials as in the case with heat engines. A fuel cell based hybrid cycle consists of combining a fuel cell with a heat engine to maximize the overall system efficiency. Overall system efficiencies greater than 60% on natural gas on an LHV basis may be achieved (cycles approaching 75% efficiency on natural gas on an LHV basis have been identified [example: Rao and Samuelsen, 2003]). High temperature fuel cells such as solid oxide and molten carbonate fuel cells are most suitable for such applications. In the case of a high pressure fuel cell based hybrid, the combustor of the gas turbine is replaced by the fuel cell system [Litzinger, et. al., 2005; Agnew, G., et. al., 2005; Schonewald, 2005] while in the case of a low pressure fuel cell based hybrid [Ghezal-Ayagh, 2004], the heat rejected by the fuel cell may be transferred to the working fluid of the gas turbine through a heat exchanger (indirect cycle).

The fraction of the total power produced by the fuel cell in a Solid Oxide Fuel Cell (SOFC) hybrid based power plant is approximately 70%. Thus, for a central station power plant producing nominally 250 MW gross, the SOFC would have to generate as much as 175 MW. This represents a scale up of orders of magnitude over the currently demonstrated units, which have been limited to less than a MW size. Even if the power block is split up into four modules, the size of each SOFC stack module would still require a very large scale-up. In addition to scale-up, another challenge consists of developing materials that allow much higher current densities, orders of magnitude higher than the current values, in order to reduce the physical size

to something more manageable from a plot space and piping standpoint. Note that for a 50 MW SOFC, the estimated required cross-sectional area for oxygen ion transport or flow of current within the cells is greater than 10,000 m² with today's current densities.

For the reasons mentioned above, fuel cells will not be employed in the Baseline Case.

Gas Turbine based Cycles

A conventional gas turbine cycle consists of pressurizing a working fluid (air) by compression, followed by combustion of the fuel; the energy thus released from the fuel is absorbed into the working fluid as heat. The working fluid with the absorbed energy is then expanded in a turbine to produce mechanical energy, which may in turn be used to drive a generator to produce electrical power. Unconverted energy is exhausted in the form of heat which may be recovered for producing additional power. The efficiency of the engine is at a maximum when the temperature of the working fluid entering the expansion step is also at a maximum. This occurs when the fuel is burned in the presence of the pressurized air under stoichiometric conditions.

When natural gas is burned with air under stoichiometric conditions, however, the resulting temperature is greater than 1940°C (3500°F) depending on the temperature of the combustion air. It is therefore necessary to utilize a large excess of air in the combustion step, which acts as a thermal diluent and reduces the temperature of the combustion products, this temperature being dependent on the gas turbine firing temperature which in turn is set by the materials used in the turbine parts exposed to the hot gas, and the cooling medium (its temperature and physical properties) as well as the heat transfer method employed for cooling the hot parts. A fraction of the air from the compressor is bled off as cooling air when air is utilized for cooling, the air being extracted from the compressor at appropriate pressures depending upon where it is utilized in the turbine. From a cycle efficiency and engine specific power output (kW per kg/s of suction air flow) standpoint, it is important to minimize the amount of cooling air as well as the excess combustion air.

The necessity to use a large excess of pressurized air in the combustor as well as for turbine cooling when air cooling is employed creates a large parasitic load on the cycle, since compression of the air requires mechanical energy and this reduces the net power produced from the system, as well as reducing the overall efficiency of the system.

Some of the more promising cycle configurations and technology advancements being pursued are discussed in the following directed at increasing the performance of the basic Brayton cycle.

Humid Air Turbine (HAT) Cycle

The mechanical energy required for air compression in the Brayton cycle can be reduced by utilizing interstage cooling. However, from an overall cycle efficiency standpoint, interstage cooling can be utilized advantageously if the heat removed from the compressed air in the intercooler can be efficiently recovered for conversion to power. If the entire heat is simply rejected to the atmosphere, the overall cycle efficiency may actually decrease depending upon

the cycle pressure ratio, since it results in the consumption of more fuel to compensate for the energy lost through the intercooler. Only at very high pressure ratios can intercooling be justified in most cycles.

In the HAT cycle [Rao, 1989] a significant portion of the excess air that is required as thermal diluent in a gas turbine, is replaced with water vapor (see Figure 5). The water vapor is introduced into the system in an efficient manner, by pumping of a liquid followed by low temperature evaporation. Pumping a liquid requires less mechanical energy compared to gas (air) compression. Evaporation of the water into the compressed air stream is accomplished using low temperature heat, in a counter-current multistage humidification column, rather than generating steam in a boiler. This method of humidification permits the use of low temperature heat for accomplishing the evaporation of water. For example, water which boils at 100°C (212°F) at atmospheric pressure may be made to evaporate at room temperature when exposed to a stream of relatively dry air.

The process also reduces the parasitic load of compressing the combustion air by intercooling the compressor, while recovering most of the heat removed in the intercooler for the humidification operation. Thus, a more thermally efficient power cycle is achieved. Humidification of the compressed air also leads to a reduction of NO_x emissions. The humid air is preheated by heat exchange with the turbine exhaust in a recuperator to recycle the exhaust energy to the combustor, thereby eliminating the expensive steam bottoming cycle required in a combined cycle.

The advantages of the HAT cycle are:

- Less than 5 ppmV NO_x without post-combustion treatment
- High efficiency without a steam bottoming cycle
- Excellent part-load performance, efficiency essentially constant down to 60% of full load
- Performance quite insensitive to ambient temperature
- Water usage less than that for a combined cycle employing wet cooling tower and if desired, water may be recovered from HAT exhaust
- High specific power output
- Integrates synergistically with reliable low-cost “Total Quench” gasifier
- In coal based Zero Emission plants, the “Total Quench Gasifier” option is of choice
- In natural gas Zero Emission based plants where CO₂ is recovered from exhaust, CO₂ concentration is higher (dry basis).

Despite the HAT cycle’s potential advantages, the development of the required turbo-machinery is occurring at a very slow pace, mainly due to the very high development costs for developing the required large intercooled gas turbine. Studies sponsored by EPRI have found that the costs of developing the engine could be as high as \$700 to 800 million. Based on the current status of this technology, it will not be used in the Baseline Case but will be considered for application in the Advanced Cases to be investigated under Task 2 of the project.

Oxy-Fuel Cycles

Another promising approach is oxy-fuel combustion for ultra high temperature and high pressure “steam turbines” [Jericha, et. al., 1995; Smith et. al., 2000]. In these systems, the fuel is combusted utilizing a relatively pure O₂ stream to create a working fluid for the turbine composed mostly of water, and CO₂. The design of these systems would facilitate the capture of essentially all of the CO₂ and all of the Clean Air Act criteria pollutants such as NO_x and SO_x and other unregulated pollutants depending on the purity constraints set for the product CO₂ stream for sequestration. The syngas cleanup system will be simplified significantly resulting in efficiency and capital cost benefits if these criteria pollutants are allowed to be contained in the captured CO₂ stream leaving the plant. Only particulate cleanup would be required in the syngas cleanup process.

These cycles do not require a shift unit upstream of the power block as is done in the other cycles that consist of pre-combustion CO₂ recovery in Zero Emission power plant applications. Thus, from a thermal performance standpoint such cycles have the advantage of not by-passing the thermal energy produced during the exothermic shift reaction around the topping cycle as is done in the other cycles consisting of pre-combustion CO₂ recovery. In the pre-combustion CO₂ recovery based cases, the thermal energy generated in the shift unit enters the bottoming steam cycle directly. In Oxy-Fuel cycles, the CO₂ is captured from the exhaust of the turbine in the condenser. The disadvantage, however, is that the CO₂ is recovered at low pressure (at sub-atmospheric pressure) and requires a significant amount of compression power to pressurize the CO₂ before it may be transported for sequestration. Alternate schemes to extract the CO₂ at higher pressure should be investigated as well as system configurations that produce excess hydrogen for export.

A large amount of O₂ is also required as compared to the pre-combustion CO₂ recovery schemes. An Ion Transport Membrane (ITM) unit would be required to produce the O₂ for both the gasifiers and the power cycle in order to limit the negative effects on plant performance and cost due to the demand for a large quantity of O₂.

Development needs include the design of the combustor as well as the “steam turbine” which has many of the features of a gas turbine. An organization with significant involvement in the development of such a system in the U.S. is Clean Energy Systems, Inc.

Based on the current status of this technology, it will not be used in the Baseline Case but will be considered for application in the Advanced Cases to be investigated under Task 2 of the project.

Partial Oxidation Cycles

One form of this cycle is depicted in Figure 6. This concept is similar to a reheat cycle except that the first combustor is operated under sub-stoichiometric or partial oxidation conditions [Korobitsyn, Kers and Hirs, 1998; Newby et. al., 1997]. Following the sub-stoichiometric stage, oxidation of the fuel is completed in the second combustor after expansion in the high pressure turbine. This is an alternative scheme that may be used to limit the firing temperature while gaining efficiency. The absence of excess O₂ in the first stage combustor decreases NO_x formation. Potential challenges are (1) due to the metallurgical issues such as H₂ embitterment

and metal dusting within the partial oxidation combustor as well as the high pressure turbine, (2) soot formation within the partial oxidation combustor and (3) design of the high pressure turbine seals to contain the CO and H₂ at the high temperature and pressure. A large addition of steam may be required to circumvent Concerns 1 and 2 while a buffer gas such as N₂ (supplied by the ASU) may be required for the seals (Concern 3). Humidification of the syngas or of the oxidant (as in the case of the HAT cycle described previously) could be used to replace some or all of the steam required by the partial oxidation combustor while utilizing low temperature heat for the humidification operation in order to enhance the overall plant efficiency. The oxidant may consist of O₂ instead of air in the case of a Zero Emission plant that utilizes an Oxy-Fuel Cycle described previously.

Based on the current status of this technology, it will not be used in the Baseline Case but will be considered for application in the Advanced Cases to be investigated under Task 2 of the project.

Advanced Brayton Cycles

Some of the technological advances being made or being investigated to improve the basic Brayton cycle include the following, in addition to the changes in the basic cycle configuration such as the inclusion of reheat combustion, intercooling (which is justified for very high pressure ratio cycles) and fogging of the compressor inlet air:

- Rotor inlet temperature of 1700°C (3100°F) or higher which would require the development and use of advanced materials including advanced thermal barrier coatings and turbine cooling techniques including closed loop steam cooling
- Advanced combustor liner (combustion air and combustion products being hotter) required due to increases in rotor inlet temperatures
- High blade metal temperature in the neighborhood of ~1040°C (1900°F) while limiting coolant amount would again require the development and use of the advanced materials including advanced thermal barrier coatings
- Pressure gain combustor
- Cavity or trapped vortex combustor to reduce NO_x formation
- High pressure ratio compressor (greater than 30 to take full advantage of higher firing temperature)
- Integration capability with high temperature ion transport membrane air separation in IGCC applications.

Addition of novel bottoming cycles is yet another approach to improving the overall plant (combined cycle) performance. Overall cycle efficiencies approaching 65% on natural gas on an LHV basis may be expected (see Figure 7) utilizing these advanced technology gas turbines. Some of these developments and challenges are described in the following and then a recommendation is made regarding the selection of the power technology for the Baseline Case.

Gas Turbine Firing Temperature

Current-state-of-the-art gas turbines for land-based applications have firing temperatures (rotor inlet temperatures) that are as high as about 1430°C (2600°F) on natural gas base-loaded

operation. This increase in firing temperature has been made possible by being able to operate the turbine components (that come into contact with the hot gasses) at higher temperatures while at the same time utilizing closed circuit steam cooling. In a state-of-the-art air-cooled gas turbine with firing temperature close to 1320°C (2400°F), as much as 25% of the compressor air may be used for turbine cooling, which results in a large parasitic load of air compression. In air cooled gas turbines, as the firing temperature is increased, the demand for cooling air is further increased. Closed circuit steam cooling of the gas turbine provides an efficient way of increasing the firing temperature without having to use a large amount of cooling air. Furthermore, steam with its very large heat capacity is an excellent coolant. Closed circuit cooling also minimizes momentum and dilution losses in the turbine while the turbine operates as a partial reheater for the steam cycle. Another major advantage with closed circuit cooling is that the combustor exit temperature and thus the NO_x emissions are reduced for a given firing temperature; the temperature drop between the combustor exit gas and the turbine rotor inlet gas is reduced since the coolant used in the first stage nozzles of the turbine does not mix with the gasses flowing over the stationary vanes. Note that control of NO_x emissions at such high firing temperatures becomes a major challenge. The GE H series gas turbines as well as the Siemens and Mitsubishi G series gas turbines incorporate steam cooling although the GE turbine includes closed circuit steam cooling for the rotors of the high pressure stages.

Taking the firing temperature beyond 1430°C (2600°F) poses challenges for the materials in the turbine hot gas path. Single crystal blading has been utilized successfully in advanced turbines but in addition to this, development of advanced thermal barrier coatings would be required. Extensive use of ceramics may be predicated for firing temperature near 1700°C (3100°F).

Use of a reheat or sequential combustor in a gas turbine is an alternative scheme that may be used to limit the firing temperature while gaining efficiency. Such a scheme as depicted in Figure 8 has been commercialized by Alstom in their GT 24 and 26 engines. For a given firing temperature, the gain in combined cycle heat rate is approximately 2% with the use of a reheat combustor. Another advantage is the reduced NO_x emission due to both the lower firing temperature and the destruction of some of the NO_x that is formed in the first combustor by the reheat combustor. The challenges associated with the design of the reheat combustor are due to the combustion air that consists of a hot (> 650°C or 1200°F) vitiated (< 15% O₂ by volume) stream.

Gas Turbine Pressure Ratio

The optimum pressure ratio for a given cycle configuration increases with the firing temperature of the gas turbine. Thus to take full advantage of the higher firing temperature of the gas turbine with firing temperature greater than 1700°C (3100°F) the required pressure ratio may be in excess of 30. Another constraint to also consider is the temperature of the last stage buckets in the turbine. This temperature may have to be limited to about 650°C (1200°F) from a strength of materials standpoint since the last stage buckets in large scale gas turbines tend to be very long and a certain minimum pressure ratio would be required to limit this temperature. Development of a compressor with such a high pressure ratio may require the adoption of the aero-engine technology including twin-spools in order maintain a fuel flexible design. Note that

the pressure ratio of the gas turbine increases when firing syngas as compared to natural gas operation (syngas being a much lower heat content gas than natural gas). The increase in pressure ratio is dependent upon the amount and nature of the diluent added to the syngas for NO_x control and the degree to which the compressor inlet guide vanes are closed. Air extraction from the compressor (while supplying the extracted air to the ASU) will help in order to limit the increase in the engine pressure ratio but an upper limit exists for the fraction of air that may be extracted without affecting the amount of air remaining for combustor liner cooling purposes.

Combustor Developments

Pressure Gain Combustor. A pressure gain combustor produces an end-state stagnation pressure that is greater than the initial state stagnation pressure. An example of such a system is the constant volume combustion in an ideal spark ignited engine. Such systems produce a greater available energy in the end state than constant pressure systems. It has been shown that the heat rate of a simple cycle gas turbine with a pressure ratio of 10 and a turbine inlet temperature of ~1200°C (2200°F) can be decreased by more than 10% utilizing such a constant volume combustion system [Gemmen, Richards and Janus, 1994]. Pulse combustion which relies on the inherent unsteadiness of resonant chambers can be utilized as a pressure gain combustor. Research continues at the U.S. DOE and at NASA for the development of pressure gain combustors. Based on the current status of this technology, it will not be used in the Baseline Case but will be considered for application in the Advanced Cases to be investigated under Task 2 of the project.

Trapped Vortex Combustor. The Trapped Vortex Combustor (TVC) has the potential for numerous operational advantages over current gas turbine engine combustors [Hsu, Gross and Trump, 1995]. These include lower weight, lower pollutant emissions, effective flame stabilization, high combustion efficiency, and operation in the lean burn modes of combustion. The TVC concept grew out of fundamental studies of flame stabilization and is a radical departure in combustor design using swirl cups to stabilize the flame. Swirl stabilized combustors have somewhat limited combustion stability and can blow out under certain operating conditions. On the other hand, the TVC maintains a high degree of flame stability because the vortex trapped in a cavity provides a stable recirculation zone that is protected from the main flow in the combustor. The second part of a TVC is a bluff body dome which distributes and mixes the hot products from the cavity with the main air flow. Fuel and air are injected into the cavity in a way that it reinforces the vortex that is naturally formed within it.

The TVC may be considered a staged combustor with two pilot zones and a single main zone, the pilot zones being formed by cavities incorporated into the liners of the combustor [Burrus et. al., 2001]. The cavities operate at low power as rich pilot flame zones achieving low CO and unburned hydrocarbon emissions, as well as providing good ignition and the lean blowout margins. At higher power conditions (above 30% power) the additional required fuel is staged from the cavities into the main stream while the cavities are operated at below stoichiometric conditions. Experiments have demonstrated an operating range that is 40% wider than conventional combustors with combustion efficiencies of 99%+. Use of the TVC combustor holds special promise as an alternate option for suppressing the NO_x emissions in syngas applications where pre-mixed burners may not be employed. Research continues in this area

and based on the current status of this technology, it will not be used in the baseline Baseline Case but will be considered for application in the Advanced Cases to be investigated under Task 2 of the project. Organizations actively involved in the development of such combustors include GE and Ramgen.

Catalytic Combustor. Lean stable combustion can be obtained by catalytically reacting the fuel-air mixture with a potential for simultaneous low NO_x, CO and unburned hydrocarbons. It also has the potential for improving lean combustion stability and reducing combustion-induced pressure oscillations. The catalytic combustor can play a special role in IGCC applications to reduce NO_x emissions but such a combustor for the large scale applications with commercial guarantees is not expected to be available in the near term. Based on the current status of this technology, it will not be used in the Baseline Case but will be considered for application in the Advanced Cases to be investigated under Task 2 of the project.

Recommendation of Gas Turbine Technology for the Baseline Case

- Based on the developmental status of the above described technologies, it is recommended that for the Baseline Case, the steam cooled “H” technology gas turbine as represented by the GE 7H machine be utilized.

Other Considerations

Inlet Air Fogging. An alternate approach to reducing the parasitic load of air compression in a gas turbine is to introduce liquid water into the suction air [Bhargava and Meher-Homji , 2002]. The water droplets will have to be extremely small in size and be in the form of a fog to avoid impingement on the blades of the compressor causing erosion. As the water evaporates within the compressor from the heat of compression, the air being compressed is cooled which in turn causes a reduction in the compressor work. Note that the compression work is directly proportional to the absolute temperature of the fluid being compressed.

A benefit in addition to increasing the specific power output of the engine is the reduction in the NO_x due to the presence of the additional water vapor in the combustion air. A number of gas turbines have been equipped with such a fogging system operating on natural gas. Care should be taken, however, in specifying the water treatment equipment since high quality demineralized water is required as well as in the design of the fogging system to avoid impingement of the compressor blades with water droplets.

This technology has been proven in a number of natural gas based plants and will be considered for incorporation in the Baseline Case as a sensitivity.

NO_x Control. The name plate NO_x emission from the GE Frame 7FB gas turbine which is being offered for IGCC applications, on syngas with massive N₂ and/or moisture addition is 15 ppmV (dry, 15% O₂ basis). To achieve lower NO_x emissions, a selective catalytic reduction (SCR) unit would be required. The unreacted ammonia leaving the SCR, however, reacts with any SO₃ present to form ammonium salts that can (1) deposit in the low temperature sections of the HRSG causing fouling, and (2) result in particulate emissions. In order to limit the number

of HRSG washes to one per year to remove these salt deposits, the total equivalent sulfur concentration in the gas turbine exhaust should be limited to 2 ppmV, which is roughly equivalent to 10 to 15 ppmV total sulfur in the syngas. The SO₃ is formed by (1) oxidation within the gas turbine combustor of the H₂S and COS present in the syngas, and (2) oxidation of the SO₂ within the SCR containing a vanadium catalyst.

If an SCR is required, then the following design option may be required:

- Utilize a low vanadium content SCR catalyst.
- Install a NH₃ oxidation catalyst (developed by Engelhard) downstream of the SCR to oxidize the NH₃ slipping through the SCR catalyst into N₂ and H₂O in order to minimize the NH₃ emissions. The catalyst can reduce the incoming concentration of NH₃ from 1 - 20 ppmV to less than 0.5 ppmV (the NH₃ oxidation catalyst itself produces some SO₃, however).
- Limit the concentration of the sulfur compounds in the fuel gas to 10 ppmV. This will not be a problem for an IGCC plant designed for producing a decarbonized syngas utilizing a sour shift and an acid gas removal unit to capture the CO₂ while performing desulfurization of the syngas because most of the COS is hydrolyzed to H₂S in the shift reactors, while a very large solvent circulation rate is maintained in the acid gas removal unit to capture the CO₂ resulting in very low sulfur content in the treated syngas.

This approach will be considered for incorporation in the Baseline Case as a sensitivity for the ultra low NO_x IGCC.

Conclusions - Technology Selection – Baseline Case

The overall plant configuration proposed for the Baseline Case is depicted in Figure 9. The plant scheme consists of high pressure (HP) cryogenic air separation unit (ASU) supplying 95% purity O₂ to GE type HP total quench gasifiers. The raw gas after scrubbing is treated in a sour shift unit to react the CO with H₂O to form H₂ and CO₂. The gas is further treated to remove Hg in a sulfided activated carbon bed. The syngas is desulfurized and decarbonized in a Selexol acid gas removal unit and the decarbonized syngas after humidification and preheat is fired in GE 7H type steam cooled gas turbines. HP N₂ from the ASU is also supplied to the combustors of the gas turbines as additional diluent for NO_x control. A portion of the air required by the ASU is extracted from the gas turbines.

An ultra low NO_x (< 2 ppmvd, 15% O₂ basis) sensitivity case is developed by the inclusion of an SCR in each of the heat recovery steam generators (HRSGs). Gas turbine inlet air fogging is also evaluated as a sensitivity case.

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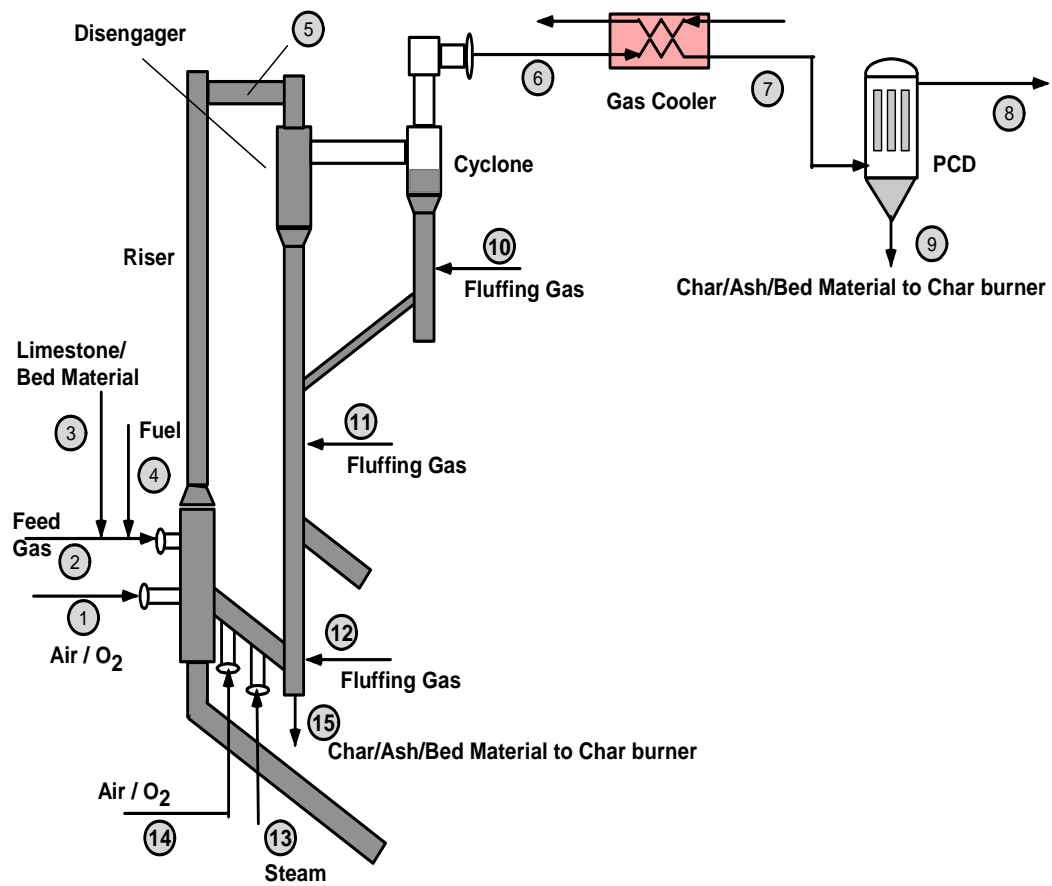


Figure 1: Advanced Transport Reactor

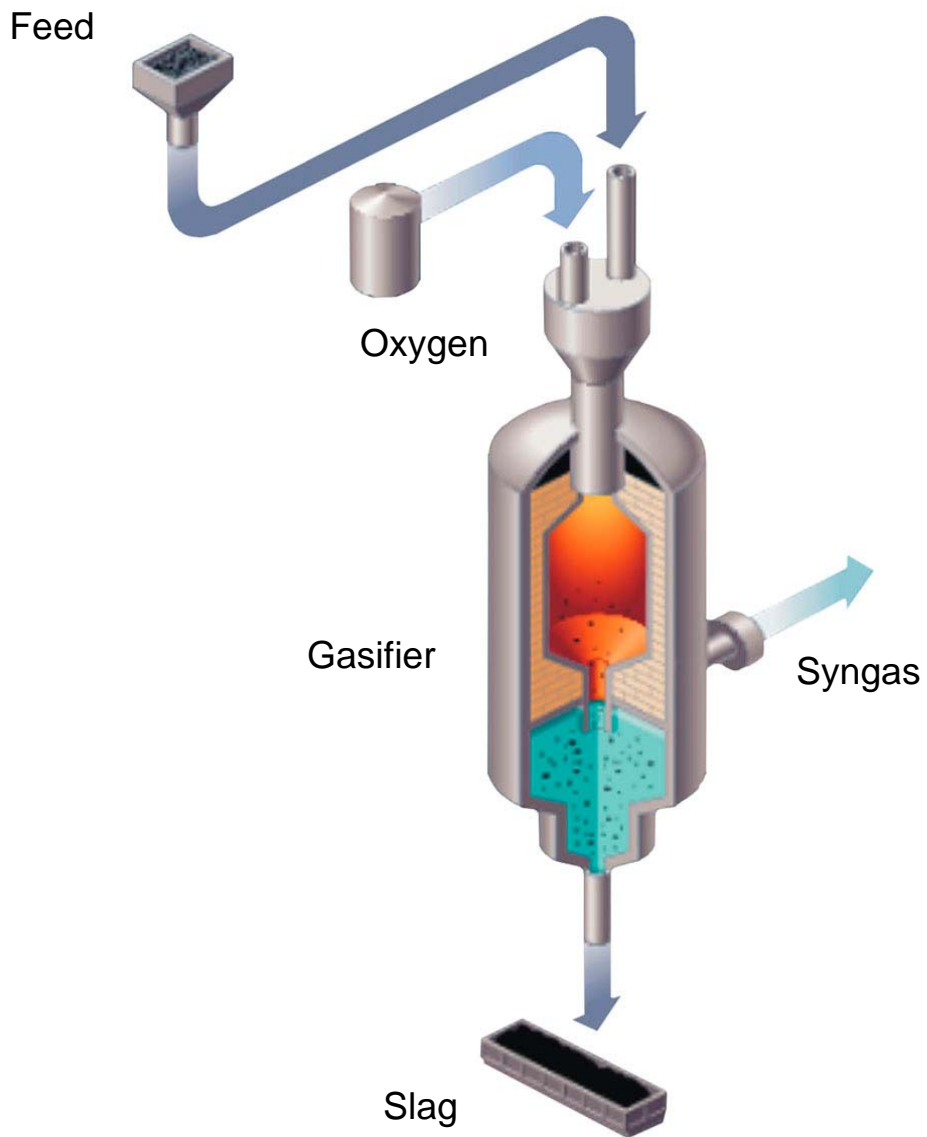


Figure 2: GE Total Quench Gasifier

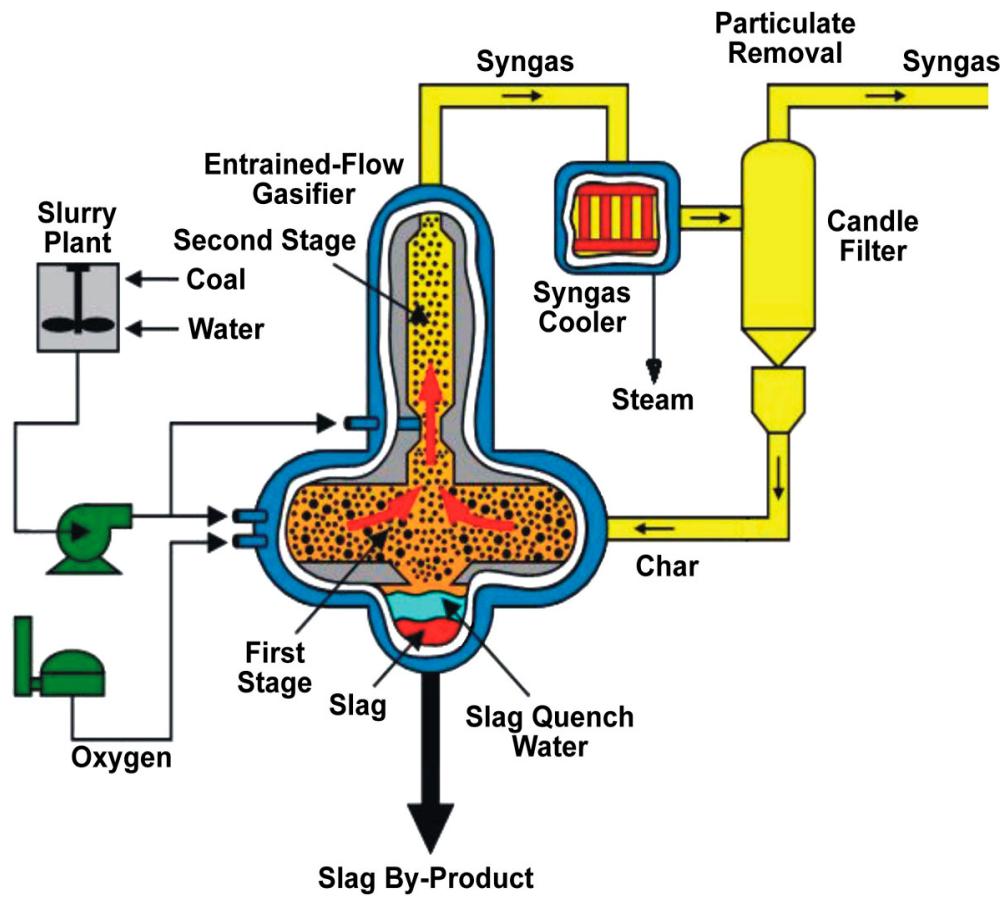


Figure 3: E-Gas Gasifier

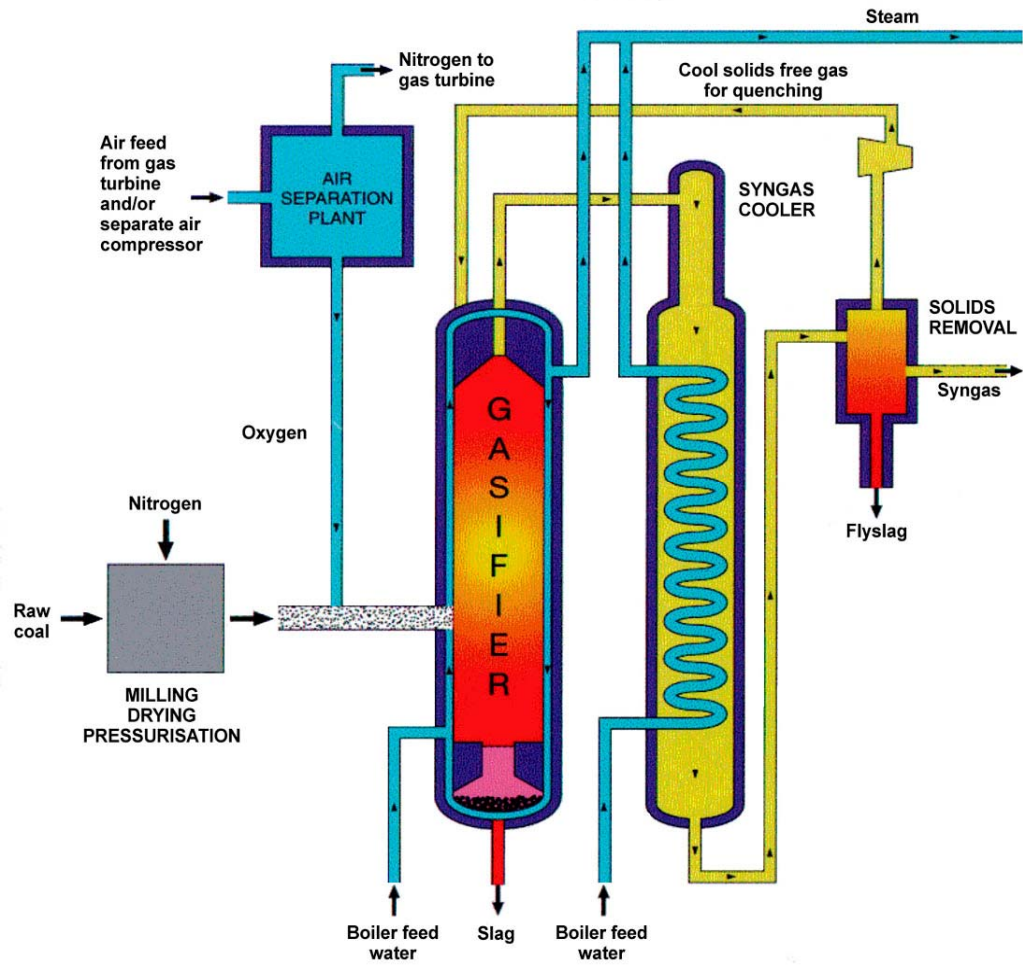


Figure 4: Shell Gasifier

Table 1: Syngas Contaminants^a

Contaminant	Concentration (ppmV)	Comments
Arsenic, as AsH ₃	<0.04	Kingsport gasification stream
	0.150-0.578	Kingsport gasification feed conc.
	0.2	UND-EERC highest vaporization
Halogens {Cl & F}	~0	Kingsport gasification stream
Chlorine	120	UND-EERC highest vaporization
CH ₃ F	2.55	Kingsport gasification feed conc.
CH ₃ Cl	2.01	Kingsport gasification feed conc.
HCl	<1	Kingsport gasification stream
Fe(CO) ₅	0.05-0.01	Kingsport gasification stream
	5.63	Kingsport gasification feed conc.
Ni(CO) ₄	0.025-0.001	Kingsport gasification stream
HCN	<1	Kingsport gasification stream
CH ₃ SCN	2.14	Kingsport gasification feed conc.
Acetonitrile	<0.5	Kingsport gasification stream
PH ₃	1.91	Kingsport gasification feed conc.
Antimony	<0.025	Kingsport gasification stream
	0.07	UND-EERC highest vaporization
Cadmium	0.011	UND-EERC highest vaporization
Beryllium	<0.025	Kingsport gasification stream
Chromium	<0.025	Kingsport gasification stream
	6.0	UND-EERC highest vaporization
Mercury	<0.025	Kingsport gasification stream
	0.0015	UND-EERC highest vaporization
Nickel	3.0	UND-EERC highest vaporization
Potassium	512	UND-EERC highest vaporization
Selenium	<0.15	Kingsport gasification stream
	0.17	UND-EERC highest vaporization
Sodium	320	UND-EERC highest vaporization
Thiophene	1.61	Kingsport gasification stream
Vanadium	<0.025	Kingsport gasification stream
Lead	0.26	UND-EERC highest vaporization
Zinc	9.0	UND-EERC highest vaporization

^a In addition to H₂S, COS, Possibly CS₂, NH₃, HCN.

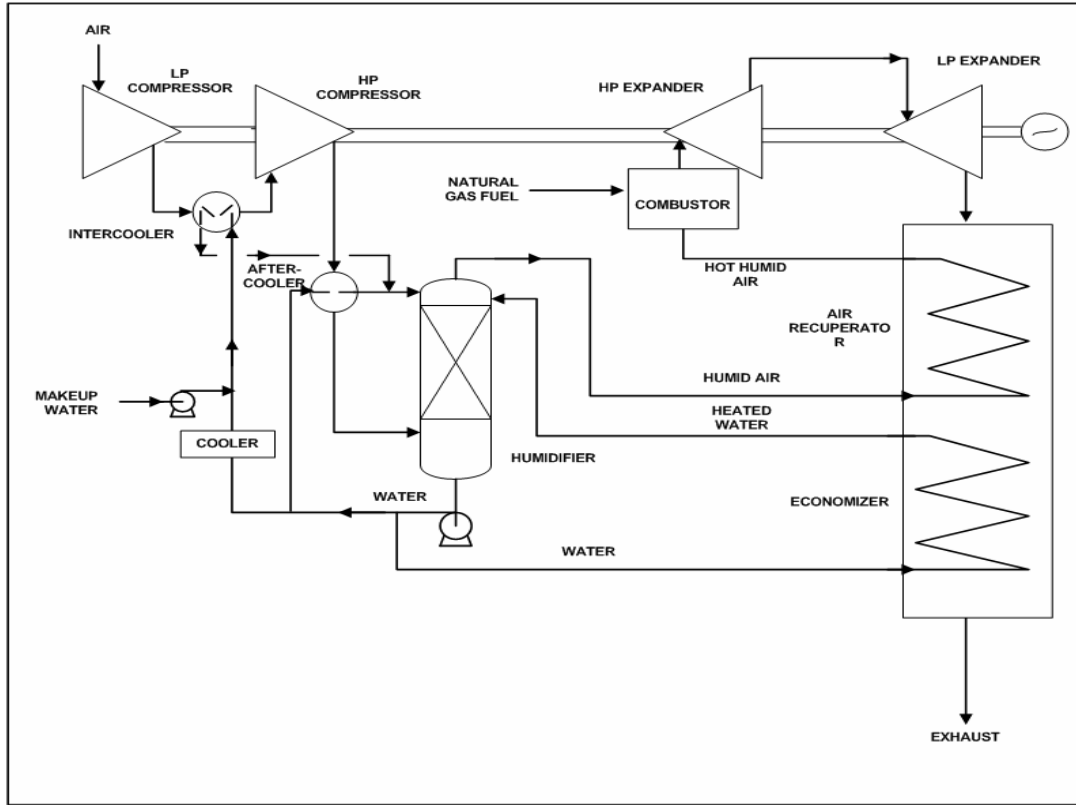


Figure 5: HAT Cycle

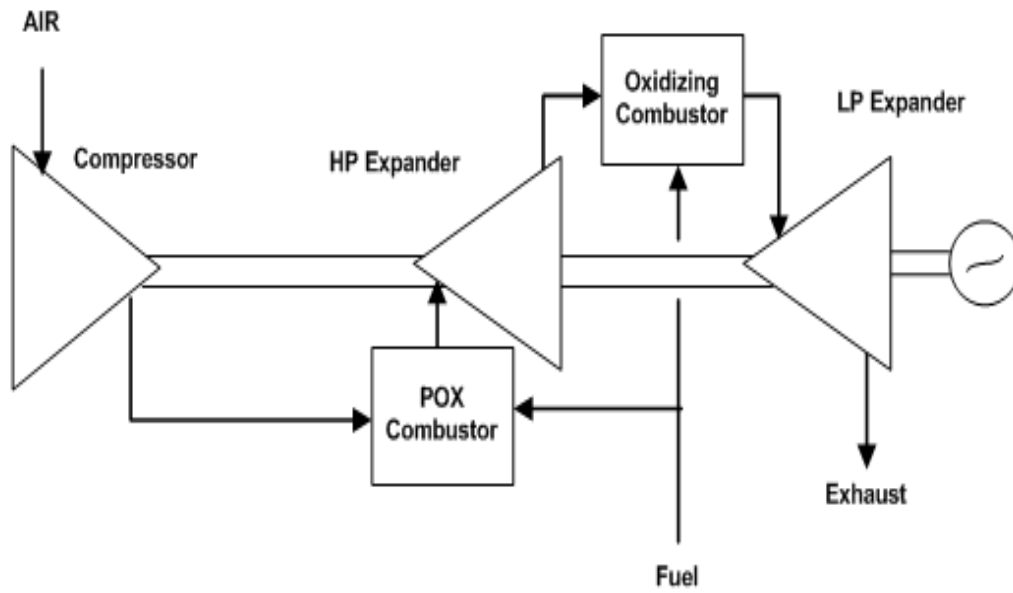


Figure 6: Partial Oxidation Cycle

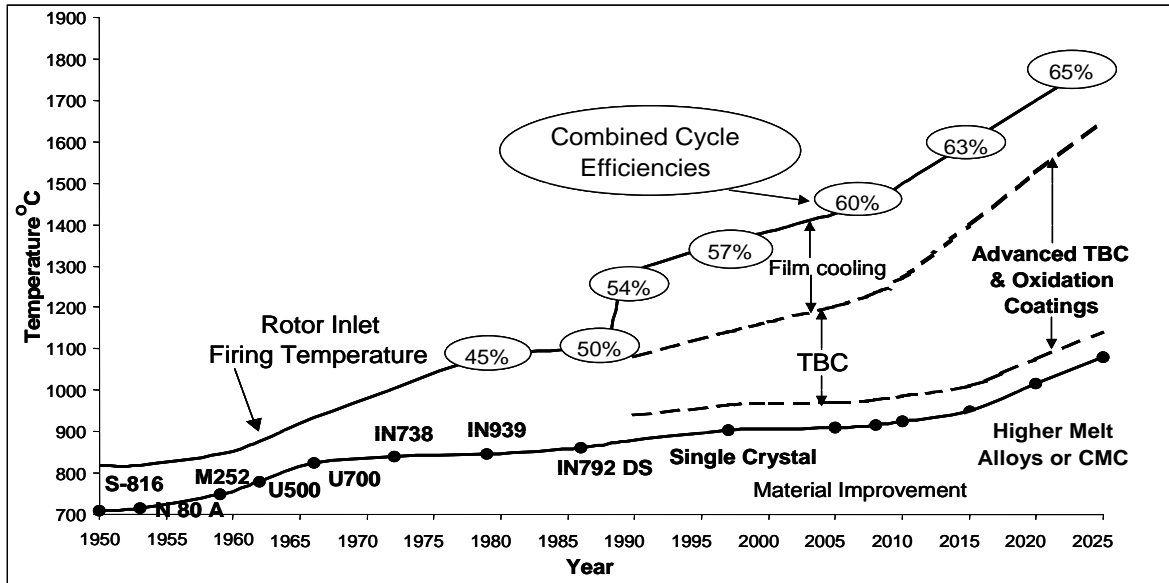


Figure 7: Impact of Firing / Metal Temperature on Efficiency

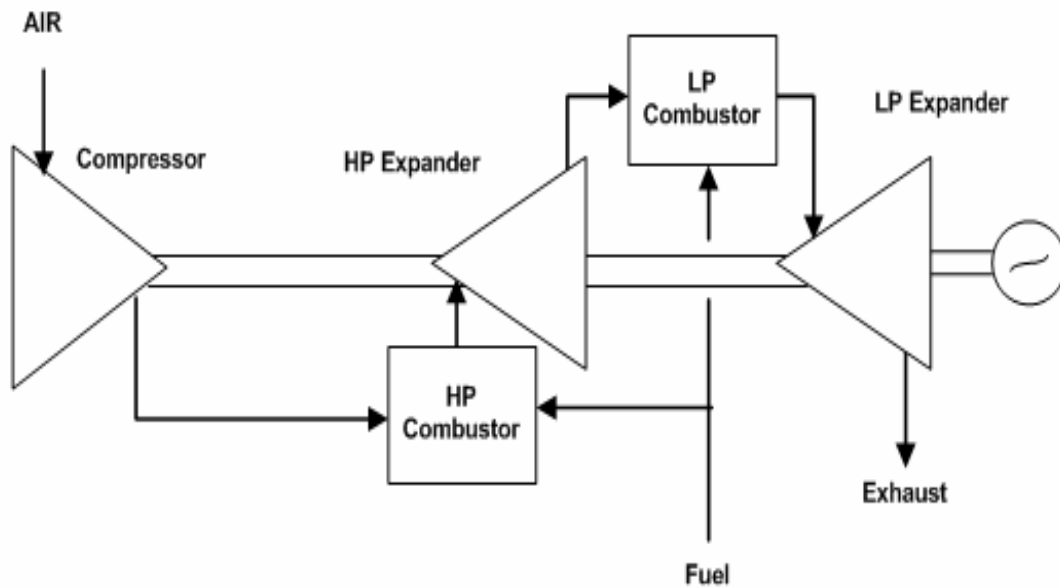


Figure 8: Reheat Gas Turbine Cycle

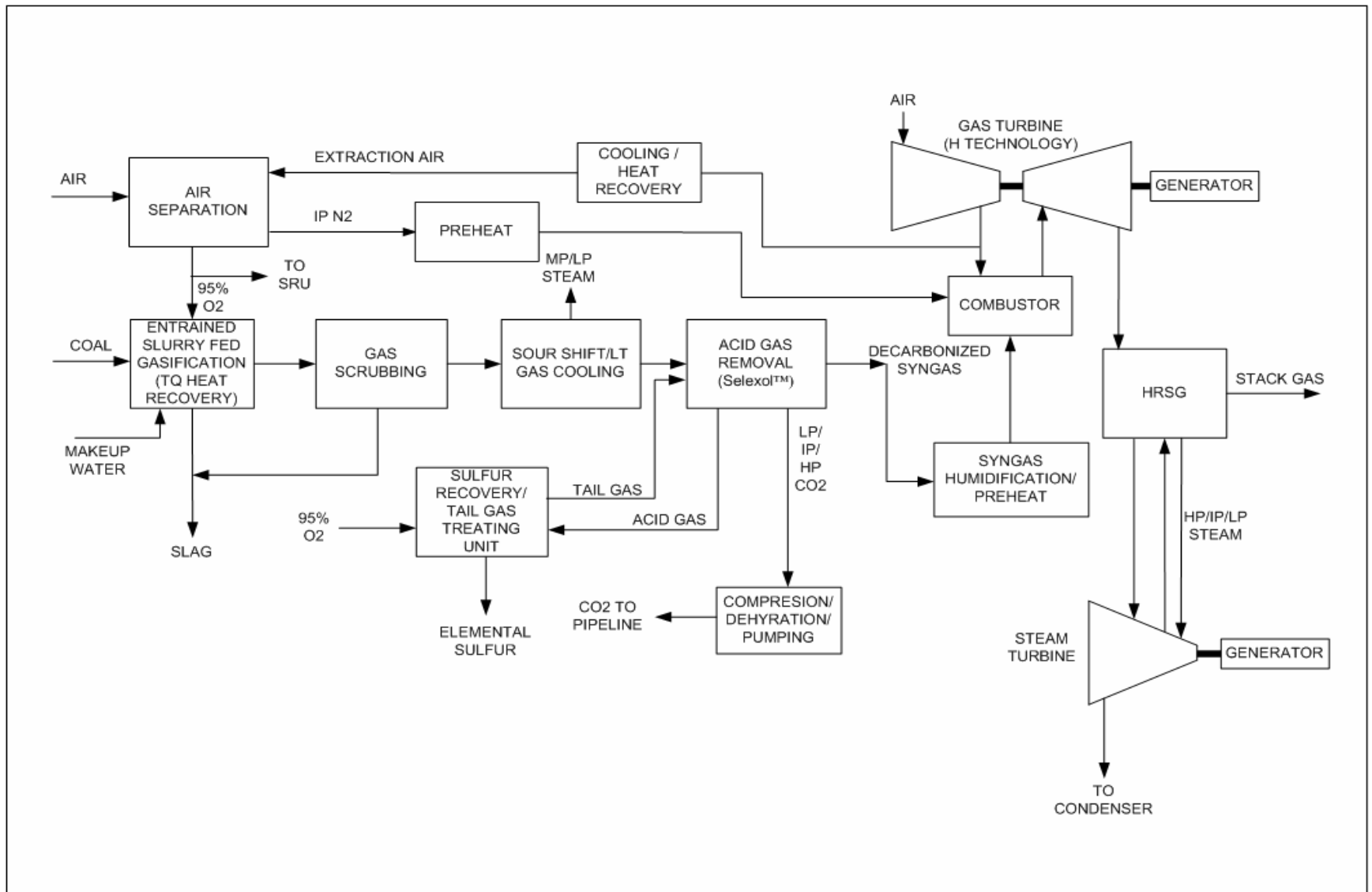


Figure 9: Overall Block Flow Diagram – Baseline Case IGCC with CO₂ Capture