



Background^{1, L2}

The worldwide focus on clean power generation and carbon capture has increased the importance of the associated technologies, which involve two distinct approaches, namely pre-combustion and post-combustion carbon capture.

In pre-combustion CO₂ capture, fuel is gasified by applying heat under pressure in the presence of steam and air and/or oxygen to form synthetic gas (Syngas). CO₂ is then captured from the Syngas, before being mixed with air in a combustion turbine, resulting in the CO₂ being relatively concentrated and at a high pressure.

In post-combustion CO₂ capture, mainly, pulverized coal is burnt in air to raise steam. CO₂ is exhausted in the flue gas at atmospheric pressure and concentrations of 10-15% v/v. This process is more challenging due to the low pressure and dilute CO₂ concentration resulting in a high volume of gas having to be treated. Also trace impurities in the flue gas tend to reduce the effectiveness of the CO₂ absorbing processes and compressing the captured CO₂ from atmospheric pressure to pipeline pressure represents a large parasitic load.

Another post-combustion capture technology, oxy-combustion, involves combustion of the fuel with near pure oxygen resulting in a flue gas stream of higher CO₂ concentration. This technology relates more to combustion, and is not discussed further in this paper.

When CO₂ is captured, power station generating efficiency is significantly reduced. Therefore a power cycle with a high thermal efficiency is essential to ensure an acceptable outcome. Power cycle efficiency is continually being improved by increasing the steam temperature and pressure; this development is limited by the availability of suitable alloys.

Historical Trend in Boiler Operation (Note: water P _C = 221 bar, T _C = 374°C)				
Operation	Year	Pressure	Temperature	Efficiency
		bar	°C	%
Subcritical	1960 - 1970	166	540	38 to 42
Supercritical	1970 - 1990	240	566	44
Ultra supercritical	1990 - present	310	600	49

Ultra supercritical (USC), once-through utility (OTU) operation is considered to be the best option for “Clean Coal Technology”. USC operation reduces the CO₂ emissions and therefore improves the economics of carbon capture and sequestration (CCS).

Pre-combustion and post-combustion CCS methods are similar, in that both require significant power for blowers, pumps and compressors. Studies are indicating parasitic power in the range 15 to 25% with the technology, plant layout, pressure drop, compressor operation, transportation, and sequestration configurations each having a significant effect. Crucial to CCS economics is the optimization of the heat integration circuits and the minimization of CO₂ stripping steam to reduce the impact on power plant parasitic power.

CO₂ is present at much higher concentrations in Syngas than in post-combustion flue gas, so CO₂ capture should be less expensive for pre-combustion than for post-combustion capture. However, there are few gasification plants in full-scale operation, and capital costs are higher than for conventional pulverized coal plants.

Process simulators are playing an increasingly important role in finding the optimum economic solutions. CHEMCAD is being used in modeling pre-combustion and post-combustion processes and has developed thermodynamics specifically for the pre-combustion and compression technologies.

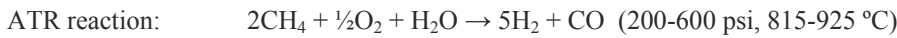
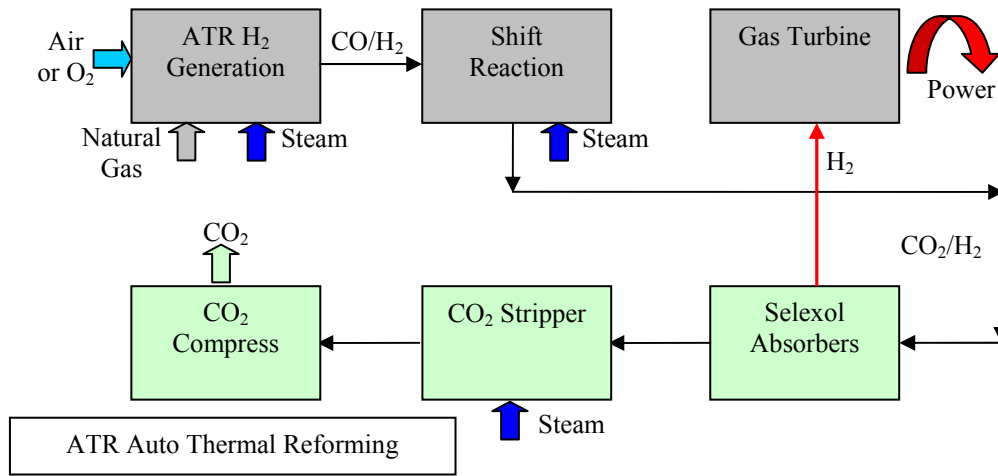


Pre-combustion Carbon Capture

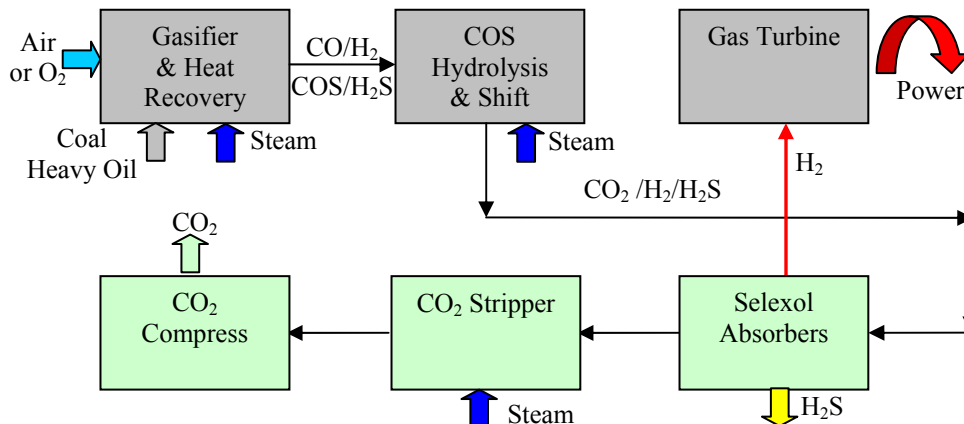
In pre-combustion CC, the fuel will be either natural gas or gasified hydrocarbon feedstock. If natural gas, it is converted into CO and H₂ by auto thermal reforming (ATR) and then CO is converted into CO₂ by the shift reaction. If hydrocarbon (coal or heavy oil), it is gasified in the presence of steam and air or oxygen at a high temperature and pressure, followed by the shift reaction to form CO₂, H₂, COS and other gaseous compounds, depending on the hydrocarbon make-up. ^{Appendix I}

A key part of this technology is the removal of CO₂ and H₂S (if present) from the Syngas by absorption in a physical solvent. The captured CO₂ can then be processed or compressed and sequestered in a suitable reservoir. Proven technology includes the Selexol[®] process that uses a solvent, which is a mixture of dimethyl ethers of polyethylene glycol. Dow Chemical Company retains the gas processing expertise, which is offered under license. Clariant GmbH offer an equivalent solvent, available from their Genosorb range. ^{Appendix II}

Syngas Plant Combined Cycle with Carbon Capture



Integrated Gasification Combined Cycle (IGCC) with Carbon Capture



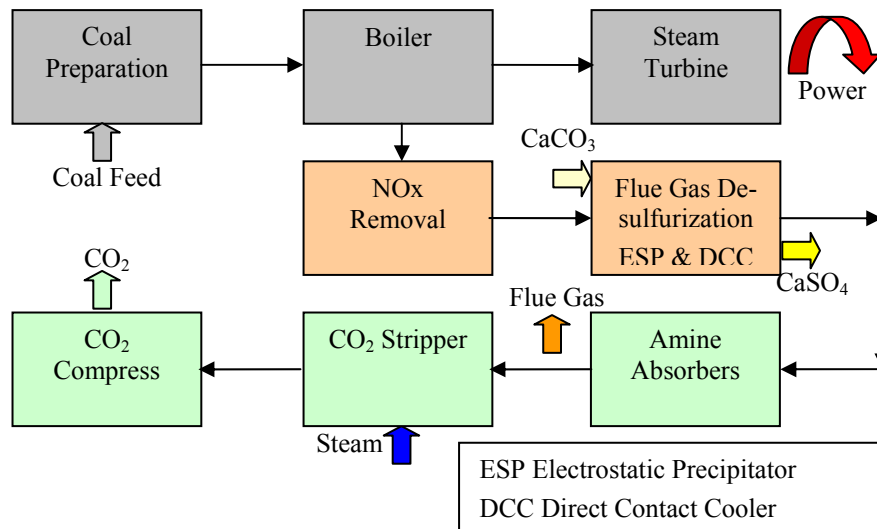


Post-combustion Carbon Capture

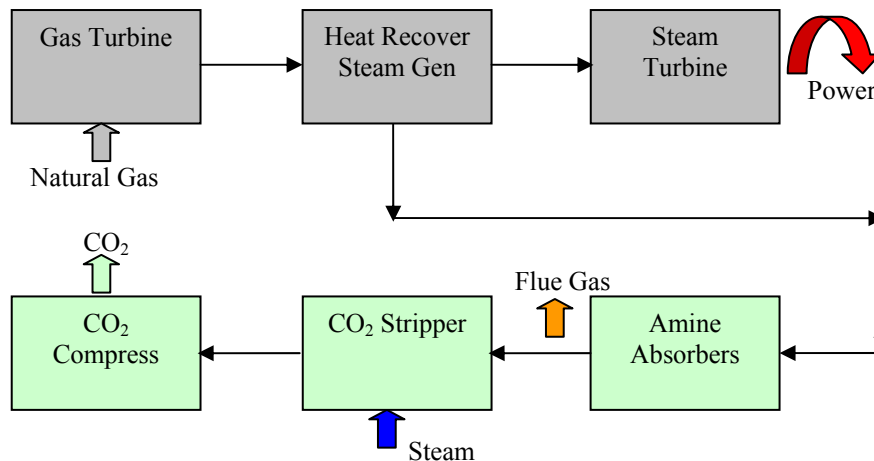
The typical fuel is either natural gas or pulverized coal. ^{Appendix I} When natural gas, it is combusted in a gas turbine, and when coal, it is combusted in a steam boiler. Alternative fuels, such as biomass and wood chippings, are now starting to be used.

Key parts of this technology are Flue Gas Desulfurization (FGD) to remove SO₂(if present) by spray scrubbing with limestone, particulate removal by Electrostatic Precipitator (ESP), direct contact cooling (DCC) with circulating water and reactive absorption of CO₂ using inhibited amine blends ^{Appendix III}. The captured CO₂ is then desorbed from the rich amine by steam stripping and then compressed for transfer and sequestration in a suitable reservoir.

Pulverized Coal Fired with Carbon Capture



Natural Gas Fired Combined Cycle with Carbon Capture



A CCGT set has a gas turbine-generator, a waste heat boiler followed by a steam turbine-generator. The combined cycle power plant (CCPP) fuel is usually natural gas, although fuel oil or Syngas are being used. The CCPP can have single-shaft or multi-shaft configurations. The single-shaft has one gas turbine, one steam turbine, one generator and one Heat Recovery Steam Generator (HRSG). The multi-shaft has one or more gas turbine-generators and HRSGs that supply steam to a separate single steam turbine-generator.



Thermodynamics

Summary ^{Appendices II, III & IV}

The CHEMCAD flowsheet will have a Global K Value Model selected, with individual UnitOps having Local K Value Model set to suit the specific process. The Global K Value Models used in CHEMCAD are summarized below:

- Pre-combustion absorption and desorption – special PSRK gas/physical solvent
- Flue gas desulfurization (FGD) gypsum process - electrolyte option with NRTL
- Flue gas desulfurization (FGD) Linde Solinox process - special PSRK
- Direct contact cooling (DCC) - Ideal vapor pressure - set as local K-value
- Post-combustion absorption and desorption at atmospheric pressure - AMINE
- Compression - Benedict Webb Ruben Starling (BWRS) with CO₂ parameters

For example, with pre-combustion absorption, flash, and compression, we would have:

Global K-value – Special PSRK and local K-value - BWRS for compression

The global enthalpy models used are AMINE for post-combustion absorption and desorption at atmospheric pressure and latent heat for all other cases.

Pre-combustion Absorption and Desorption ^{18, Appendix II}

The SELEXOL™ process is a well-proven, stable acid gas removal system based on the use of a dimethyl ether of polyethylene glycol as a physical solvent involving no chemical reaction. The favorable physical solubilities of the acid gases relative to the other light gases demonstrate the suitability of SELEXOL™ for selective removal of H₂S and for capturing CO₂. The process is designed to take advantage of the solubility difference of H₂S and CO₂. The solubilities shown in the Table are for single components only and are approximate for multi-component systems.

Selexol Solvent Relative Solubility of Gases ^{Ref. 18}	
Components	Solubility Ratio
H ₂ (Least soluble)	1.0
N ₂	1.5
CO	2.2
CH ₄	5.0
CO ₂	75
COS	175
H ₂ S	670
CH ₃ SH	1,700
SO ₂	7,000
H ₂ O	55,000
HCN (most soluble)	95,000

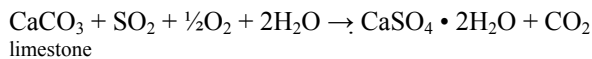
SELEXOL is now included in the CHEMCAD library component database. The PSRK model combines an equation of state approach with an activity coefficient. This has allowed for the development of a special PSRK gas/physical solvent package which has been specifically developed for the SELEXOL™ process. This is selected on the Thermodynamic Settings K-value Models screen.

**CO₂ Compression and Transport** Appendix IV

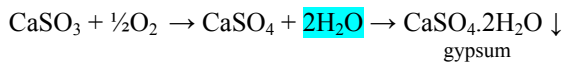
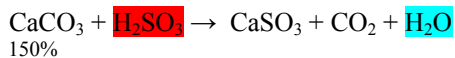
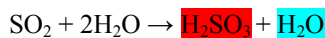
In this system CO₂ is close to the super-critical state where the temperature is greater than the critical temperature making fugacity calculation difficult. The Benedict Webb Ruben Starling equation of state has been used, as this allows parameters specific to the properties of CO₂ to be used.

Post-combustion FGD Process

Conventional wet scrubbers utilize a wet limestone process, with in-situ forced oxidation to remove flue gas SO₂ and produce a gypsum by-product according to the following overall reaction:



This overall equation is made up of the following sub-reactions:



CaSO₄·2H₂O (dihydrate) solubility in water is 0.21g / 100 g solution.

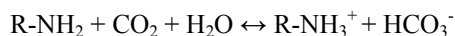
Crushed and milled limestone is mixed with water to form a 10 – 15% w/w slurry. To achieve > 99% oxidation of CaSO₃ to CaSO₄ a 3:1 stoichiometric ratio of oxygen to absorbed SO₂ (moles O₂ / moles SO₂) is required⁽⁴⁾. The reactions operate at a pH between 5.0 and 9.0; above the high pH limit precipitation of CaCO₃ will take place.

CHEMCAD NRTL – Electrolyte K value option breaks the molecules into specific electrolyte species and considers the ionic reactions. CaCO₃ and CaSO₄ are designated as components that can form a solid.

Post-combustion Absorption and Desorption 13, p 87-92, Appendix III

An aqueous solution of mono-ethanolamine (MEA) is used for the reactive absorption of CO₂ at atmospheric pressure.

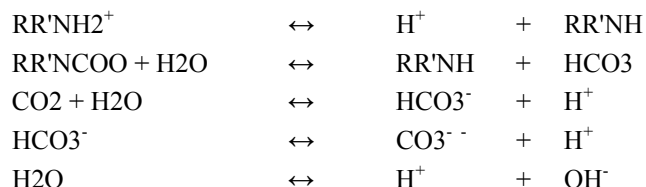
The reaction mechanism is as follows:



In CHEMCAD the K-value was set for AMINE which uses the Kent Eisenberg method to model the reactions. The following amines are included in the AMINE model allowing for further investigation if desired.

Diethanolamine (DEA), Monoethanolamine (MEA), Methyl diethanolamine (MDEA)

The chemical reactions in the CO₂-Amine system are described by the following reactions:



where R and R' represent alcohol groups. The reaction equations are solved simultaneously to obtain the free concentration of CO₂. The partial pressure of CO₂ is calculated by the Henry's constants and free concentration in the liquid phase.

**Pre-combustion SELEXOL® Process** ^{13, p 1202, 22}

SELEXOL® is a physical solvent designed to provide effective CO₂ removal and selective absorption of H₂S and COS from a variety of natural gas and Syngas streams. The physical absorption process is more sensitive to the operating temperature and pressure, as compared with the amine process, being more efficient at high pressure and low temperature.

Advantages include:

- Physical absorption rather than absorption by chemical reaction
- Chemically and thermally stable, less degradation reduces costs
- Low viscosity, enhances mass transfer
- High flash point gives ease of handling and safe conditions
- Low vapor pressure results in low solvent loss, reduces raw material costs
- No heat of reaction and small heat of solution, eliminates interstage cooling
- No on-site formulation required
- Non fouling, inherently non-foaming and low corrosion
- High selectivity for H₂S/COS over CO₂, eliminates need for separate FGD
- High loadings at high CO₂ partial pressure, reduces solvent recirculation rate
- High affinity for water so simultaneously dehydrates process gas streams
- Requires little heat input, solvent regeneration by pressure let down
- Material of construction mainly carbon steel due to non-aqueous nature

Disadvantages include:

- Requires gas cooling to ~100°F (Post-combustion process also requires DCC)
- Sensitive to operating temperature and pressure, but can be used to advantage
- Absorption process may require some refrigeration

The absorption process is carried out at high pressures resulting in significant economies of scale as compared to low pressure post-combustion carbon capture. There is no requirement for the DCC, inlet blower and absorber interstage cooling. Solvent recirculation rates are reduced significantly and process flow configurations are available that do not require steam for solvent regeneration.

Solvent recirculation rates are a key driver of capital cost and should be minimized by reducing the contact temperature. This is achieved by taking advantage of the Joule Thompson effect as CO₂ pressure is reduced and using of heat exchangers to recover refrigeration from process streams, cooling from hydraulic turbines and auxiliary refrigeration plant.

The absorption of H₂ and CH₄ in the rich solvent is minimized by flashing the solvent at an intermediate pressure, nominally ~½ the absorber pressure, and recompressing the flash gas to recycle to the absorber gas inlet.

The feed gas will almost always contain water of saturation which will accumulate in the solvent until a balance is achieved. Several techniques are available for control of water build up.

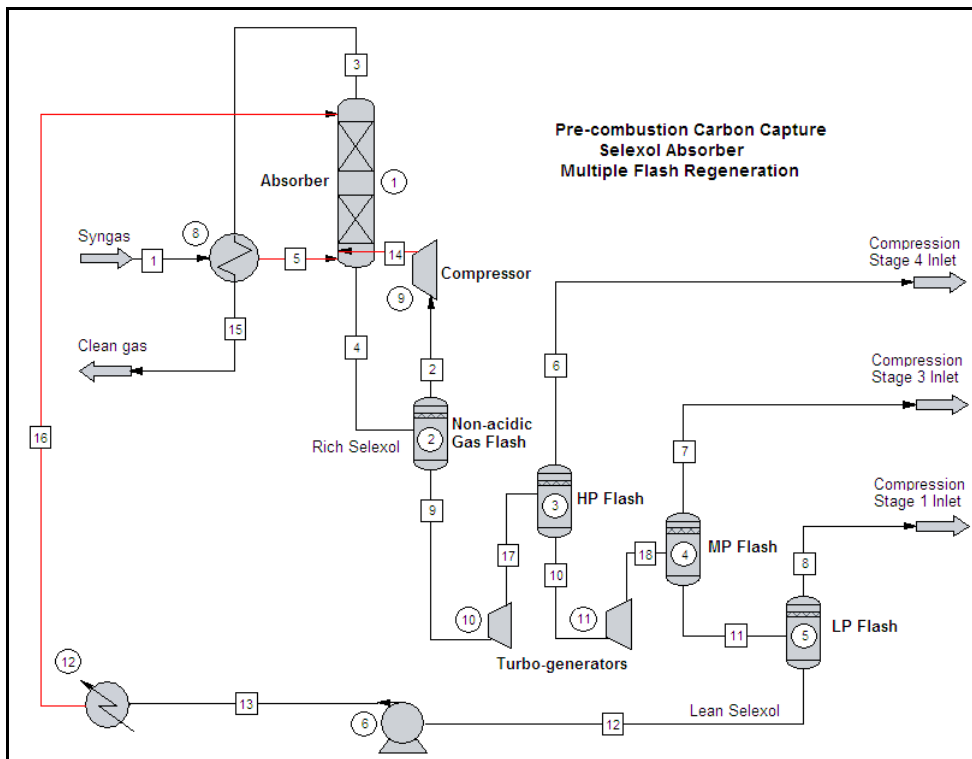
This process can be configured in many ways depending on whether H₂S and COS are present and the required levels of H₂S and CO₂ removal. There is extensive design and operating experience available with several main contractors offering unique solutions. Typical modeling parameter ranges are shown at the end of this section.



Pre-combustion SELEXOL® Process ^{13, p 1191, 22}

The simplest CO₂ capture scheme is to regenerate the solvent by carrying out multiple flashes at reducing pressure to recover the CO₂. The flash pressures will be determined by the subsequent compression stage pressures, with it being desirable to flash at the highest pressure to minimize compression power. Gases flashed at the highest pressures will contain most of the non-acidic gases and are usually recompressed and returned to the absorber inlet. To achieve a greater than 95% CO₂ capture the final flash pressure required will be approaching atmospheric. Pressure let down through turbo-expanders can generate up to half the pumping power required for SELEXOL circulation. This approach not only reduces power consumption but provides cooling of the regenerated solvent which increases the absorption efficiency. Often sufficient auto-refrigeration is available to avoid the use of ancillary refrigeration equipment.

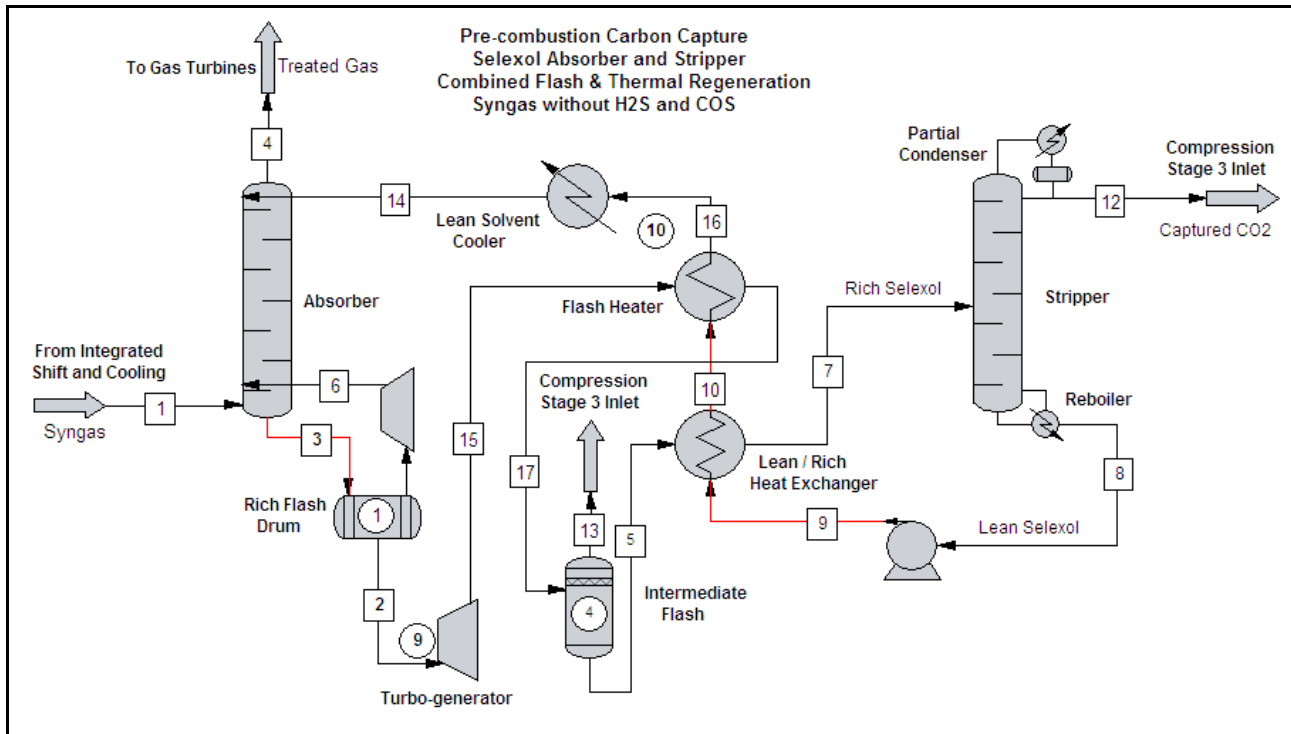
The flow diagram²⁴ below shows a process to remove CO₂ from a gas stream using this pressure letdown approach.



This process flow scheme eliminates the requirement for extracting steam from the power plant steam cycle. The CHEMCAD process simulator optimizer tool can be used to determine the flash pressures for most efficient H₂ and CH₄ recovery and CO₂ capture to minimize compression power. Solvent regeneration using a combination of multiple flashing at reduced pressure and thermal stripping can result in an optimal economic solution, depending on the site constraints.

Pre-combustion SELEXOL® Process ^{13, p 1202, 22}

In the case of CO₂ capture from a Syngas plant with natural gas as the fuel, not containing H₂S, the following process flow scheme is typical. There are many variations of this process flow scheme being dependent on the solvent used, the composition, pressure, and temperature of the feed gas, and the treating requirements.

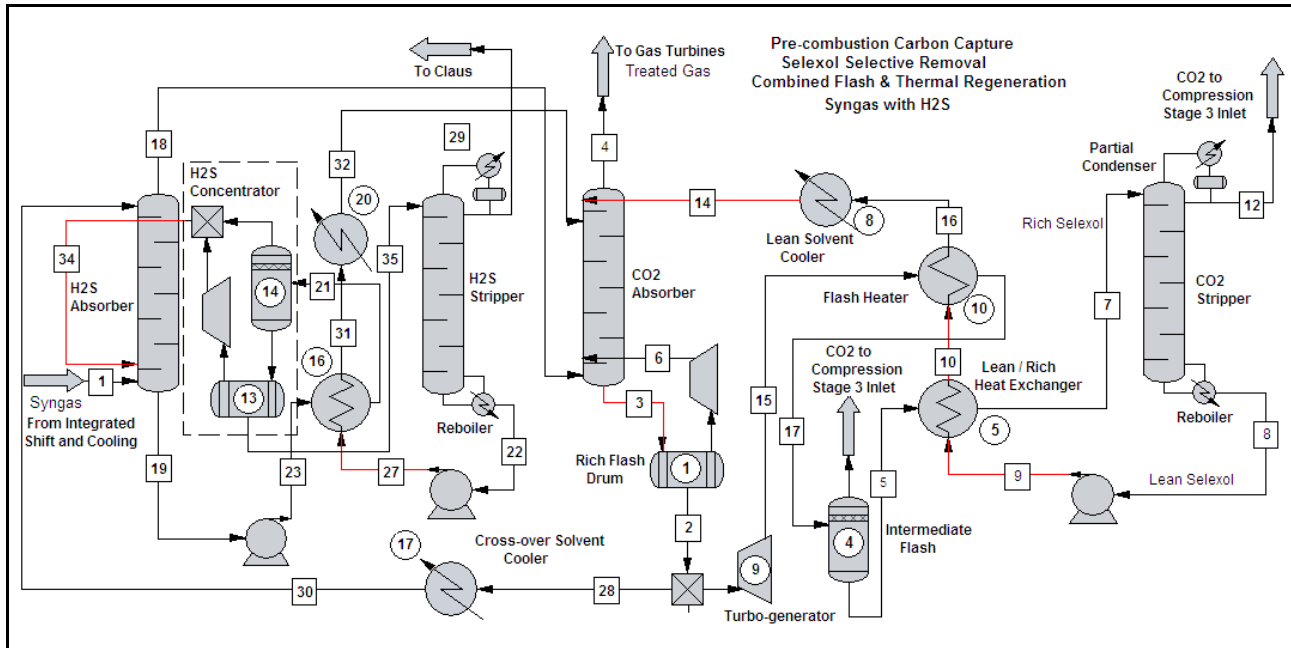


This process flow scheme can capture > 95% CO₂ with < 1% H₂ losses and can be optimized by adjusting the Rich Flash Drum and Intermediate Flash Drum pressures. The design objective is to achieve the maximum CO₂ capture at the highest pressure and to minimize stripper steam usage. The heat exchanger network objective is to provide the maximum temperature at the Intermediate Flash drum consistent with achieving a Stripper feed temperature >105 °C. The Lean Solvent Cooler will probably require auxiliary refrigeration to achieve acceptable absorption conditions.

The Stripper bottoms temperature is adjusted to drive off the absorbed CO₂ and can be expected to be in the range 120 °C to 130 °C. The Stripper off-gas temperature to compression should be ~ 37 °C.

**Pre-combustion SELEXOL® Process** 13, p 1202, 22, 27

In the case of CO₂ capture from gasified coal, containing H₂S, the following process flow scheme provides selective removal of H₂S and > 95% CO₂ capture. This process flow scheme is discussed in detail in Reference 27, link L12.



Key features of this process flow scheme are summarized:

Syngas from the gas cooling section is contacted with CO₂ saturated SELEXOL from the CO₂ Absorber bottoms preventing additional CO₂ pick up in the H₂S Absorber and minimizing the temperature rise, all of which enhances selectivity for H₂S.

The rich H₂S solvent from the H₂S Absorber is flashed at high pressure which preferentially flashes the CO₂ and enriches the H₂S content in the acid gas leaving the H₂S stripper, which is fed to the Claus unit for sulfur recovery. Adjustment of the flash pressures in the H₂S concentrator section of the flow scheme forces the H₂S content in to the range 20 to 50 mol %, with the Claus requiring > 20 mol %.

The CO₂ Absorber scheme is similar to the previous flow scheme with the exception that the CO₂ Absorber Lean solvent is supplemented with the H₂S Stripper Lean solvent.

In this scheme there are many objective parameters that require optimization including solvent circulation rates and temperature, theoretical stages, energy consumption and steam usage. CHEMCAD provides powerful optimization facilities ideally suited to this task.



Pre-combustion CO₂ Capture Model Parameters ^{11, 25, 26}

There are many configurations of pre-combustion process plant which are dependent on the Syngas composition, process objectives and site constraints. The following table provides general information for the Water Shift Gas stream and details for CO₂ absorption and regeneration using simple flashing without any heat input. If pipeline quality gas is required CO₂ recovery will require thermal regeneration which is discussed in the post-combustion carbon capture section. For a more detailed discussion on the operating parameters refer to paper by R. Van Deraerschot.²²

Pre-combustion CO ₂ Capture Modeling Parameter Ranges		
Parameter	Range	Units
Water Gas Shift CO to CO ₂ Conversion ⁽²⁶⁾	95 - 97	%
H ₂ ex Water Gas Shift ⁽²⁶⁾	53-55	mol % dry
CO ex Water Gas Shift ⁽²⁶⁾	1-2	mol % dry
CO ₂ ex Water Gas Shift ⁽²⁶⁾	38-41	mol % dry
Water Gas Shift Pressure Drop ⁽²⁸⁾	2	bar
Pressure ex Water Gas Shift	35 - 70	bar
Temperature ex Water Gas Shift	200 - 450	°C
Temperature ex Syngas Cooler	15 to 37	°C
Absorber Theoretical Stages ^{Note 3}	Performance driven	Dimensionless
Stage Efficiency	0.1 - 0.3	Normalized
Absorber Pressure Drop	0.2 - 0.5	bar
Absorber L/G ^{Note 3}	0.5 - 2.0	mol L / mol G
Typical CO ₂ Loading ^{(25) Note 4}	11.0 (L/G = 1.1)	scf CO ₂ /gal Selexol
Absorber Bottom Temperature ^{(25) Note 1}	-5 to 25	°C
Absorber Top Temperature	-12 to 10	°C
Rich Flash Drum Pressure	1/3 to 1/2 Absorber	Bar
High Pressure Flash ⁽¹¹⁾	20 - 30	bar
Medium Pressure Flash ⁽¹¹⁾	10 - 13	bar
Low Pressure Flash ⁽¹¹⁾	Vac - 4.5	bar
Stripper Bottoms Temperature	120 - 130	°C
CO ₂ to Compression Temperature	37	°C
Turbo Generator Efficiency ^{Note 2}	75	%
Pump Head	0.5 - 2.0	bar
Pump Efficiency	60 - 80	%
CO ₂ Capture Separation Factor	95	%
CO ₂ Pressure to Storage	152	bar
H ₂ S Concentration to Claus Process	20 to 50	mol %
Claus Process Operating Pressure	0.7	bar

Notes ⁽¹¹⁾

The absorption capacity of Selexol for acid gases increases as the temperature decreases. Pressure let down through the turbo generators provides auto cooling however additional refrigeration can result in higher efficiency and more economic plant.

Expansion of the rich solvent through turbo generators can provide a significant proportion of the lean solvent pumping power.

Trade off between the number of theoretical stages and circulation rate from Kremser⁽²⁵⁾.

Pikes Peak Plant⁽²⁴⁾ initial design was based on 23.9 scf/gal equivalent to L/G 2.3.

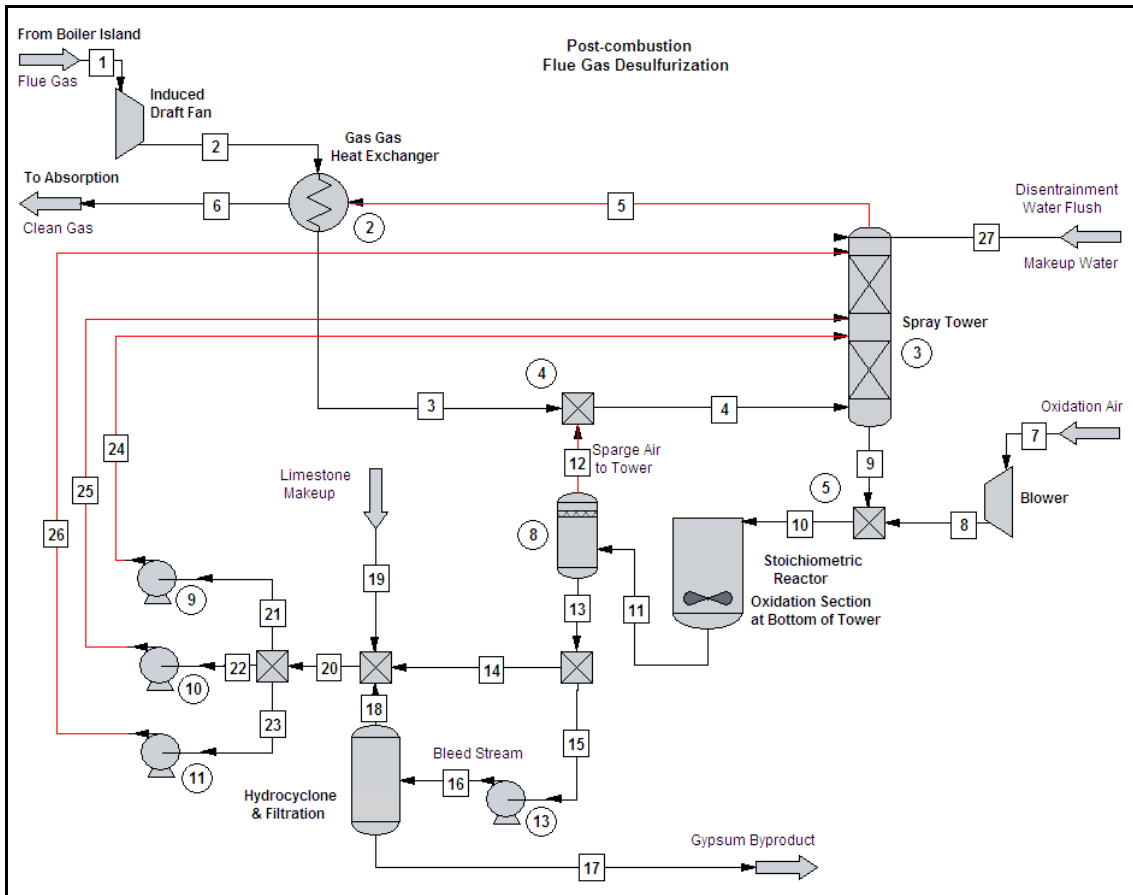


Post-combustion Flue Gas Desulfurization

FGD units normally use spray towers to contact the flue gas with an atomized limestone slurry. The slurry is pumped through spray nozzles to form droplets to provide a large interfacial surface for mass transfer. A reaction tank is provided, at the tower base, to allow for CaSO_3 to CaSO_4 conversion by introducing oxidation air through sparge grids with separate agitators or lances, which are open pipes in front of an agitator, or a combination of the two techniques. Operational problems include scaling and plugging of the spray nozzles.

SO_2 removal can be increased by increasing the liquid flow rate, increasing the pH of the feed slurry or by using an additive. It is considered^{13, p519} that the pH in the reaction tank should be controlled in the range 5 – 5.8 and that air sparge rates of 3x stoichiometric should be used. Reaction tank volume is sized⁴ to give a $10\text{h}^{1-\text{Alstom}}$ to 15h retention time to achieve the 99% conversion from CaSO_3 to CaSO_4 . Increasing the slurry level can have a significant affect on the oxidation due to increase in the residence time. The development of a generalized design approach, based on fundamentals, is difficult, so spray contactors are usually designed on the basis of previous experience.

A simplified post-combustion FGD flowsheet is shown. A stoichiometric reactor gives better convergence than a kinetic reactor with the SO_3 ion being set as the key component. True components, CaSO_4 and CaCO_3 , are identified as having the potential to form a solid. A component separator, set for solids split, removes all solids in the filtration loop.



Linde AG have developed the Solinox^{13-p602, 20} process, which is based on physical absorption using Clariant Genosorb 1900. This is a gypsum free FGD method which overcomes the mounting problems associated with the sale and disposal of FGD gypsum.



FGD Model Considerations

The circulating liquor consists of limestone in the form of dissolved CaCO₃ and a recycle slurry consisting primarily of a 15% w/w concentration of CaSO₄ and CaSO₃. Fresh slurry make-up has a water content of 20% w/w water. Spray tower scrubbers³ require high liquid to gas(L/G) ratios, in range 3.0 litre/m³ (22.4 gal/1000 ft³) and even as high as 10.7 litre/m³(80 gal/1000 ft³)⁴. The model has been based on three spray bank levels, each being supplied by dedicated pumps providing 2 bar differential head at 70% efficiency and using the minimum L/G value of 3.0 litre/m³.

The tower diameter is calculated from the gas side velocity. The maximum velocity allowed depends on the droplet particle size, which if too small leads to excessive liquid entrainment and, if too large poor mass transfer and wall wetting. The selection is a trade off between fan and pumping power which impacts severely on the FGD economics. Acceptable gas velocities vary in the range of 1.8 to 3.0 m/s. with recent designs claiming velocities as high as 4.5 to 6 m/s. A reduction in tower diameter, or resorting to parallel stream operation, has a significant impact on the capital and running costs. The type of gas eliminator influences the allowable gas velocity, which if excessive can result in liquid being entrained. Typical mist eliminators (zigzag-mesh pad-woven pad) use velocities in the range of 3.0 to 4.5 m/s and horizontal mesh pads up to 7.0 m/s.^{10, p5-45}

A spray tower will typically have a tray above the flue gas inlet, to ensure good gas distribution across the tower and several spray banks followed by a disentrainment section. If three spray banks are used, then 5 theoretical stages are allowed with initial stage efficiencies in the 0.5 to 0.65 range. Adjusting the efficiency profile allows the column to be optimized. The height (**Z**) of a tower can be determined from the number of transfer units (**NTU**) and height of transfer unit (**HTU**) concept, where **Z = NTU x HTU** and since the scrubbing process is gas film controlled the following also applies:

$$NTU = \ln (Y_1/Y_2) \quad NTU = -\ln (1 - \text{fractional efficiency})$$

Typical **HTU**, based on the overall gas film coefficient, for SO₂/water system is 0.829 m,¹⁰ allowing tower height to be estimated after allowing for mechanical construction constraints for the installation of the tray, spray banks, and disentrainment sections.

A correlation, proposed by Lunde^{13, p34} indicates that to realize two overall gas transfer units, the overall power required is 0.1 hp/1000 scfm (2.63E-03 kw/m³). Typical forced oxidation power consumptions and comparative values with other performance factors are shown in the following tables.

Forced Oxidation Spargers -Typical Energy Consumption ⁶		
Case	Grid Site	Lance Site
Dispersion Power, (kW)	41	192
Compressed Air Power, (kW)	326	212
Totals, kW	367	404



FGD Model Parameters 3, 4, 6 & 7

Operating Conditions: SO ₂ Absorption by Limestone in Spray Tower with Forced Oxidation ^{13-p517}		
Parameter	Value	Units
SO ₂ in Feed	3600	ppmw
SO ₂ Removal	90	%
Solids in Slurry	15	%
Gas Velocity	10	ft/s
L/G	96 (12.8)	gal/1000cf (litre/m ³)
pH of Feed Slurry	5.3	
Sump Reaction Retention Time	6	m
Stoichiometric Ratio	1.1	Limestone (mol)/ SO ₂ absorbed (mol)
Final By-product Solids	85	%

The following table shows typical model parameter values.

FGD Spray Scrubber Unit – Typical Parameter Ranges		
Parameter	Range or Factor	Units
Flue Gas ID Fan Head	0.01 – 0.05	bar
Flue Gas ID Fan Efficiency	60 – 85	%
Spray Tower Pressure Drop	0.005 -0.01	bar
Liquid to Gas Ratio	3.0 – 10	litres / m ³
Liquor Rate	Flue Gas Flow - L/G	kg/h
Pump Head	1.5 – 4.0	bar
Pump Efficiency	60 – 80	%
Slurry Water Composition	10 - 30	% weight basis
Tower Theoretical Stages	Performance driven	Dimensionless
Stage Efficiency	0.2 – 0.7	Normalized
Spray Banks	Vendor	
Forced Oxidation Method	Vendor	
Lance Power	Vendor	kW / m ³
Number of Lances	Tank size	
Oxidation Air Flow Basis	3.0	mole O ₂ / mole SO ₂
Lance Air Power	Vendor	kW / m ³
Air Blower Efficiency	60 - 85	%
Limestone Bond Index	10.0	kWh/ dry short ton ^(=2000lb)
Crusher Power	2.0 – 4.0	kWh/ dry short ton
Wet Grinding Power	Includes crusher	kWh/ dry short ton



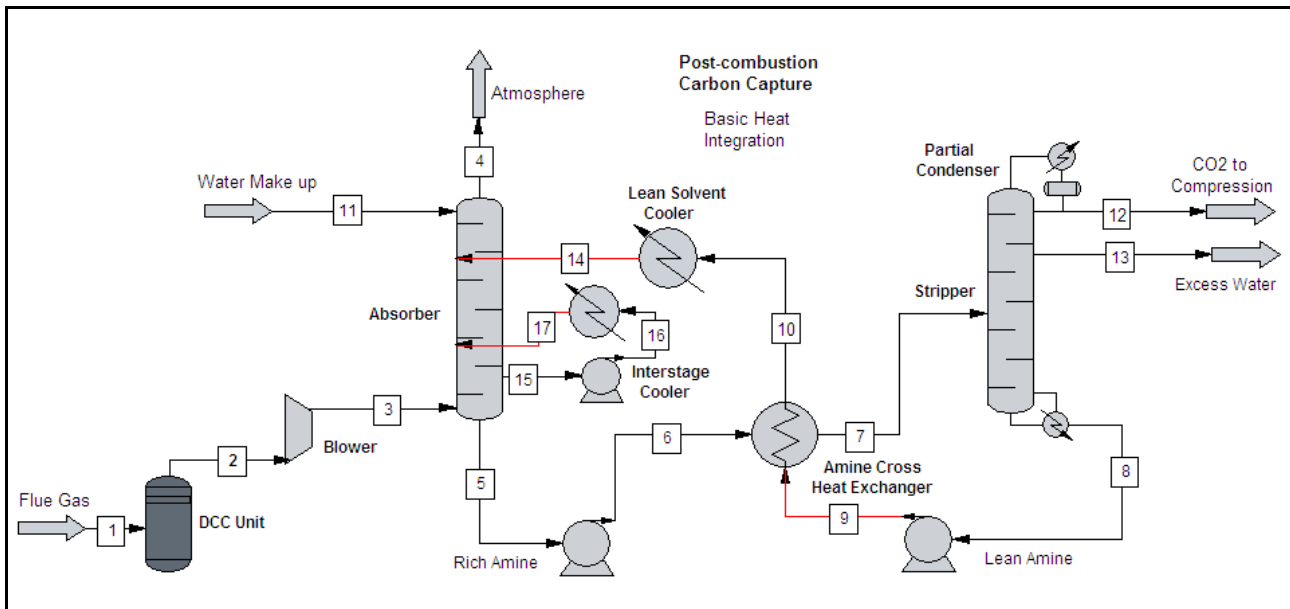
Post-combustion Carbon Capture^{1, 11, 13}

Chemical absorption of CO₂ with amines provides the most cost effective means of obtaining high purity (>99% CO₂) vapor from flue gases in a single step. The process is well established in gas sweetening and hydrogen production, but these processes are carried out at high pressures unlike with flue gas applications. Several alkanolamines such as MEA (monoethanolamine), DEA (diethanolamine), and MDEA (methyldiethanolamine) have been used, with the selection being determined by the application. High-efficiency FGD is essential, as amines react rapidly with SO₂^{13, p241} to form sulfite which does not generally stay in solution as a heat-stable salt because of its high reactivity.

The specialty amine aqueous solution strength can vary in the range 15 to 50% and has a significant affect on the process economics. Generic amines^{L3, L11}, such as MEA and DEA, are more corrosive and strengths are limited to 30%. Steam consumption is highly dependent on this selection, with lower concentrations requiring more steam. Amines degrade^{13, p232} in the presence of O₂ and CO₂ to form products which can reduce absorption capacity, increase solution viscosity, increase foaming and cause corrosion. Inhibitors are added to reduce this corrosion.

Amine losses^{13, p231} in low pressure amine contactors can be significant, with MEA having substantially higher vapor pressure than other amines. The water wash at the top of the absorber is used to minimize amine losses. The Lean Amine Feed temperature has a major influence on the flue gas temperature and water concentration and hence losses.

A simplified post-combustion CO₂ capture flowsheet using amine solution is shown. The heat integration circuit is basic and various schemes have been developed, which split the rich amine stream prior to the cross heat exchanger and feed to a separate heat recovery circuit which is then returned to the absorber as a rich amine feed. Flowsheet convergence is improved by breaking the rich amine stream feed to the stripper.



If the flowsheet is connected directly to the compression section then a dummy heat exchanger is required, prior to the compression section inlet, to allow for a local K of BWRS, modified for latest CO₂ parameters, to be specified.



Amine Absorber¹³

The CO₂ uptake in the absorber is influenced by the tray efficiency profile. Typically efficiencies are quoted for the bottom tray 37%, top tray 14% and a maximum efficiency 45% on the 15th tray from the bottom^{13, p120}. It should be noted that these values are for high pressure absorption. The heat of reaction generates considerable heat in the liquid phase with most of the reaction taking place at the bottom of the column. A typical temperature “bulge” is formed due to cool inlet gas absorbing heat from the rich solution at the bottom of the column and later losing heat to the cooler lean solution near the top. The lean solution temperature determines the water emission to atmosphere. The bulge is sharper and lower in the column for primary amines such as MEA.

The circulating liquor rate depends on the liquor selection, amount of MEA to satisfy the reaction stoichiometry and the packed tower loading for mass transfer which depends on the tower internals selection. Typical absorption liquor rate, quoted in the literature, is ~0.5 mol CO₂/mol amine which is equivalent to 1.87 mol L/mol G and 1.7 mol L/mol G was used to initialize the model. Typical regeneration liquor rates are ~0.2 mol CO₂/mol amine.

CO₂ Stripper¹³

Typical stripping columns contain 12 to 20 trays below the feed stage and 2 to 6 trays above to prevent loss of amine. Some foaming may occur at the feed tray so the trays above serve to remove entrained amine droplets. Column convergence is improved by setting the damping factor to 0.5 and by using simple estimations for initialization. The stripping of CO₂ from MEA solutions is aided by increasing the temperature (raising the pressure) or by reducing the water content.

Column bottom parameter could be set either by heat input, bottom flow rate draw or temperature. Temperature specification, set at 120 °C, allows calculation of column heat duty and bottoms flow with a varying feed rate. Bottom temperature was selected, though column bottoms flow could also be used as the composition is known and hence the total flow can be derived from the MEA feed flow. Reboiler heat flux should be limited and recirculation rate should be kept high and elevated temperatures avoided. Reboiler temperature should not exceed 120 °C to minimize amine thermal degradation. Typical reboiler steam rates are in the range 1 to 1.5 lb/gal of circulated solution. The rate of CO₂ desorption is not materially affected by the rate of stripping steam flow. The reboiler duty^{13, p123} has to be adequate to provide heat for the following:

Sensible heat to raise feed to lean solution temperature leaving the reboiler

Reverse the amine-acid gas reaction and dissociate the amine-acid gas compounds

Latent heat and sensible heat to convert reflux water into steam which serves as the stripping vapor

Column top parameter could be set either by heat duty or temperature. Reflux ratio was not specified as the top parameter due to partial condenser. Temperature was selected and set at 37.8 °C, which allowed reflux ratio and heat duty to be calculated. Typical reflux ratios^{13, p124} vary in the range 3:1 to <1:1 with MEA requiring a higher reflux ratio typically > 2:1. In this case reflux ratio refers to water (moles) in acid gas leaving column to CO₂ (moles) stripped. The surplus water take off flow (set in ratio to flow leaving the stage) directly affects the reflux ratio and hence the reboiler duty; this parameter is adjusted to obtain column convergence conditions. Specifying flow can lead to convergence problems.

An example in the source^{13, p125} quoted 20% amine solution rich feed temperature at 105 °C and reflux water returned to column at a temperature of 54.4 °C. The column temperature profile increased rapidly to 116 °C and then slowly increased to a reboiler temperature of 120 °C with a top column pressure of 1.66 bara.


Post-combustion Carbon Capture ^{1, 11, 13}

The following tables show typical model parameter values.

Post-combustion CO ₂ Capture Model Parameter Values			
Parameter	Input Value	Range or Factor	Units
ID Fan Head	0.371	0.25 – 0.5	bar
Flue Gas ID Fan Efficiency	70	60 – 85	%
Flue Gas Inlet	51	45 – 55	°C
MEA Solution Strength	30	15 – 50	% w/w
Absorber Theoretical Stages	12.0	Performance driven	Dimensionless
Stage Efficiency	0.3	0.1 – 0.3	Normalized
Absorber Pressure Drop	0.35	0.2 – 0.5	bar
Absorber Bottom Heat Exchanger	Case Value		MW
Absorber Top Heat Exchanger	Case Value		MW
Lean Liquid to Gas Ratio	1.7	1.5 – 1.8	mol L / mol G
Semi-lean Liquid to Gas Ratio	1.7	1.5 – 1.8	mol L / mol G
Absorber Bottom Temperature ⁽¹¹⁾	50	50 – 60	°C
Absorber Top Temperature ⁽¹¹⁾	35	40 – 45	°C
Stripper Theoretical Stages	20	Performance driven	Dimensionless
Stripper Top Pressure	1.65	System driven	bar
Stripper Pressure Drop	0.3	0.2 – 0.5	bar
Stripper Reboiler Pressure	2.0		bar
Stripper Condenser Duty	Case Value		MW
Stripper Reboiler Duty	Case Value		MW
Stripper Feed Temperature ⁽¹¹⁾	105	105	°C
Stripper Bottom Temperature ⁽¹¹⁾	110	110	°C
Stripper Top Temperature ⁽¹¹⁾	120	120	°C
Stripper Rundown Temperature	37.8		°C
Stripper Condenser	Partial Mode		
Condensate Rundown Split	Adjust for convergence		Dimensionless
Steam Pressure	3.0	3.0 to 4.0	bar
Pump Head	0.5	0.5 – 2.0	bar
Pump Efficiency	70	60 – 80	%

Absorber Stage Configuration		Stripper Stage Configuration	
Make up Water	1	Water take off	1
Top Pump Around	4 to 1	Rich MEA Feed	2
Lean MEA	4	Flash Steam	4
Semi-lean	Not assigned		
Bottom Pump Around	10 to 10		
Flue Gas Inlet	12		



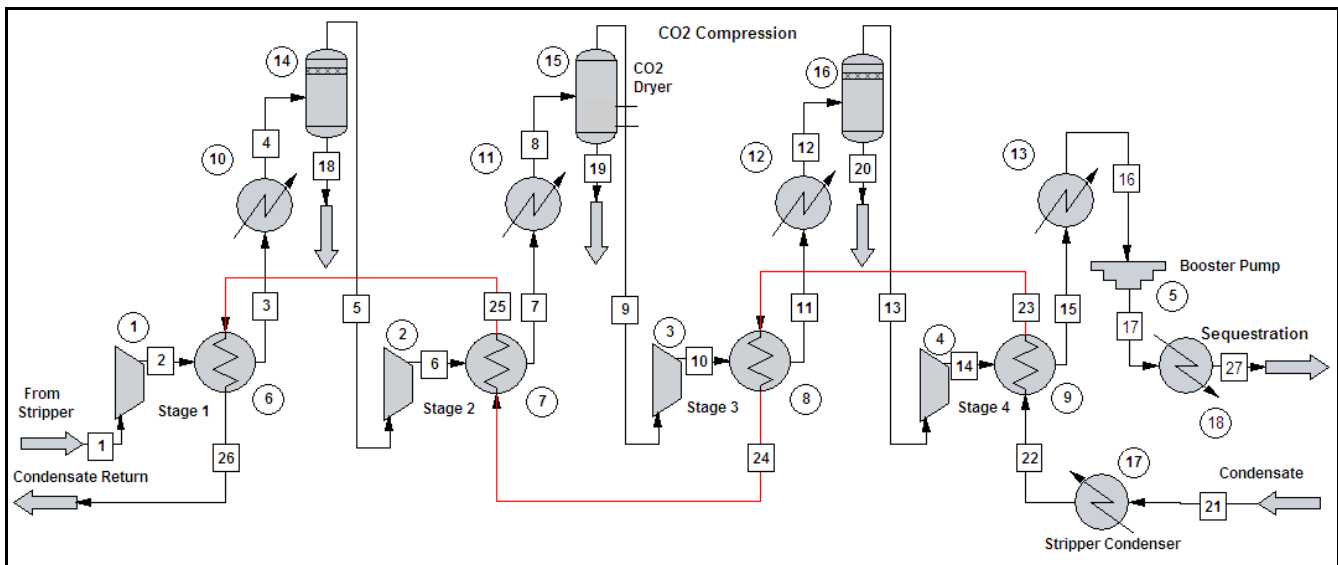
CO₂ Compression and Transport ^{1,9}

A typical pressure profile for the compression stages is shown in the table. A fixed inlet temperature of 40 °C was set for each stage. Turbine condensate from the boiler island was taken for stripper condenser cooling and compressor interstage cooling. Turbine condensate is typically available from the power plant at ~30 °C and can be returned at ~14 °C. The cooling circuit has been optimized to obtain the maximum heat extraction from the turbine condensate.

CO ₂ Compression Typical Model Parameters		
Parameter	Input Value	Units
Compressor Efficiency	75 (60-85)	%
Stage 1 Compression Ratio	3.0	Dimensionless
Stage 2 Compression Ratio	3.0	Dimensionless
Stage 3 Compression Ratio	3.0	Dimensionless
Stage 4 Compression Ratio	2.5	Dimensionless
Final Pressure	110	bar
Stage 1 Discharge Temperature	182	°C
Stage 2 Discharge Temperature	184	°C
Stage 3 Discharge Temperature	187	°C
Stage 4 Discharge Temperature	164	°C
Final Discharge Temperature	35	°C

Model stage compressor power absorbed and temperature rises can be validated using the theory presented in Appendix V: Heuristics for Process Equipment Design.

A typical CO₂ compression flowsheet is shown. The CO₂ dryer is modeled using a component separator.



**Appendix I: General Process Input Data****Coal Combustion**

Typical data¹⁴ are shown for coal used in power generation to allow initial estimates to be made for flue gas compositions resulting from burning coal.

Washed Coal as Fired	
Moisture, (% w/w)	7
Ash, (% w/w)	8
Carbon, (% w/w)	77.1
Hydrogen, (% w/w)	3.5
Nitrogen, (% w/w)	1.2
Sulfur, (% w/w)	1.0
Oxygen, (% w/w)	2.2
Calorific Value (Btu/lb), Gross	13200
Calorific Value (Btu/lb), Net	12790
Theoretical Air Requirements per kg fuel	
kg air	10.09
m ³ air, 0°C, 760 mmHg	7.8
Waste Gas per kg fuel	
m ³ wet waste gas, 0°C, 760 mmHg	8.08
CO ₂ content of dry waste gas %	18.9
Composition of Wet Waste Gas	
CO ₂ , (% v/v)	17.8
H ₂ O, (% v/v)	5.7
Oxides of N and S, (% v/v)	0.3
N ₂ , (% v/v)	76.2
Dew Point, °C	35

Natural Gas Fired Combined Cycle Plant

Consider a 1000-MW combined cycle gas turbine (CCGT) station burning natural gas with a molecular weight of 17.82 and net calorific value of 19826.4 Btu/lb. There are 3 Siemens V94.3A gas turbines (233 MWe each), 3 heat recovery steam generators, and 1 steam turbine (330 MWe) giving a total station output, allowing for 15 MW parasitic power, of 1014 Mwe.

The gas flow to one GT is 108376 lb/h and operates with a stoichiometric air/fuel ratio of 15.85; this gives an air flow of 4971022 /lb/h. At these conditions, the total flue gas flow is 4233 lb/s at a temperature of 113 °C and ~ 14.7 psia. With composition as shown, this will represent the feed to a retrofitted post-combustion carbon capture facility.

Component	Mass/Mass Fuel	Volume % (Dry)
CO ₂	2.59	14.24
O ₂	6.95	3.86
N ₂	35	81.9
SO ₂	0	0
H ₂ O	2.33	0

**Syngas Production** ^{21, Chapter 5}

Syngas produced from coal, gasified in the presence of steam and air, will consist primarily of CO and H₂. Increasing the gasification temperature increases the CO and H₂ content. Adding oxygen results in auto-thermic gasification, with no external heat being required, increases the CO and CO₂ content. Gasifier efficiency is determined by comparing the chemical energy in the Syngas relative to the chemical energy in the coal and is known as cold gas efficiency. Recent developments are mainly aimed at increasing the operating temperature and pressure. Typical performance data^{21, Table 5.6} of some demonstration gasification processes are shown.

Process	O ₂ kg/kg coal	Type	T _{reactor} °K	T _{exit} °K	Cold gas η%	P bar
Lurgi-Slag	0.52	Moving	>2200	700	88	25
Dow	0.86	Entrained	1600-1700	<1300	77	22
Shell	0.89	Entrained	2200	1200	81	30



Appendix II: Physical Property Data – Selexol and Genosorb

The Selexol™ process can be carried out using a polyethylene glycol dimethyl ether (PEGDME) manufactured by Dow Chemical Company. The physical and thermodynamic properties are summarized in the table. CHEMCAD Selexol is component 2277.

Selexol Physical Properties ²² (CHEMCAD library values)		
Property	Value	Units
Density at 77 °F	8.6 (8.595 at 60 °F)	lb/ gal
Vapor Pressure at 77 °F	0.0007 (0.00775)	mm Hg
Freezing Point	-8 to -20 (-21.46)	°F
Specific Heat at 121 °F	0.51 (0.505)	Btu/lb.°F
Viscosity at 77 °F	5.8 (7.2)	cp
Flash Point	304	°F
Molecular Weight	(266.33)	

Clariant makes an equivalent solvent called Genosorb 1753. The closest component in the CHEMCAD library is tetra ethylene glycol dimethyl ether (1483), which is used by Clariant to report solubility data being limited to one data point. Further information on Clariant products can be downloaded from the following link:

<http://www.glymes.com/businesses/glymes/internet.nsf/vwWebPagesByID/11A16FD250E225CDC125715B004B8A7E>

A literature survey has sourced the following solubility data for CO₂ in Selexol and TEGDME, which are quoted in the source system of units.

Basis	Coefficient	Primary Unit	Temp °C	Source Reference
Henrys Law $k_H = c_a / p_g$	3.1	N cm ³ /g @ 1 bar	25	Clariant data with TEGDME
Henrys Law $H = p_g / x_a$	3.6	M Pa	25	A. Henni, A. Chakma Canadian Journal Chem Eng Vol. 83, April 2005 ⁽¹⁶⁾
	4.7	M Pa	40	
	6.5	M Pa	60	
Henrys Law $k_H = c_a / p_g$	0.1686	M / atm	21	J.W. Sweny, J.P. Valentine Sept. 1970, Chem Eng ⁽¹⁵⁾

Units converter: <http://www.epa.gov/athens/learn2model/part-two/onsite/henryslaw.htm>

This converter is used with the following units conventions for a temperature at 25 °C:

H_{px} (= p_g/x_a in atm.) or H_{yx} (= y_g/x_a dimensionless) = 0.0000180 H_{pc} (= p_g/c_a in atm.m³/mol)

The heat of absorption for CO₂ in Selexol is 160 Btu/lb (-16.4 kJ/mole) solute and for H₂S 190 Btu/lb (-15.03 kJ/mole) solute.

**Appendix III: Physical Property Data for MEA, DEA, and MDEA (Manufacturer's Data)**Reference: Amines and Plasticizers Ltd ^{L3} http://www.amines.com/mdea_comp.htm

Comparison of Amines			
Solvent	MEA	DEA	MDEA
Concentration %	15	30	35-50
Solvent Circulation GPM	100	100	100
Acid Gas Removal Capacity MOL/HR	49.8	58.6	87.5
Capacity Increase % (MEA BASE = 100)	100	118	175

Heat of Reaction with H ₂ S and CO ₂		
Amine	Heat of Reaction (Btu/lb)	
	H ₂ S	CO ₂
MDEA	450	577
DEA	493	650
MEA	650	820

Selectivity and Capacity			
Amine	Selectivity*	Capacity	
		Mol H ₂ S/Mol Amine	Mol CO ₂ /Mol Amine
MDEA	3.85	0.10	0.12
DEA	2.27	0.09	0.32
MEA	0.89	0.07	0.50

*Selectivity is defined as ratio of (mole percent of H₂S removed to mole percent of H₂S in feed gas) to (mole percent of CO₂ removed to mole percent of CO₂ in feed gas).

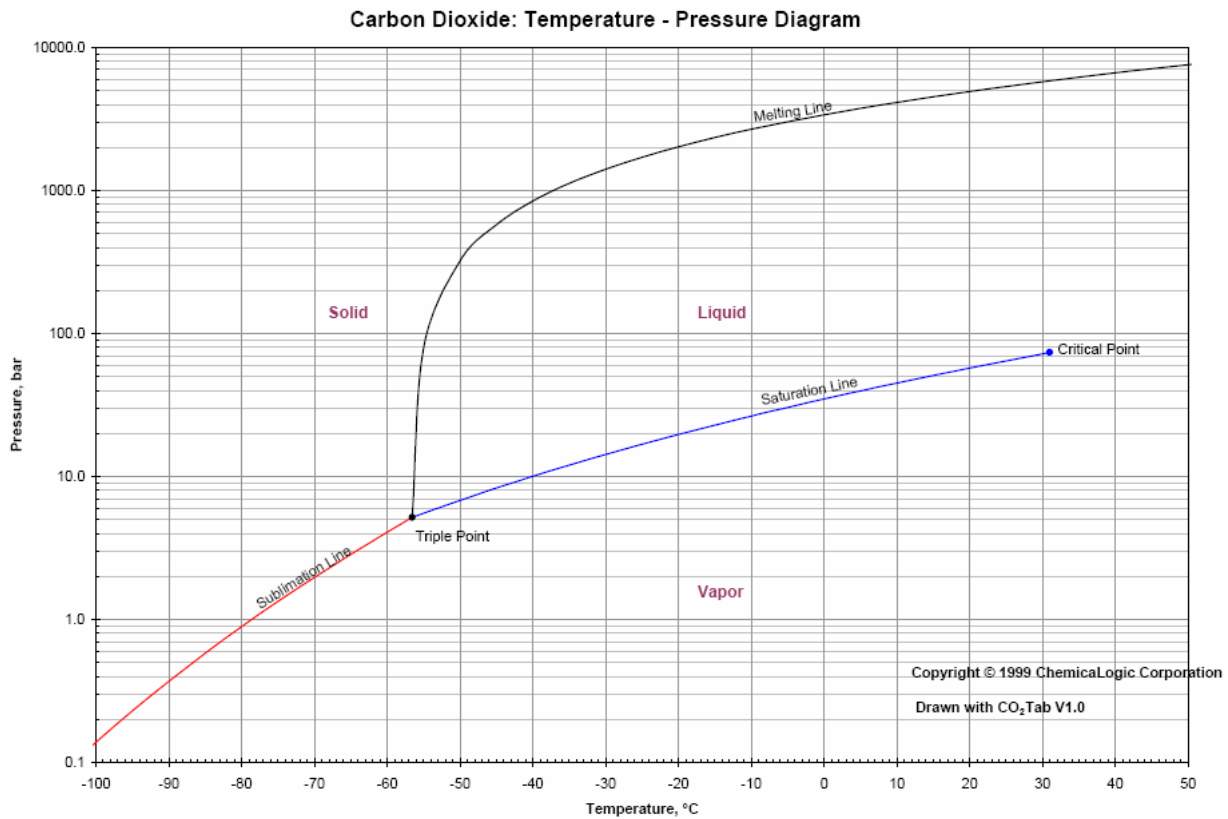
Recommended Ranges of Amines Concentration – Rich and Lean Amines			
Amine	Conc. Weight %	Rich Loading Mol/Mol	Lean Loading Mol / Mol
MDEA	35-55	0.45-0.55	0.004-0.01
DEA	25-30	0.35-0.40	0.05-0.07
MEA	15-20	0.30-0.35	0.10-0.15

Corrosion	
Solvent	Corrosion Rate MPY
30% Wt MEA	32
50% Wt DEA	25
15% Wt MEA	13
20% Wt DEA	8
50% Wt MDEA	3



Appendix IV: Physical Property Data for Carbon Dioxide

Species	Critical Temperature	Critical Pressure	Critical Volume
	°C	bar	m ³ / kmol
CO ₂	31.05	73.81	0.093



Benedict Webb Ruben Starling equation of state allows parameters to be set for CO₂ as follows:

γ	5.15515E-09	[(m ³ mol ⁻¹) ²]	1.322771343	[ft ⁶ /lbmol ²]	1 ft ³ [=]	0.0283168	m ³
A ₀	0.27706	[(m ³ mol ⁻¹) ² Pa]	10310.929341961	[psia ft ⁶ /lbmol ²]	1 lb mol [=]	453.59237	g mol
B	0.00004987	[m ³ mol ⁻¹]	0.798842083	[ft ³ /lbmol]	1 psia [=]	6894.76	Pa
C ₀	14024.79	[(m ³ mol ⁻¹) ² K ² Pa]	1691084688.96	[psia R ² ft ⁶ /lbmol ²]	1 R [=]	0.555555556	K
a	0.000013837	[(m ³ mol ⁻¹) ³ Pa]	8248.737608	[psia ft ⁹ /lbmol ³]			
b	4.119E-09	[(m ³ mol ⁻¹) ²]	1.056902503	[ft ⁶ /lbmol ²]			
c	1.503505	[(m ³ mol ⁻¹) ³ K ² Pa]	2903992124.50	[psia R ² ft ⁹ /lbmol ³]			
α	7.74781E-14	[(m ³ mol ⁻¹) ³]	0.318451808	[ft ⁹ /lbmol ³]			



Appendix V: Heuristics for Process Equipment Design

In modeling, “Rules of Thumb,” or heuristics based on experience, are used for estimating many parameters before more specific data is available.

Compressors and Fans ^{5,9}

Practical pressure rises are:

Fans – 12 in wg, Blowers < 40 psig and compressors for higher pressures.

Outlet temperature : $T_{out} = T_{in} \left(\frac{P_{out}}{P_{in}} \right)^{(k-1)/k}$ where $k = C_p/C_v$

Exit temperatures should not exceed 350 to 400 °F.

Compression power requirement for each stage is given by:

$$W = \left(\frac{1000}{24 \cdot 3600} \right) \left(\frac{m Z_s R T_{in}}{M \eta_{is}} \right) \left(\frac{k_s}{k_s - 1} \right) \left[(CR)^{\frac{k_s - 1}{k_s}} - 1 \right]$$

W = stage compression power [kW]

m = CO₂ mass flow [tons/day]

Z_s = average CO₂ stage efficiency

R = gas constant [8.314 kJ/kmol-K]

T_{in} = CO₂ temperature at stage inlet [K]

M = CO₂ molecular weight [kg/kmol]

η_{is} = isentropic efficiency of compressor

k_s = C_p/C_v average ratio of specific heats for stage

CR = P_{out}/P_{in} the compression ratio for stage

Optimal compression ratio (CR) for each stage is given by Mohitpour as follows:

$$CR = (P_{cut-off} / P_{initial})^{1/N_{stage}}$$

Typical efficiencies for reciprocating compressors are 65% at compression ratio of 1.5, 75% at 2.0, and 80-85% at 3-6.

Efficiencies of large centrifugal compressors are 76-78% and rotary compressors 70%.

Mills ⁷

Crushing is used from limestone size of 3/4” x 0” size down to 1/8” x 0” size, with power consumption in the range of 2 – 4 kWh/dry short ton where a short ton is 2000 lbs.

Grinding starts at 1/8” x 0” size, with horizontal ball mill power consumption of 32 kWh/dry short ton of limestone processed.

Wet grinding in a vertical ball mill can achieve 25 kWh/ dry short ton.



Absorbers and Strippers

Tray efficiencies for gas absorption and stripping can be as low as 10 – 20%.⁵

Large spray towers generally yield one equilibrium stage. The height of a gas limited transfer unit is in the range 1 to 3 m. Enhanced transfer takes place at the time of droplet formation with 75 to 95% approach to equilibrium stripping in a 1.4-m tower.^{8, 14-56}

Scrubber Type	Pressure Drop ("wc)	Gas Velocity (feet/sec.)	Liquid Pressure (psig)	Footprint Dia. for 60,000 acfm (feet-inches)
Spray Tower	2 to 4	6 to 8	20 to 60	12-6 to 14-6
Tray Tower	4 to 6	6 to 8	5 to 10	12-6 to 14-6
Packed Tower	3 to 4	6 to 8	10 to 20	12-6 to 14 -16
Venturi with Separator	8 to 12	-200 at throat	5 to 10	11-6

Pumps⁵

Centrifugal pumps: single stage for 15-5000 gpm, 500 ft max head.

Centrifugal pumps: multistage for 20 – 11,000 gpm, 5500 ft max head.

Efficiency 45% at 100 gpm, 70% at 100 gpm and 80% at 10,000 gpm.



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Power Plant Carbon Capture with CHEMCAD

Links

- L1 <http://www.co2captureandstorage.info/>
IEA data
- L2 <http://www.netl.doe.gov/technologies/index.html>
DOE reports
- L3 http://www.amines.com/mdea_comp.htm
Amine data
- L4 <http://www.ieagreen.org.uk/reports.html>
IEA reports
- L5 <http://www.glymes.com/businesses/glymes/internet.nsf/directname/home>
Clariant data
- L6 http://www.co2captureandstorage.info/networks/capture_workshops.htm
Networks
- L7 <http://www.netl.doe.gov/publications/>
DOE conferences
- L8 <http://www.gasification.org/Docs/Workshops/2007/Indianapolis/03Ciferno%20Pre%20and%20Post%20Combustion%20CO2%20Capture%20Summary.pdf>
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Dow data source
- L10 <http://www.co2storage.org.uk/>
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- L11 <http://www.rite.or.jp/English/lab/chemical/090622results-e/csiro2009-e.pdf>
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Acknowledgements

This technical paper has been prepared for Chemstations by J. E. Edwards of P&I Design Ltd, (Teesside, UK), who would like to acknowledge the support of Mott MacDonald, (Brighton, UK).