

Exploring the many carbon capture options

IMTE AG Consulting Engineers

Carbon capture and sequestration each have many technical hurdles remaining to be scaled in coming years. Capture and reuse of CO₂ to enhance oil recovery preceded the current clamor over climate change and is often pointed out as a viable way to handle the gas. This article explores the first part of the process—options for CO₂ separation and capture.

It has been more than ten years since the first commercial CO₂ capture and sequestration system motivated by greenhouse gas reduction was placed into service. In 1991, Norway became the world's first country to impose a tax on CO₂ emissions from point sources, to the tune of \$55/ton.

Five years later, Statoil began injecting CO₂ beneath the bottom of the North Sea to avoid the stiff carbon tax. Today, the state-owned firm is injecting about a million tons of CO₂ per year, in the process saving about \$55 million a year in taxes. That's a pretty good ongoing return on an \$80 million investment.

In North America, EnCana's Weyburn field tertiary oil recovery project dwarfs all similar sequestration projects. The CO₂ byproduct of the Great Plains Synfuels Plant in North Dakota is collected and transported north to an oil field in Saskatchewan through a 200-mile pipeline and injected underground, extending the field's productive life (Figure 1).

The CO₂ acts much like a solvent, removing oil trapped in cracks of reservoir rock. In Saskatchewan, the results have been impressive: a two-thirds increase in oil production from the field since CO₂ flooding began in 2000. The project is expected to permanently store 20 million tons of CO₂ over its lifetime.

The differences between these two projects go well beyond their technical details and original motivation. The current U.S. plan for carbon capture and sequestration lies somewhere between Norway's top-down regulatory approach and the free-market partnership between Weyburn and Great Plains Synfuels. Washington envisions meeting the carbon challenge with government-industry partnerships seeded by federal money that industry would match.

In the U.S., there are seven regional carbon sequestration partnerships spanning 40 states (Table 1), and they are poised to scale up their research and pilot plant operations as the third phase of a multi-decade effort.

The partnerships spent much of 2003-2005 characterizing the regional opportunities for capture and storage of CO₂ in North America and publishing the National Carbon Sequestration Atlas and Geographic Information System and other materials. Phase 2 began in 2005 with field evaluations that will continue through 2009.

Phase 3 is the deployment phase; several high-volume (up to 1 million tons/yr) sequestration pilot projects are scheduled to be built in North America between now and 2016.

The U.S. Department of Energy (DOE) sequestration program is funding a diverse portfolio of around 70 different R&D projects with a projected 2007 budget of around \$74 million.

Many of the projects enjoy strong industry support; the private sector is providing 39% of their funding, on average. U.S. investment in the sequestration R&D program to date is on the order of \$260 million.

First things first

Over the past 160 years, atmospheric levels of CO₂ have risen from around 280 ppm to 360 ppm. The increase has been caused primarily by skyrocketing growth in combustion of fossil fuels by vehicles, factories, and power plants.

Predictions of global energy use this century suggest continued increases in carbon emissions and atmospheric concentrations of CO₂ unless major changes are made in the ways we produce and use energy, as well as how we manage carbon.

In the U.S., power generation accounts for about 40% of national, man-made CO₂ emissions. Creating a power plant that emits no carbon (the goal of DOE's FutureGen effort) will require the simultaneous development of carbon capture and sequestration technologies.

Sequestration projects such as the ones in Norway and the U.S. described above will be only marginally useful unless the tonnage of CO₂ emitted by power plants can be reduced considerably. Likewise, a CO₂-capturing integrated gasification combined-cycle (IGCC) plant without a place to safely store the gas will accomplish just as little.

State-of-the-art conventional generation technologies are still growing in thermal efficiency, and we could see a further improvement of 4% to 5% over the next decade or so (Table 2).

New alloys being developed for ultra-supercritical boilers and steam turbines may push the efficiency of plants based on them to 50-52% by 2020, and to 52-55% by 2050. Table 2 also lists the range of CO₂ emissions for each of the power generation technologies considered.

Many CO₂ capture options

Power engineers would be wise to gain a understanding of the growing role that coal gasification in general, and IGCC in particular, will play in clean electricity production worldwide over the next decade. At present, it appears that the carbon-capture portion of future IGCC plants will be based on one of four general technological approaches:

- Post-combustion CO₂ capture
- Oxy-fuel combustion
- Pre-combustion de-carbonization
- A potpourri of novel concepts that resist categorization

Each technology has advantages and disadvantages. Some have been proven in the chemicals production industry, and others, while holding much future promise, are still in the laboratory development stage. The remainder of this article explores these four categories in greater detail.

Post-combustion CO₂ capture

The first approach—the simple addition of a separate post-combustion CO₂ capture system to a power plant—is the most straightforward technique. End-of-pipe treatment of flue gases produced by conventional fossil fuel-fired plants belongs in this category.

However, the technique's economic efficiency is rather low. The huge volumes of flue gas containing relatively little CO₂ must be handled by conventional absorption processes requiring very large and expensive equipment.

What's more, the efficiency penalty that the technique imposes on the power plant is huge, on the order of 25-35%. Yet post-combustion capture seems eminently suitable for retrofitting to existing facilities because it does not affect the upstream (fuel) part of the plant.

Many commercial technologies being proposed for CO₂ capture are not new, and have proven effective as components of industrial processes. Many of those processes are technologically mature and available.

For example, chemical and physical absorption are ready to CO₂ capture in bulk quantities today—but at a prohibitive cost. R&D studies suggest that chemical absorption may be more suitable than physical absorption for post-combustion de-carbonization. Physical absorption may be a better fit with pre-combustion de-carbonization—the third technology approach (more on this later).

Pros and cons of amines. Alkanolamines are considered by many as the best candidates for post-combustion de-carbonization of flue gases. They have been well proven well as de-carbonization solvents in the gas processing, chemicals, and petroleum industries for more than 50 years.

Figure 2 is a flow diagram of a typical process of this sort. The upstream absorption stage cools the CO₂ stream and removes particulates from it. Next, the cooled and cleaned stream enters the absorption tower, where it makes contact with the alkanolamine solvent in counter-current flow.

The gas to be absorbed enters the absorber at its bottom, flows up, and leaves at the top. The solvent enters the top of the absorber, flows down, and emerges at the bottom. CO₂ is chemically bound to the solvent by the exothermic reaction of the gas with the amine in the solvent.

The liquid amine CO₂-rich solvent then leaves the bottom of the absorber and passes into the stripping tower via a cross heat exchanger. In the CO₂ stripper, the mixture is heated with steam to liberate the CO₂ from the solvent as the acid gas. This step is carried out at lower pressure than the previous absorption step, to enhance desorption of CO₂ from the liquid.

The CO₂ is now ready for the further steps of compression, transport from the power plant to a storage site, and sequestration. The hot lean amine solution then flows through the cross heat exchanger, where it is contacted with the rich amine solution from the absorber. The lean amine solution from the cross heat exchanger is then returned to the top of the absorption tower.

Amine absorption has been practiced at large scale in the natural gas processing industry to remove H₂S and CO₂ from the fuel. Adapting the technique to flue gas de-carbonization is problematic, for two reasons.

First, CO₂ is present in large quantities in flue gas, but H₂S is only an impurity to be removed from natural gas. Second, de-carbonization of natural gas must address the presence of H₂S—but there is no H₂S in flue gas.

The greatest obstacle to post-combustion de-carbonization is the low pressure (atmospheric) of the flue gas. Only chemical solvents with high reaction energies like alkanolamines can economically scrub CO₂ under such low partial pressures.

The term “amine” refers to group of organic compounds that can be derived from ammonia (NH₃) by replacing one or more H atoms by organic radicals. Amines are classified according to the number of hydrogen atoms replaced.

Primary amines (RNH₂) include monoethanol amine (MEA) and diglycolamine (DGA). There is considerable industrial experience with primary amine chemical absorption solvents, especially with MEA.

MEA, one of the most frequently used solvents for CO₂ capture, has been the traditional solvent of choice for CO₂ absorption and acid gas removal in general. It is the cheapest technique, but it generates the most reaction heat: 1.9 MJ/kg.

Because MEA’s molecular weight is the lowest of the primary amines, it has the highest theoretical absorption capacity. But it also the lowest boiling point, so there may be solvent carryover in the CO₂ removal and regeneration steps. Another drawback of MEA is its high reactivity with COS and CS₂, which degrades the solvent. In addition, the CO₂ itself is a strong corrosive agent.

Techniques based on primary amines have been used in industry. An example is the Fluor Daniel Econamine FG process, which uses MEA concentrations of around 30% by weight to successfully remove 80-90% of the CO₂ from the flue of an ABB Lummus process. In the latter process, the MEA concentration is around 20% by weight.

Secondary amines (R₂NH) include diethanolamine (DEA) and di-isopropylamine (DIPA). Secondary amines have lower capture reaction heat and enjoy some advantages over primary amines.

For example, the reaction heat of CO₂ with DEA is only 1.5 MJ/kg, compared to 1.9 MJ/kg for primary amines. This makes the use of secondary amines more economical in the regeneration step than using MEA. However, secondary amines share the other downsides of primary amines.

Tertiary amines (R₃N) amines—including triethanolamine (TEA) and methyl-diethanolamine (MDEA)—are even less reactive. They require the least heat to liberate the CO₂ from the solvent. For example, MDEA’s capture reaction heat is just 1.3 MJ/kg.

Because tertiary amines react more slowly with CO₂, they must be circulated more quickly than primary and secondary amines. On the upside, tertiary amines degrade and corrode more slowly than primary and secondary amines.

Oxy-fuel combustion

The second approach to carbon capture is oxy-fuel combustion, which also is called oxy-fuel de-carbonization or O₂/CO₂ firing. It is a much more elegant technique than post-combustion CO₂ capture because pure oxygen is used as the oxidant instead of air. Nitrogen is completely eliminated from the process. Instead of nitrogen, CO₂ recycled in a semi-closed cycle serves as the working fluid (Figure 3, top).

Oxy-fuel combustion is much more promising for new installations than post-combustion CO₂ capture. Although the air separation (oxygen generation) unit consumes a lot of energy, its overhead is mitigated by the elimination of the need for final CO₂ separation—the technique's biggest plus.

CO₂ is produced in a high sequestration-ready concentration in the range of 80-98%. Water alone must be removed from the flue gas, by simple condensation.

There is a broad, ongoing, and worldwide R&D effort to reduce the cost of oxygen generation. Most of the advanced processes being investigated are based on operating membranes at high temperatures.

Scale-scale test rigs have confirmed that overall plant efficiency and economics can be improved by oxy-fuel combustion. Larger-scale work is being done in glass and steel melting furnaces. At this point, it appears that oxy-fuel combustion could be retrofit to existing steam power plants without incurring exorbitant costs.

Figure 4 illustrates how oxy-fuel combustion could be incorporated into a combined-cycle cycle to enable carbon capture. The key elements of this process are:

- An air separation/oxygen generation unit (not shown).
- A gas turbine designed to operate with a CO₂/H₂O working fluid.
- A control system for maintaining stoichiometry between the streams of fuel and oxygen injected into the combustion chamber. Doing so is necessary to keep unreacted fuel and oxygen from reaching downstream of the chamber.
- A Rankine cycle circuit.
- A condenser/separator, for segregating the carbon dioxide from the water.
- A compressor/pumping/heat exchanger system, needed to pump the CO₂ to its final destination.

For power plants fueled by natural gas, this concept would represent another alternative to pre-combustion capture. The only problem with implementing the scheme: it would be harder to operate the gas-fueled gas turbines with a CO₂ working fluid than it would be for turbines firing a hydrogen-rich fuel.

Accordingly, retrofitting existing gas-fired combined-cycle plants with an oxy-fuel system would not be economic because the turbines would have to be redesigned. Greenfield projects, by contrast, may indeed prove more feasible.

Pre-combustion de-carbonization

Removal of the carbon prior to the combustion stage of an IGCC plant is our third carbon capture option (Figure 3, bottom). First, a fossil fuel is transformed to a synthetic gas (syngas), essentially a mixture of CO + H₂. Next, the CO in the syngas is converted to H₂ + CO₂ by a water-gas-shift (WGS) reactor. Finally, the CO₂ is separated by conventional methods.

The big advantage of pre-combustion carbon removal is that the CO₂ separation step consumes much less energy than in other processes because it takes place in a smaller reaction volume and at lower volumetric flow rates, elevated pressure, and higher component concentration. The higher concentrations make the capture process far less energy-intensive. The energy generation penalty, typically 10-16%, is roughly half that of post-combustion CO₂ capture.

Pre-combustion carbon capture is a lot more cost-effective than post-combustion capture and slightly more effective than oxy-fuel capture. Technologies for pre-combustion capture of CO₂ via gasification are well established in the process industries.

They can be considered a segment of H₂ production processes commonly used and proven in NH₃ production, oil refining, and methanol synthesis. Figure 5 is a simplified flow diagram of an IGCC system, firing a heavy fuel feedstock, integrated with pre-combustion carbon capture.

An advantage of pre-combustion capture is that the syngas produced as the first step of the process can be used as fuel in a turbine cycle. Doing so would produce a flue gas stream high enough in CO₂ concentration to allow the use of simple, inexpensive separation techniques.

Figure 6 is similar to Figure 5, but it shows the syngas generation options that would be available to an IGCC plant using natural gas as feedstock. Commercial gas turbines are optimized to burn either natural gas or fuel oil. Tailoring them to burn hydrogen would certainly require a redesign, but it might not be substantial.

When natural gas is the feedstock, syngas can be produced by either of the technologies shown in Figure 5. The CO is reacted with steam in a catalytic process of the WGS reaction to produce CO₂ and the highest possible amount of H₂.

Following the conversion and the removal of condensate, the gas mainly consists of H₂ with CO₂. The CO₂ can then be separated by chemical or physical absorption and disposed of or put to use. The H₂ can be used as chemical feedstock or as fuel for a combined-cycle plant or a fuel cell.

Chemical vs. physical solvents. Chemical or physical gas absorption equipped with a stripping regeneration stage—generally called cold gas cleanup (CGC)—is used for syngas desulfurization by all currently operating IGCC plants, with the sole exception of the Piñon Pine Power Project (funded by the DOE and Sierra Pacific Power Co.) in Nevada.

Elevated pressures and relatively high concentration of CO₂ in the syngas are the prime cost drivers for pre-combustion carbon removal technologies. Moreover, strong-affinity

chemical solvents have to be used to capture such small concentrations of CO₂ in such a big volume.

Absorption of CO₂ by MDEA is very efficient. Unfortunately, the stronger the capture, the more heat is required to release the CO₂ in the regeneration stage. Apart from this disadvantage, strong chemical degradation sensitivity to SO₂ and NO₂ exists. In the presence of oxygen, corrosion also becomes more aggressive.

Despite these drawbacks, the commercial use of the alkanolamine MDEA is currently popular at IGCC plants. Projects such Plaquemine (1986), Wabash River (1995), Tampa Electric (1996), Puertollano (1997), ISAB Energy (2000), Motiva Delaware (2000), and Piensa (2006) employ MDEA for the same reason: it is highly effective at removing sulfur from syngas.

Of course, this does not mean that MDEA will retain its edge over physical solvents. Preliminary experience suggests that physical solvents may be more effective for this purpose.

Physical solvents. If the CO₂ concentration and pressure could be increased, the CO₂ capture equipment would be smaller and physical solvents could be used, with lower energy penalties for regeneration.

Using physical solvents, CO₂ concentration can be three times higher while pressure upstream the gas turbine is typically 20 times higher.

Volume concentration of the CO₂ is therefore 60 times higher, compared to typical flue gas from a coal plant. The advantage in this case is lower heat consumption in the solvent regeneration step: no additional heat is necessary, and the stripping is driven mainly by the pressure release (flash distillation).

The **Rectisol** process with intermediate water-gas-shift is one of the most effective procedures for pre-combustion CO₂ capture from IGCC plants firing a heavy fuel.

It offers multiple benefits such as desulfurization, additional H₂ generation via WGS, H₂ separation, and CO₂ capture—all in a single, integrated train.

This process configuration has been applied in the Pernis refinery/127-MW IGCC project operated by Shell Gasification Solutions. The Pernis plant, in the Netherlands, is the first IGCC facility equipped with CO₂ separation, although the separated CO₂ is presently vented.

Thanks to this arrangement, Pernis could be considered the only sequestration-ready IGCC plant in the world.

Single-circuit Rectisol processes also are running at the 350-MW Vresova IGCC project in the Czech Republic and at Global Energy Inc.'s Schwarze Pumpe station in Germany.

Selexol is another physical solvent competitive with Rectisol. There are 55 Selexol operating units in syngas and natural gas service in the world. In operating IGCC plants, Selexol isn't as popular, however.

On the other hand, if H₂ production or CO₂ capture is the priority, Selexol moderately outperforms Rectisol. Table 3 lists the IGCC projects (principally at refineries) currently using Selexol.

Figure 7 is a flow diagram of the process being used at Farmland Industries, Inc.'s ammonia plant in Coffeyville, Kansas.

Emerging concepts

The fourth and last category of carbon capture technologies comprises novel concepts based on techniques at the pilot or laboratory stage of development. Processes that use membranes, chemical looping, or hydration to separate CO₂ are examples of these promising (in the longer term) technologies.

Ion transport membranes (ITMs) can selectively move oxygen ions and thus separate oxygen from any gas mixture. Ion transport is a very economical but very energy-intensive cryogenic process that uses ceramic, non-porous, mixed-conducting membrane media. The membrane itself uses conductors made of mixed-metal oxides.

The membrane conductivity state is initialized at high excitation temperatures, typically 800C to 900C. At these temperatures the ITMs exhibit both electric and oxygen ion conductivity. In stoichiometric terms, they are oxygen-deficient and thus create oxygen vacancies in their crystal lattice.

The ion transport mechanism is based on the principle of ionic exclusion. First, oxygen from the air adsorbs on the surface of the membrane. The membrane then dissociates, ionizes, and releases electrons.

The oxygen anions occupy vacancies in the lattice and diffuse through the membrane, driven by an oxygen chemical-potential gradient. This gradient is proportional to the difference between the respective oxygen partial pressures on opposite sides of the membrane.

At the permeate surface of the membrane, the oxygen ions release their electrons, which subsequently recombine and desorb from the surface as neutral oxygen molecules.

The interest in ITMs is based on the possibility of indirect CO₂ capture directly in the gas turbine's combustion chamber. Oxygen is separated from air using an ITM, fuel is added, and combustion takes place at the opposite (permeate) side of the membrane. This arrangement mimics a gas turbine combustor with inherent CO₂ separation.

The flow rate of oxygen across the membrane surface is proportional to the difference of concentrations (partial pressures) of oxygen on both sides. The lower the concentration on the permeate side, the better the whole process is driven. A big advantage of the process is that oxygen on the permeate side is permanently withdrawn as the consequence of combustion.

The idea of integrating ITMs with a gas turbine was originally proposed by Norsk Hydro. The concept was further developed by Alstom, which has proposed using it in the EU-sponsored AZEP Advanced Zero Emission Power Plant) project.

Chemical looping makes it possible to perform both fuel combustion and CO₂ separation in a single piece of equipment. It is a closed-circuit ion transfer process that uses a metal oxide to transfer oxygen from the combustion air to the fuel. As with ITMs, direct contact between fuel and combustion air is avoided.

The process (Figure 8) is made possible by two fluid reactors operating as an oxygen exchanger with interconnected fluidized beds. In the fuel reactor, the metal oxide is reduced by reaction with the fuel.

Its outlet gas consists of CO₂ and H₂O. In the air reactor, the reduced metal oxide is oxidized by air. Its outlet gas consists of nitrogen and a reduced amount of oxygen.

The net chemical reaction (pseudo-combustion) of the two reactors is the same as for normal combustion with the same amount of heat released. The advantage is that CO₂ is inherently separated off, eliminating the need for auxiliary power.

CO₂ hydration processes are our final example of novel, emerging technologies. CO₂ hydrates are especially compatible with water-gas-shift reactors.

The process relies on water's ability to create hydrates in the presence of CO₂ at high pressure and very low temperature. As Figure 9 shows, CO₂ is hydrated in the formation reactor, which receives nucleated water from another reactor.

The nucleation process creates enough active nuclei centers in a solvent, in this case water. Next, the nuclei promote massive hydration of CO₂, creating the hydrate slurry. Finally, the CO₂ is separated from its hydrate slurry.

The upside of the process is that this separation can be accomplished efficiently, at low capital and operating costs. The downside of the process is that it requires ammonia cooling.

TABLES

Table 1. Regional carbon sequestration partnerships. *Source: U.S. EPA*

| | |
|--|--|
| California Energy Commission | www.westcarb.org |
| New Mexico Institute of Mining and Technology | www.southwestcarbonpartnership.org |
| Montana State University | www.bigskyco2.org |
| University of North Dakota, Energy & Environmental Research Center | www.undeerc.org/pcor/ |
| University of Illinois, Illinois State Geological Survey | www.sequestration.org |
| Battelle Memorial Institute | www.mrcsp.org |
| Southern State Energy Board | www.secarbon.org |

Table 2. CO₂ emissions of various power generation systems. *Source: IMTE AG Consulting Engineers*

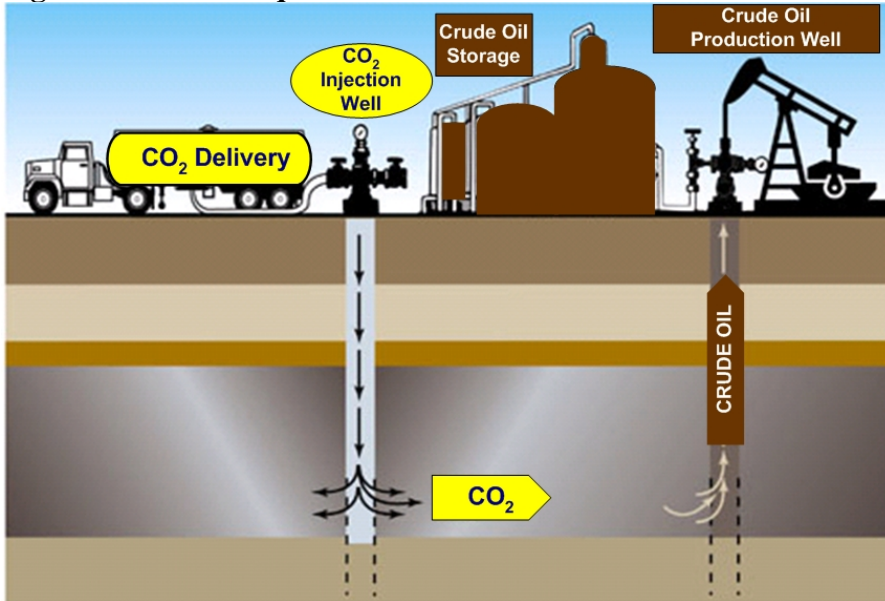
| Technology | CO₂ emissions Tons/MWh | Typical thermal efficiency over next decade, % |
|---|--|---|
| Combined-cycle gas turbine plant firing natural gas | 0.35 – 0.40 | 54 |
| Combined-cycle gas turbine plant firing oil | 0.45 – 0.55 | 48 |
| IGCC plant | 0.60 - 0.80 | 43 |
| Pulverized coal plant with flue gas desulfurization | 0.70 – 1.00 | 41 |
| Pressurized fluidized-bed combustion plant | 0.75 – 1.05 | 40 |
| CO ₂ recycle system | 0.90 – 1.20 | 34 |

Table 3. Gasification projects currently using Selexol. *Source: IMTE AG Consulting Engineers*

| Plant name/owner | Country | Start-up date | Feedstock | Gasification process | End product |
|--|----------------|----------------------|--------------------|-----------------------------|--------------------|
| SCE Cool Water | U.S. | 1984 | Bituminous coal | Texaco | Ammonia |
| Mitteldeutsche Erdöl-Raffinerie GmbH | Germany | 1985 | Visbreaker residue | Shell | Methanol |
| Coffeyville Resources Refining & Marketing | U.S. | 2000 | Petroleum coke | Texaco | Ammonia |
| api Energia S.p.A | Italy | 2001 | Visbreaker residue | Texaco | Electricity |
| Sarlux srl | Italy | 2001 | Visbreaker residue | Texaco | Electricity |
| Total Fina Elf/Texaco | France | 2006 | Refinery residue | Texaco | Hydrogen |

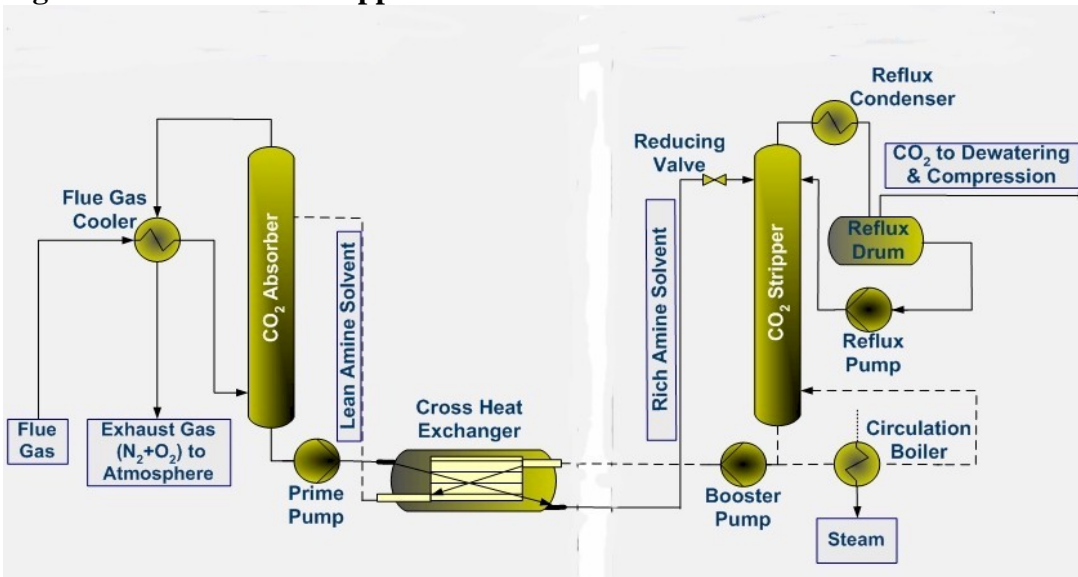
FIGURES

Figure 1 - Before sequestration.



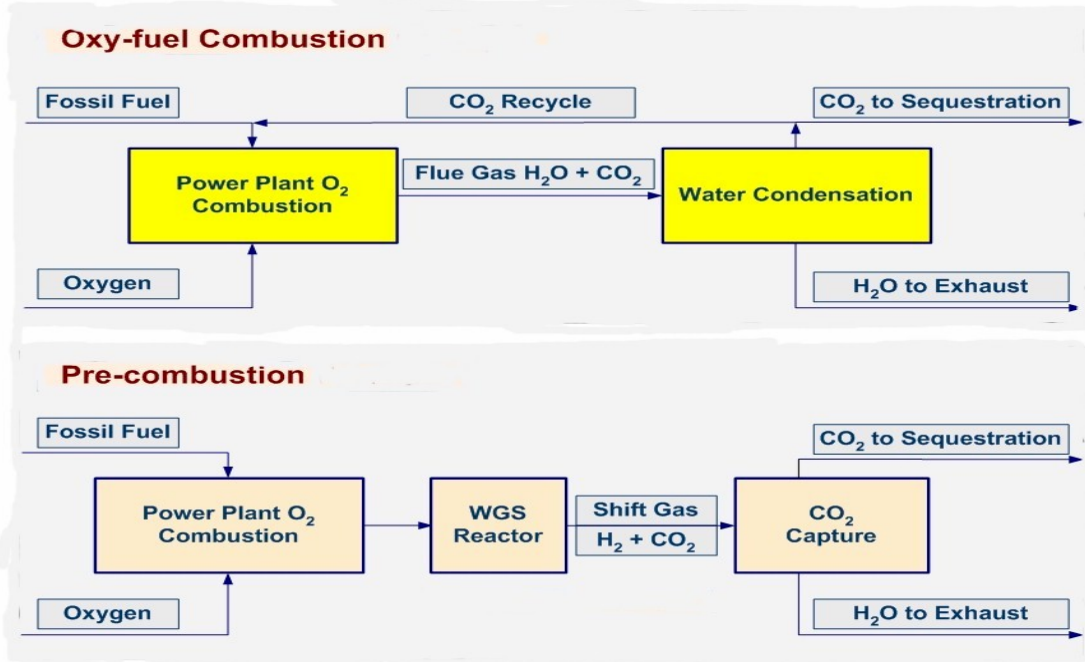
The typical process for injecting CO₂ into a depleted oil field to increase its output. Source: IMTE AG Consulting Engineers

Figure 2 - After-the-fact approach.



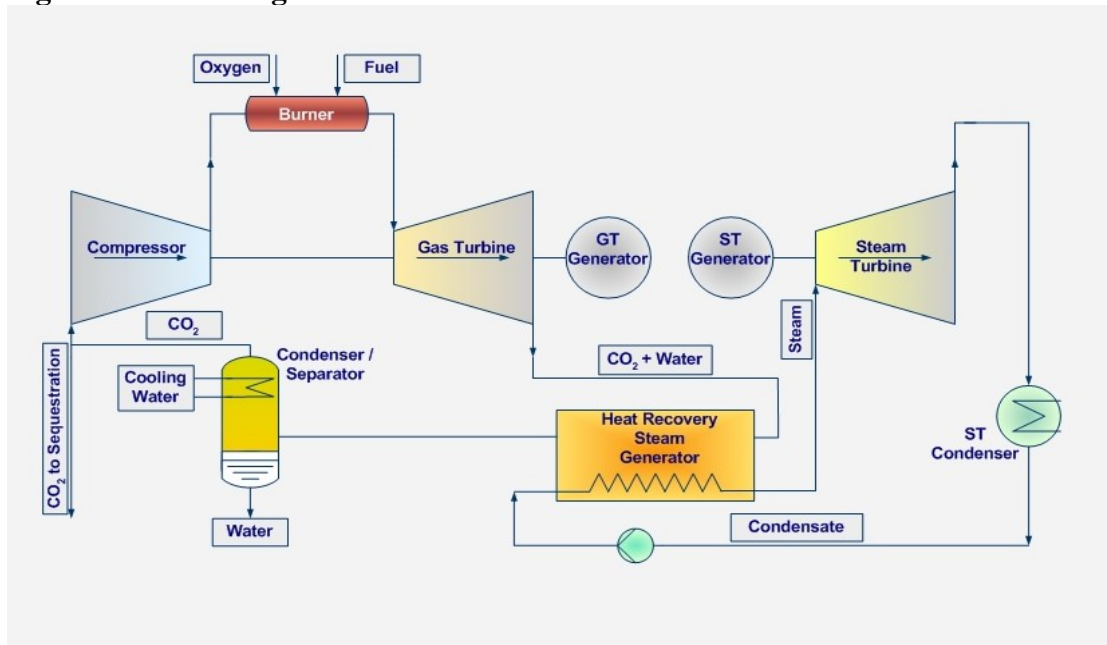
The process flow of a typical flue gas decarbonization system. Source: IMTE AG Consulting Engineers

Figure 3 - More options.



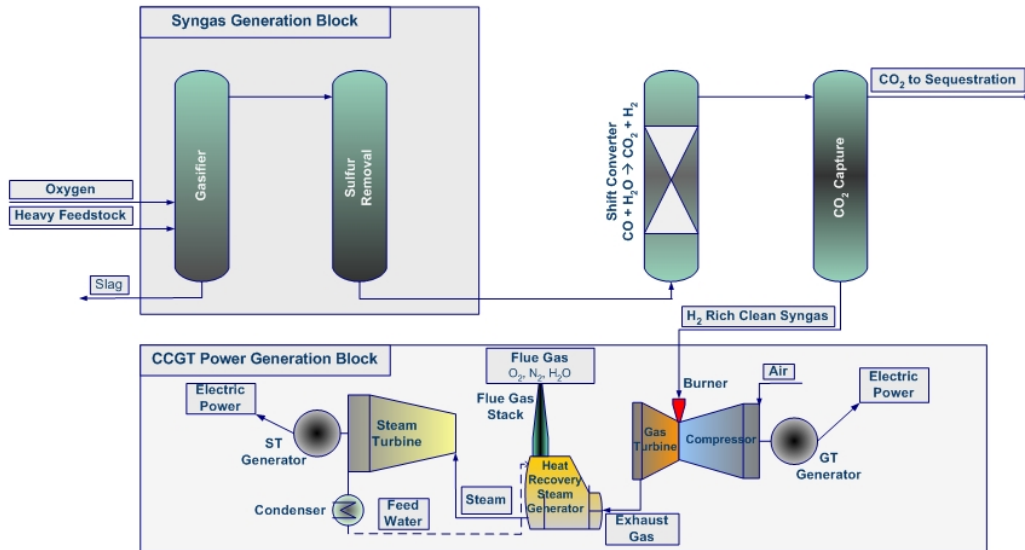
Oxy-fuel and precombustion options for power plant CO₂ capture and sequestration.
 Source: IMTE AG Consulting Engineers

Figure 4 - Semi-tough.



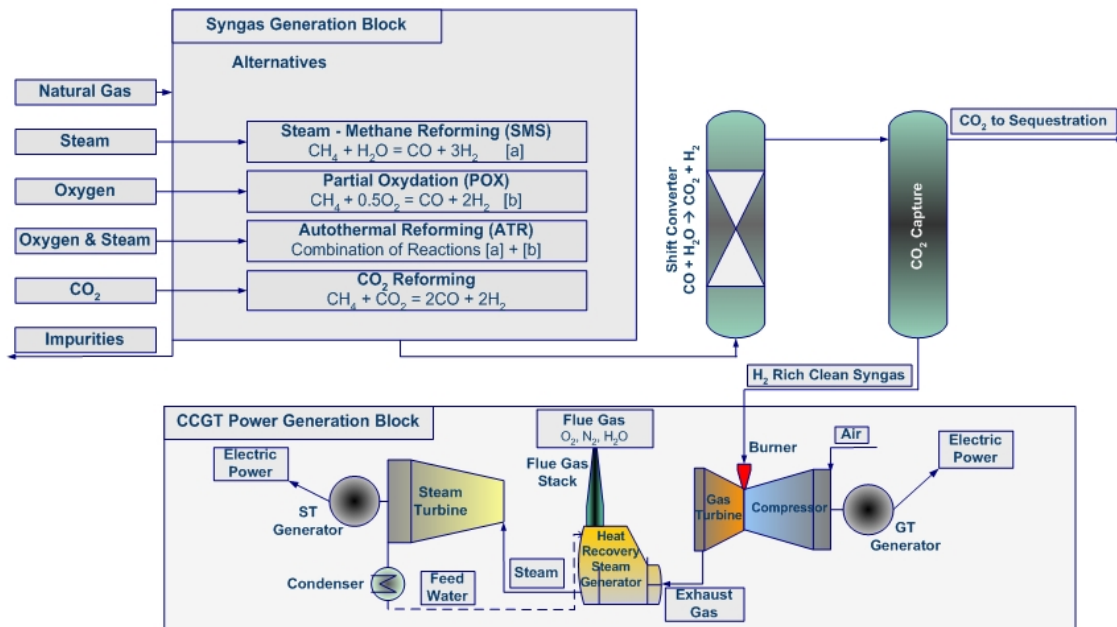
One possible way to retrofit a combined-cycle plant with an oxy-fuel combustion system that circulates CO₂ in a semi-closed loop. Source: IMTE AG Consulting Engineers

Figure 5 - Heavy duty



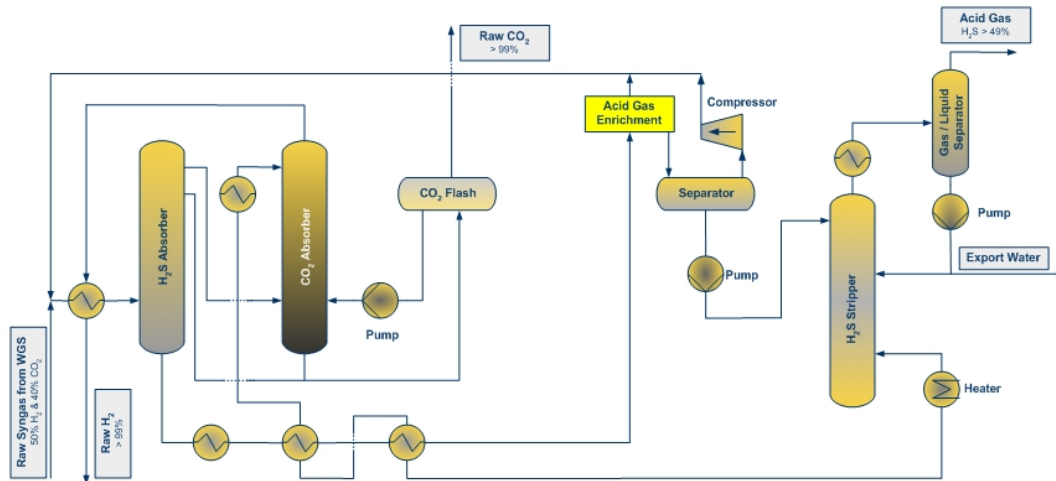
A flow diagram of an IGCC plant with a heavy fuel feedstock. *Source: IMTE AG Consulting Engineers*

Figure 6 - Lighter fare.



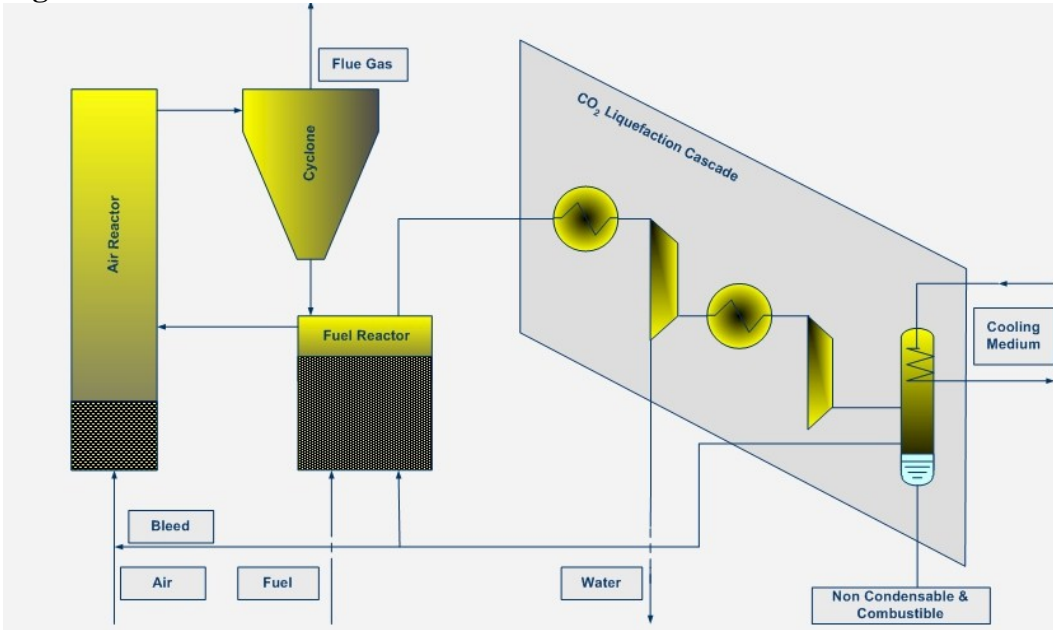
A flow diagram of an IGCC plant firing natural gas and equipped for pre-combustion capture of CO₂. *Source: IMTE AG Consulting Engineers*

Figure 7 - Selexol selected.



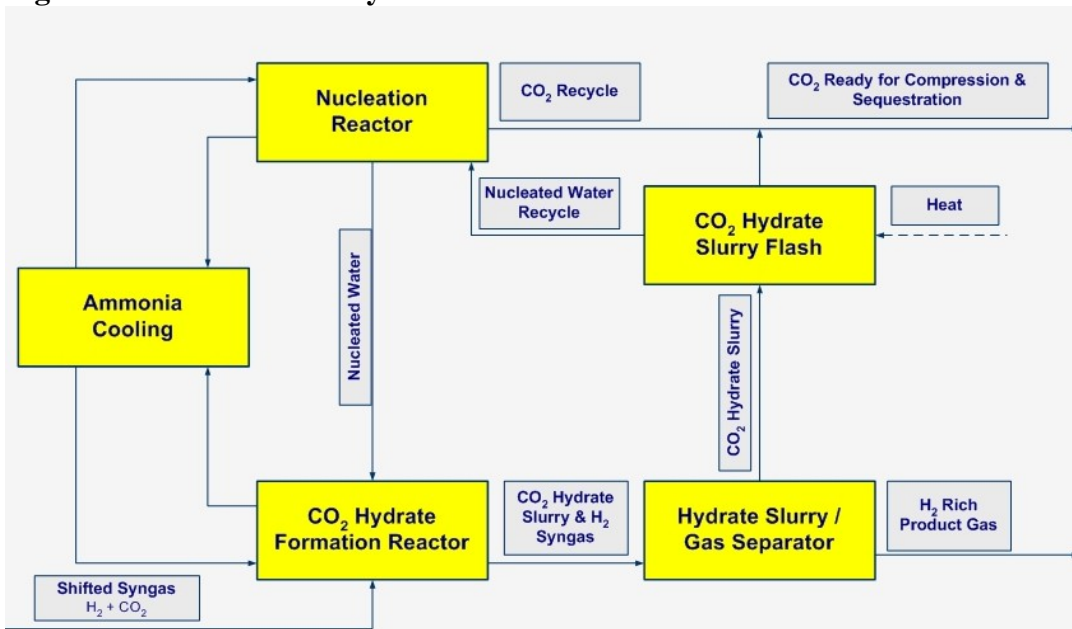
The process flow at Farmland Industries' ammonia plant in Coffeyville, Kansas. The plant uses Selexol to treat syngas. *Source: IMTE AG Consulting Engineers*

Figure 8 - Indirect combustion.



The flow of a chemical looping system. *Source: IMTE AG Consulting Engineers*

Figure 9 - Remember to hydrate.



9. Remember to hydrate. The flow of a CO₂ hydration process. Source: IMTE AG Consulting Engineers