

## Hybrid Power for Cracking Power Plant CO<sub>2</sub>

“Sequestration” (pumping enormous volumes of CO<sub>2</sub> underground and hoping it won't leak out) is impractical for several technical and political reasons. The clear and convincing case against carbon sequestration can be found in a recent [GAO report](#) on the field.

A preferable approach is molecular dissociation, known as cracking. By electrolysis, CO<sub>2</sub> can be cracked into solid carbon and oxygen gas, making treasure out of trash. Simultaneous electrolytic cracking of CO<sub>2</sub> and water can produce syngas (CO + H<sub>2</sub>), which can be converted to liquid vehicle fuel.

So how much cracking energy will be required, and where will it come from? As we discuss below, the enormous cracking energy for coal plant CO<sub>2</sub> should be provided by wind, solar, and other renewable energy sources, in a hybrid power system. Coal provides base load power, and renewables crack the coal emissions.

### *Post-Combustion Carbon Capture and Disposal at Pulverized Coal Plants*

Although IGCC may be the clean coal technology of the future, presently nearly all coal plants are of the type where the coal is burned to raise steam, and the steam pushes a turbine to turn a generator. Post-combustion carbon dioxide capture and disposal remains an unsolved problem. Despite growing alarm over global climate change, and the fact that coal-fired power plants are the main source of CO<sub>2</sub> emissions, policymakers are paralyzed because coal plants are essential for providing the base load power that keeps the electricity grid reliable and thus powers the modern way of life. Coal power is here to stay, notwithstanding the clamor for replacing it with unreliable wind and solar power. The United States, fortunately, has abundant coal reserves.

The generators at coal plants run all the time, because getting them up to speed takes days. A “spinning reserve” is therefore available when supply exceeds demand. At times of low power demand, such as at night, power is very cheap. Various schemes for energy storage, to avoid wasting this excess energy, have been proposed, such as pumping water into elevated reservoirs. What about using this excess energy to crack at least some of the CO<sub>2</sub>? NO<sub>x</sub> and SO<sub>x</sub> could be electrolytically cracked as well.

### *IGCC Clean Coal Plants*

Integrated Gasification Combined Cycle (IGCC) power plants convert a carbonaceous fuel, such as biomass or coal, into syngas, a mixture of carbon monoxide and hydrogen (CO + H<sub>2</sub>). The conversion occurs in a gasifier at temperatures over 700 °C. Preferably, the gasifier is supplied by oxygen instead of air, for higher energy density (heating value) in the syngas. Obtaining oxygen for oxygen-blown gasifiers requires a cryogenic air separation unit (ASU), which is a large parasitic load on the plant, of 380 kWh/ton of O<sub>2</sub> (1.368 GJ/ton, or 43.78 kJ/mol).

The output of the gasifier is scrubbed of SO<sub>x</sub> and particulates, then separated into carbon dioxide (CO<sub>2</sub>) and syngas (CO + H<sub>2</sub>). Syngas can be processed by Fischer-Tropsch synthesis into liquid vehicle fuel (synfuel), or may be fuel for direct combustion. A water-gas shift reactor may increase the hydrogen content of the syngas stream and minimize the CO content by the reaction  $\text{CO} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + \text{H}_2$ . Syngas from the gasifier goes into a combustor which produces hot gas which expands through the gas turbine, generating electricity. The gas turbine exhaust is still hot, so its waste heat is used to raise steam for a bottoming cycle which generates more power. Hence the name “combined cycle”: a Brayton cycle (gas turbine) combined with a Rankine cycle (steam turbine).

### *Syntrolysis, the Simultaneous Electrolysis of CO<sub>2</sub> and H<sub>2</sub>O*

Carbon dioxide capture, which is its separation from the gasifier output or from flue gas, is conventionally done by amine scrubbing or by cryogenic separation. An alternative is Vorsana's radial counterflow vortex separation. Whatever the means used for separating the CO<sub>2</sub> into a relatively pure stream, the problem remains of what to do with it once it is captured.

The volume of CO<sub>2</sub> emissions from a modest size (250 MW) coal-fired power plant is 1.7 million tons per year, which occupies a space (at STP) of approximately a cubic kilometer. Cramming worldwide CO<sub>2</sub> emissions from power plants underground (“sequestration”) is not a feasible alternative because the amount of space required is enormous, transportation to suitable injection sites is prohibitively expensive, and the injected CO<sub>2</sub> might eventually leak out with fatal results.

Instead of sequestration, and instead of the bottoming Rankine cycle of IGCC (which wastes water), an alternative is to feed the separated CO<sub>2</sub> from the gasifier and the shift reactor, mixed with steam, into a cracker to produce syngas and oxygen.

Simultaneous electrolysis of carbon dioxide and water has been dubbed “syntrolysis” by Stoots, et al. at the Idaho National Laboratory, who have demonstrated a small-scale solid oxide electrolysis cell (Stoots, et al. U.S. Pat. App. No. 20080013338 published Jan. 31, 2008). Cracking is the dissociation of the CO<sub>2</sub> and H<sub>2</sub>O molecules in the process  $\text{CO}_2 + \text{H}_2\text{O} \Rightarrow \text{CO} + \text{H}_2 + \text{O}_2$ .

The oxygen from cracking CO<sub>2</sub> could be recycled into the gasifier, saving the cost of cryogenic separation in the ASU. The ASU accounts for approximately 30% of the operation and maintenance cost of the IGCC plant, and its operation depends on parasitic energy from the plant. For each mole of CO<sub>2</sub> cracked, a mole of O<sub>2</sub> is produced. The air separation unit uses 43.78 kJ/mol O<sub>2</sub> so cracking a ton (22,727 moles) of CO<sub>2</sub> to yield 22,727 moles of O<sub>2</sub>, saves 0.99 GJ. For each metric ton of oxygen (31,250 moles) produced in IGCC plants, the energy saved is therefore 1.368 GJ.

Oxygen recycling for combustion, even in a conventional powdered coal plant, will reduce the volume of smokestack emissions by 75% through eliminating the nitrogen ballast

from air combustion which frustrates carbon capture methods such as amine scrubbing. For post-combustion carbon capture, that is a big plus. So the benefit of oxygen recycling will at least partially offset the cost of carbon cracking, even in existing pulverized coal plants.

### *Energy Storage and Grid Connection Problems of Renewables*

Wind, solar, and tidal power are collectively known as renewables. The good thing about renewables is that they produce no emissions. The bad thing is that they are intermittent, and there is no technology available for storing the energy they produce. Because they are intermittent, they cannot be connected to the grid, and their power goes to waste.

Storing the energy from renewables has been a major unsolved problem. Batteries are impractical, and hydrogen as a medium of energy storage faces what look to be insuperable difficulties because the tiny hydrogen molecule leaks out and causes fire danger. Therefore stringent controls are mandated, making hydrogen difficult to transport and store. Hydrogen as a vehicle fuel will not happen for many years, if at all, and even stationary fuel cells are not widely deployed. See the excellent discussion of the storage, production, and distribution problems of hydrogen, and of the limitations of fuel cells, in *The Hype About Hydrogen* (Island Press 2004), by Joseph Romm, who oversaw hydrogen and transportation fuel cell issues at the Department of Energy during the Clinton administration. Some other means than hydrogen or batteries needs to be found to put wind and solar power to use.

Popular enthusiasm about renewables as a solution to the global climate change problem ignores the fact that renewables provide power intermittently. The grid requires reliable power supply, known as base load power, which is always available to meet demand. Connecting more than 20% renewables to the grid impairs reliability, and thereby imperils economic prosperity, so a different use, other than powering the grid, needs to be found for renewable power.

## **HYBRID POWER SUMMARY**

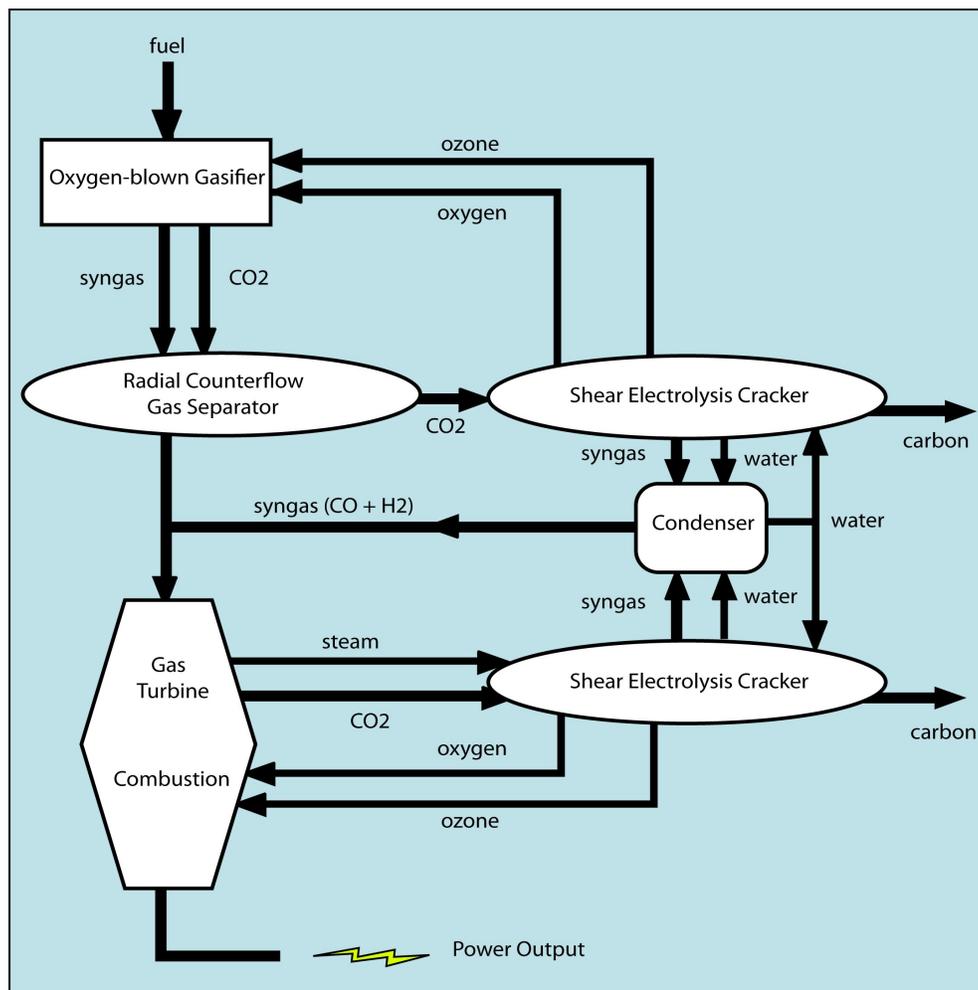
The carbon dioxide, NO<sub>x</sub>, and SO<sub>x</sub> in coal-fired power plant flue gas or in IGCC gasifier output are cracked by electrolysis, and the power for electrolysis comes from renewables. The oxygen from cracking is recycled into the plant. Solid carbon from CO<sub>2</sub> cracking is recovered as a valuable product.

Carbon dioxide thus becomes a form of grid energy storage for renewables such as wind and solar. It is stored on site or transported, then cracked whenever renewables are available. At least some of the coal plant's emissions can be eliminated by integrating renewables in this way, instead of trying to connect them to the grid.

## **DETAILED DESCRIPTION**

Below is a flow diagram of the hybrid power system applied to a gasification power

plant. This is not necessarily IGCC because there is no steam bottoming cycle, but otherwise it shares the common feature that fuel is gasified instead of being burned directly. Gasification power plants include those facilities which treat coal, biomass, landfill, or other carbonaceous fuels in a gasifier, producing syngas (a mixture of carbon monoxide and hydrogen) which can be processed into liquid fuel by the Fischer-Tropsch synthesis. A fraction of the output of the gasifier is  $\text{CO}_2$ .



SYSTEM AT IGCC POWER PLANT FOR CARBON AND OXYGEN RECYCLING

A gas separator separates  $\text{CO}_2$  from the gasifier output, leaving a stream of syngas, and the  $\text{CO}_2$  thus captured becomes feed to a cracker where the captured  $\text{CO}_2$  is decomposed. Radial counterflow solutions are available from Vorsana for both the gas separator and the cracker; these components are shown here as oval components.

The dissociation energy ( $D(\text{O}-\text{CO})$ ) required to remove the first oxygen atom from worse than useless carbon dioxide ( $\text{CO}_2$ ), so as to form the useful carbon monoxide ( $\text{CO}$ ), is 5.5 eV per

molecule, which is 127 kcal/mol, or 531.4 kJ/mol. That is even more than the large amount (493 kJ/mol) required for water electrolysis. Removing the second oxygen atom, to produce bare carbon atoms for nanotubes or other forms of solid carbon, requires 257 kcal/mol, or an additional 1075 kJ/mol.

Cracking a metric ton (a million grams, or 1.1 short tons (2000 lb.) in English units) of carbon dioxide (22,727 moles) to carbon monoxide and oxygen takes a total energy input of 12.08 GJ. To crack a one mole input of a mixture of 1/2 mole of CO<sub>2</sub> and 1/2 mole of water (H<sub>2</sub>O) requires 512.2 kJ/mol, which produces 1/2 mole of CO plus 1/2 mole of H<sub>2</sub>, (i.e. one mole of syngas) and 1/2 mole of O<sub>2</sub>.

Some of the required cracking energy (512.2 kJ/mol) for the CO<sub>2</sub>-H<sub>2</sub>O mixture is already present as internal energy, or heat, in the feed to the cracker. If the CO<sub>2</sub> from the gasifier of an IGCC plant were to be fed into syntrolysis, along with the CO<sub>2</sub> and water from the gas turbine exhaust at a temperature of 600 °C (900 K), the internal energy (heat) is 29.92 kJ/mol or 0.68 GJ/ton of CO<sub>2</sub>. The enthalpy of carbon dioxide at 900 K is 37,405 kJ/kmol of which the internal energy (heat) is 29,922 kJ/kmol, 29.92 kJ/mol. Since there are 22,727 moles per ton, the internal energy in a ton of CO<sub>2</sub> turbine exhaust at 900 K is 22,727 mol/ton x 29,922 J/mol = 0.68 GJ/ton.

Steam at 900 K has an internal energy of approximately 3290 kJ/kg or 59.22 kJ/mol. Adding the waste heat in a mole of CO<sub>2</sub> to the waste heat in a mole of steam gives 89.14 kJ for 2 moles of mixture, or 44.57 kJ/mol of mixture. Instead of using the waste heat in the gas turbine exhaust for a Rankine cycle, that 44.57 kJ/mol internal energy is conserved for carbon cracking, reducing the required 531.4 kJ/mol to 486.83 kJ/mol for cracking one mole of CO<sub>2</sub>-water mixture to produce one mole of syngas and 1/2 mole of O<sub>2</sub>.

The oxygen is recycled into the gasifier, resulting in an energy saving of 21.89 kJ per mole of mixture ( 43.78 kJ/mol O<sub>2</sub> from the air separation unit / 2). Subtracting the energy savings from oxygen recycling and the internal energy present in the feed to syntrolysis, the net required cracking energy per mole of CO<sub>2</sub>-water mixture is 465 kJ/mol.

The energy density (heating value) of syngas ranges from 5 to 12 MJ/kg depending on the process used in gasification, with oxygen-blown gasification yielding the highest energy density. The syntrolysis product here should be on the high end because the gasifier is oxygen-blown by the recycled oxygen from carbon cracking. Let's say the energy density of syngas from syntrolysis is 12 MJ/kg or 12 kJ/g. Multiplying 12 kJ/g by 30 g (28 grams in a mole of CO + 2 grams in a mole of H<sub>2</sub> = 30 grams in 2 moles of syngas), gives 360 kJ for 2 moles of syngas, and there is one mole of syngas produced by one mole of CO<sub>2</sub> - water mixture, so the energy contribution by recycled syngas is 180 kJ per mole of CO<sub>2</sub> - water mixture.

A combustor burns the output of the gasifier, to drive a gas turbine. Recycled into the plant at 85% thermal efficiency, the useful energy (power + heat) in this syngas product is 153 kJ/mol . So at least part of the energy expended in electrolysis can be recovered. The result of the combustion of pure syngas is hot CO<sub>2</sub> and water, which is suitable for recycling back into the

cracker. Or the syngas could be immediately output for synthesis of vehicle fuel. Here we examine the utility of recycling syngas for power and heat. Subtracting the heating value of the recycled syngas, as well as the energy savings from recycling oxygen and the internal energy of the feed, the net required cracking energy per mole of CO<sub>2</sub>-water mixture is 312 kJ/mol.

*Summarizing:* Each mole of CO<sub>2</sub>-water mixture (comprising 1/2 mole of CO<sub>2</sub> and 1/2 mole of H<sub>2</sub>O) requires 312 kJ/mol of cracking energy input for syntrolysis.

### *Coal Energy for Cracking CO<sub>2</sub>?*

Bituminous coal (carbon content 60%) has an energy density (heating value) of 24 GJ/ton. Conventional powdered coal plants, even without carbon capture and storage, have a 30% efficiency in converting the coal energy into electricity because waste heat in the steam turbine exhaust is dumped into the atmosphere as latent heat in the vapor from the cooling tower. IGCC plants use heat energy as well as electrical energy in cogeneration. The cogeneration (heat + power) efficiency of IGCC can be as high as 85% so the useful energy in a ton of coal is 20.4 GJ/ton. Both heat and power are conserved in the cycle described here, so assuming 85% efficiency, the energy in a ton of bituminous coal can crack 65,384 CO<sub>2</sub>-water mixture moles ( $20,400,000,000/312,000 = 65,384$ ). Of the 65,384 moles of mixture cracked by the 20.4 GJ or useful (heat + power) energy in a ton of coal, half, 32,692, are moles of carbon dioxide. There are 22,727 moles per ton of CO<sub>2</sub>, so the 32,692 moles of CO<sub>2</sub> cracked by the ton of coal's 20.4 GJ are 1.4 tons of carbon dioxide.

Cracking one ton of carbon dioxide in syntrolysis, with recycling of syngas and oxygen, requires 0.72 tons of bituminous coal delivering 14.57 GJ of useful energy. Each mole of CO<sub>2</sub> cracked by syntrolysis, taking into account all energy savings from recycling oxygen and syngas, as well as the internal energy of the feed, requires an energy expenditure of 641 kJ/mol. This is higher than the energy expenditure for cracking CO<sub>2</sub> alone.

The extra coal (0.72 tons/ton of CO<sub>2</sub>) for cracking adds to the CO<sub>2</sub> load. Each ton of the extra bituminous coal (60% carbon) for cracking produces 2.2 tons more CO<sub>2</sub>. Each of those additional tons requires 0.72 tons of coal, and so on, adding rather than subtracting emissions.

If water cracking is avoided, and carbon dioxide is cracked directly without syntrolysis, it is still the case that more carbon dioxide is produced by the cracking coal than is cracked by it. Cracking a ton of carbon dioxide (22,727 moles) takes a total energy input of 12.08 GJ (5.5 eV per molecule = 531.4 kJ/mole, x 22,727 = 12.08 GJ), and the internal energy is 0.68 GJ/ton, so 11.4 GJ/ton is the net energy input required for cracking a ton of carbon dioxide. A ton of bituminous coal has a useful energy of 20.4 GJ/ton when its energy is used at 85% thermal efficiency for heating and electricity. Those 20.4 GJ can crack approximately 1.8 tons of CO<sub>2</sub>, so each ton of CO<sub>2</sub> requires 0.56 tons of coal. Oxidation of the carbon in the cracking coal adds 2.2 more tons of CO<sub>2</sub>, so, although 1.8 tons have been cracked, 2.2 tons have been added, for a net 0.4 additional tons of CO<sub>2</sub>. As with syntrolysis, using coal energy for cracking to reduce coal CO<sub>2</sub> emissions creates a bigger problem than it solves.

Only when the cracking coal is less than 0.45 tons of bituminous coal per ton of CO<sub>2</sub> is there the same amount of CO<sub>2</sub> produced as is cracked. But this is a running in place situation where no power is coming out of the plant, and all coal energy is being used to crack coal emissions.

The conclusion that can be drawn from the foregoing is that much more carbon dioxide is produced by the cracking coal than is cracked by it. Using a better grade of coal, such as anthracite (92-98% carbon, 29 GJ/ton) does not change the result that the cracking coal creates more CO<sub>2</sub> than it cracks.

Clearly some additional energy input, besides coal, is needed for CO<sub>2</sub> cracking, which is the only hope (because sequestration is not going to work) for avoiding global climate catastrophe from the coal plant emissions necessary for reliable electricity.

*Renewables + Coal = Hybrid Power.*

Renewables can provide the additional energy input for carbon cracking. Although not reliable enough to connect directly to the grid for more than 20% of its power, wind and solar nevertheless can mitigate the emissions of the coal which provides the base load power.

A hybrid power generation system takes the best features of fossil fuels (high energy density, always reliable) and renewables (no emissions, no fuel cost) to offset the worst features of the other (CO<sub>2</sub>, intermittency), so as to provide reliable power with minimal emissions. Carbon dioxide would become, in effect, a way to take advantage of intermittent renewable energy which would otherwise be wasted because it cannot be connected to the grid. At least some of the CO<sub>2</sub> produced by the plant could be rendered harmless, and even converted into valuable products.

The CO<sub>2</sub> could be transported to a location where renewables are available, for cracking off-site, or renewables power could be transmitted to emission sites for cracking CO<sub>2</sub> stored there. The problem of connecting renewable power to the grid is avoided by using that power to clean up after coal. Captured and stored CO<sub>2</sub> becomes, in effect, a medium of renewable energy storage.

If syntrolysis is practiced by renewables, the syngas produced by cracking could be processed into liquid vehicle fuel (synfuel), and synfuel also becomes the energy storage medium for renewables.

Wind is a rapidly growing sector, with 94,000 MW of installed capacity as of 2008 which is projected to grow to 253,000 MW by 2012. Wind sector growth will be useless at some point because wind power is not reliable and there is no energy storage. Currently, new coal plants are stalled by emissions problems. If wind could overcome the emissions problems of coal, and coal could continue to provide reliable base load power for the grid, then the potential of wind could be put to use and new coal plants could be approved.

An example: For a coal gasification plant using bituminous coal at 50% efficiency (i.e. a gas turbine, without the water-wasting Rankine cycle, and using all of the waste heat for cracking), each MWh (3.6 GJ) of power output requires 0.3 tons of coal. So a 250 MW coal plant would use 75 tons of coal for an hour of operation, providing 250,000 kilowatt-hours of power. The 75 tons of coal produce 165 tons of CO<sub>2</sub> emissions. The help needed from wind power to crack 165 tons by direct carbon dioxide cracking without syntrolysis (requiring cracking energy of 11.4 GJ/ton of CO<sub>2</sub>) is 1881 GJ, which is 522,500 kWh of wind power. A wind farm producing 100 MW could crack the emissions from an hour of coal operations in 18810 seconds, or a little over 5 hours. But these 5 hours of wind power could come at any time and at any place. Storage of CO<sub>2</sub> at the power plant would buffer the feed to wind-driven crackers, or the CO<sub>2</sub> could be transported to places where wind is abundant. Even if only half of the CO<sub>2</sub> emissions could be cracked by renewable power, still there would be quantifiable progress.

The solid carbon produced by complete CO<sub>2</sub> cracking is a valuable product. Each ton of recovered solid carbon could be well worth the energy expenditure for carbon cracking. A profit incentive based on the value of carbon cracking byproducts would be a greater stimulus for rapid progress in reducing carbon dioxide emissions than scolding or punitive taxation. It is easily foreseeable that utilities will just pay any carbon tax and pass on the added cost to the consumers, rather than spending money to reduce their emissions. Hybrid power would provide existing coal plants a profit incentive to implement post-combustion carbon capture and treatment, where moral suasion or legal penalties must fail.

Once we recognize that sequestration won't be a solution to emissions, and hydrogen won't be a solution to renewable energy storage, it becomes clear that carbon cracking in hybrid power generation is worthy of investigation. The prospect of converting trash to treasure should insure quick adoption, and quick reduction of CO<sub>2</sub> emissions, around the world.

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Patent Pending

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