How To Remove CO_2, NOx and SOx From Flue Gases and Make A Profit

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Abstract

This paper address 10 of the topics listed for the APCSEET conference. What will be demonstrated is how flue gases can be cleaned up in a manner that is very cost effective for the power generation industry. We approached this problem in a totally different way to those that are currently being tried around the world, in that the greenhouse gases and other unwanted gases are sequentially condensed from the flue gases. The net result is that the combustion air that enters the power generating process at around 400ppm of CO_2, leaves the process at about 200ppm of CO_2, i.e. the ambient air is also being cleaned of CO_2. Thus we can turn a coal (or any other fossil fuel) fired power station into a zero CO_2 emitting power station, fuel and/or chemical producer. The sequential condensation process is based on pulse combustion driven thermoacoustic refrigerators. The system is referred to as a PUTAR, because of the configuration that we have developed for the refrigerator. Although the PUTAR is not quite as efficient as a compressor system, it is cheaper both to operate and build and has no moving parts to wear out. What differentiates the PUTAR process of CO_2 removal from power station flue gases is that it enables the steam generation efficiency to be increased and also the steam turbine efficiency to be increased. The net result is that the increase in the generated electricity more than pays for the PUTAR process of CO_2 removal. The PUTAR process of CO_2 removal can be applied to both post and pre-combustion capture of CO2, but the post-combustion is the better option because it is more cost effective and removes more of the CO_2 than does pre-combustion capture. Although the PUTAR system was originally developed with existing power stations in mind, when applied to a pulse combustion driven coal gasification system and power station we derive the most energy efficient power station. It out-performs a gas turbine/ steam turbine system for power generation at 5.19MW-h / tonne coal. The net result (without taking into account the fuel and/or chemical production profits) is that the Levelised Cost of Electricity (LCOE) ends up being less than at present and does not have to increase, as is the case with other proposed methods of CO_2 removal.

Introduction

Most developing countries are actively pursuing different methods of removing CO_2 from exhaust gases as a result of burning fossil fuels, to mitigate the effects of global warming. Australia is the invidious position of having the largest CO_2 output per head of population because of its dependence on cheap electricity produced from burning its large reserves of both black and brown coal. This paper is mainly about electricity production via fossil fuel fired boilers and CO_2 removal, although the proposed system can be applied to other carbon intensive industries such as aluminium production with similar cost

benefits.

There is a large body of opinion that thinks that the cost of capturing CO_2 will result in a doubling of the cost of electricity. There is another group who think that it is unnecessary to worry about CO_2 emissions as global warming is an artifact. Nobody (apart from ourselves) has considered the possibility that a CO_2 removal process can actually lead to reduction in electricity prices. There are other instances where pollution legislation has resulted in the pollutant becoming the main product and the original product a by-product [1] and the same is true in this instance with CO_2 being the pollutant and electricity the original product.

The CO_2 capture process falls into two camps - the pre-combustion capture and the post-combustion capture. The method that is proposed here falls into the latter camp. It has been modeled on both types of systems, with the post-combustion capture coming out in front in terms of electricity produced per unit of fuel.

The Proposed System Of CO_2 Capture

The current method of CO_2 removal that is in vogue is amine scrubbing of the flue gases. There are other methods that also need to be looked at, not only in their effectiveness in removing CO_2, but also the knock-on effect that they have on the electricity production. Some other possible routes to are listed in Table 1 below. It is well known in chemical engineering unit operations that gas scrubbing is an energy intensive process, which accounts for the fact that the amine process consumes a large portion of the electricity production and is not likely to be substantially reduced [2] enough to make it even worth considering as a potential solution. In one case of amine scrubbing of flue gases in a power station it was estimated that on a full scale operation half the station power electricity production got consumed [3]. There are two studies on carbon capture [4,5] that have been relied on for the comparisons between the options in this paper. The common figure from these studies is 30% of the produced electricity. According to House *et.al.* [6], the minimum energy penalty is 11% for this process.

Possible Routes to CO_2 Removal	Percentage CO_2 Removed	Electricity Used
Amine scrubbing of the flue gas	85	30%
Oxy-firing of the boiler	85	15%
Feeding the flue gases to growing algae	50	4%
Carbon adsorption filters	90	4%
Chemical looping	100	6%
Condensing out gases from the flue gases	100	can generate up to 45% extra

TABLE 1 Possible Routes to CO_2 Removal

Oxy-firing falls into the pre-combustion capture camp. Its main advantage is is that it markedly reduces

the quantity of flue gas to be treated, but it requires an air separation plant to provide the oxygen for the combustion process, which invariably results in the CO_2 production of this process escaping. Proponents of this process claim that it produces a pure stream of CO_2 , but it still has the potential to produce NOx in the flue gas from traces of nitrogen in the oxygen and also from the fuel nitrogen.

The algae route for CO_2 removal percentage depends on (a) the load factor of the power station, (b) the sunshine hours during the day and (c) the quality of the CO_2 in the flue gas, i.e. the presence of other gases and the partial pressure CO_2. A very generous figure has been assumed in this case.
Carbon [7] and zeolite [8] adsorption filters, using nano-technology, and chemical looping [9,10] are still in their infancy and offer better prospects than the previous three process.

The last process involves refrigerating the flue gases. This is not to dissimilar from the LNG process. By paying attention to the heat flows and using plate heat exchangers, we can shuffle the "hot" and "cold" steams and minimise the cooling required. This is not a route that has been examined in detail as far as we know. It has been dismissed as being impractical because of the volumes of flue gases to be handled, a criticism that could equally be applied to the amine capture process. The condensation process can be applied to existing power stations and other industries, such as aluminium, to remove CO_2 , but it is best applied to new power stations.

It is clear from Table 1, that on a technical basis only the condensing process has any merit. The question is - does it have it on an economic basis?

The Consequences

Starting with the current state of most coal fired power stations [11], approximately one third the of the energy going into the power station goes up the stack in the flue gas and one third lost to the cooling towers or cooling pond and the remainder appearing as electricity. The combustion air for the process now contains about 400ppm of CO_2 and the flue gases about 110000ppm of CO_2.

With the condensation process for CO_2 removal, the flue gases have to be cooled down. This is carried out by heat exchanging the flue gases with the incoming combustion air via a plate heat exchanger system. Plate heat exchangers have been chosen because of their compactness, low pressure drop and small temperature difference that they can operate with. This process gives us the first consequence, which is the boiler efficiency is improved and as a result leads to either less fuel being used or more steam generated for the same amount of fuel. Depending on how well the heat transferred to the incoming combustion air is retained by the time the combustion air gets into the boiler will determine how much the efficiency of the boiler is improved. With a new greenfields power station or well insulated and designed pipework, this could result in 46% more steam being available. Half this figure has been taken for the analysis in the next section.

The second consequence of this CO_2 removal process centres on the use of the coolant for the steam turbines. Once the CO_2 is removed from the flue gases, it is in a solid state and has to be changed to a gaseous state at elevated pressures to be dealt with by other storage or conversion processes. This is achieved by heating the cold solid CO_2 in a confined vessel with ethylene as the heat transfer fluid at 0°C and the CO_2 at -100°C. The effect of this is to increase the Carnot efficiency of the steam turbine by 5 percentage points leading to more electricity being capable of being generated from the same amount of steam.

The third consequence and this is of importance in Australia, is that no make-up water is required where wet cooling towers are used.

These three consequences result in extra cash flow being generated, that is enough to pay for this CO_2 removal process and more. There is a fourth consequence and that is that the remnant flue gas that is rejected to the atmosphere only contains at the most about 200ppm of CO_2. Thus not only does this condensation process remove all the CO_2, but it also removes some of the CO_2 that entered the power station in the combustion air. This is summarised in Figure 1.

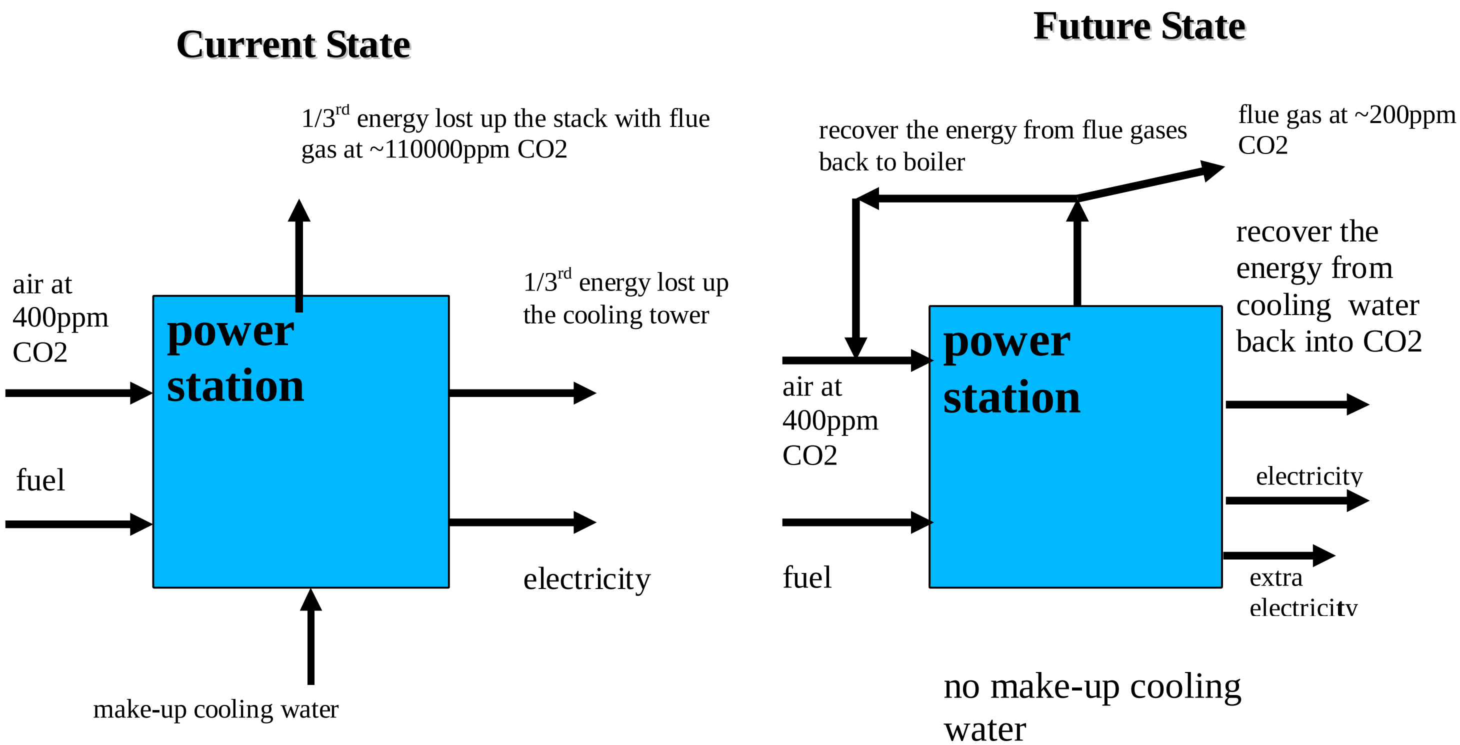

Figure 1. The consequences of using a condensation process for CO_2 removal.

The condensing process is therefore the only process that ends up being able to generate more electricity from the same quantity fuel than before.

What is a PUTAR?

PUTAR stands for **P**ulse-combustion-driven **U**-tube **T**hermo **A**coustic **R**efrigerator. This is a thermo-acoustic refrigerator driven by pulse combustion heaters with no moving parts, unlike compressor driven refrigeration systems. It operates by condensing out of the flue gas all gases condensation below 155°C in a sequential manner, such that the condensed gases are captured separately.

Heat is added at the top end via pulse combustion heaters and heat is also removed at the top end to set up a large temperature difference driving a Stirling engine. The tubes themselves are filled with helium at 3MPa (30atm). The large temperature difference sets up an acoustic wave, which travels up and down the tubes with an amplitude of ± 0.3MPa. At the bottom of the tubes is a Stirling heat pump and an interconnected orifice that throttles the helium flowing through and thus cooling it. Temperatures down to below -200°C are possible to obtain.

There are no moving parts in this refrigerator and hence the operating costs are very low. Because of the

simplicity of the design, the capital cost are lower than conventional vapour compression refrigeration systems. The various gases that can be condensed out (this list is by no means complete) are given in Table 2. The gases with an asterisk beside them are produced in negligible quantities from pulse combustion burners and can be ignored. The highest concentration is NO at ~1ppm. An artist's impression of a PUTAR is shown in Fig 2. It is based on the single tube TASHE from Ubas and van Wijngaarden [12] and overcomes the problems that they and others have faced with this unit. We have changed the top end by using pulse combustion heaters, which have 2 orders of magnitude higher heat transfer coefficients. This allows us to reduce the size of the regenerator at the top and also increase the thermal efficiency of the system. The acoustic impedance at the 'cold' end has been changed so that the time phasing always works, no matter what the conditions. Each tube assists the other and in doing so also improves the thermal efficiency of the refrigerator lowering the pressure drop that the helium gas experiences as it moves up and down the tubes.

Gas	Condensing temperature (°C)	Freezing point (°C)
H_2O	100.0	0.0
NO_2*	21.2	-11.2
SO_2*	-10.0	-73.0
H_2S*	-60.2	-86.0
CO_2	-65.0	-78.5
N_2O*	-88.5	-91.0
NO*	-152.0	-160.9

Table 2. Some flue gas properties.

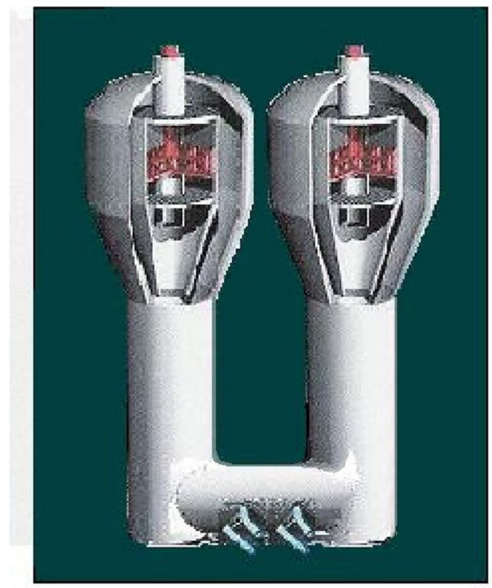

Figure 2. 200tCO_2 /day PUTAR

The Proposed Advanced Power Station

A schematic of the proposed new power station is shown in Fig 3. All the heating in this plant is by pulse combustion as it gives the highest efficiency and lowest emissions. There are three parts to this advanced power station:

1. the pulse combustion driven gasifier,
2. the super critical steam pulse combustion boiler, and
3. the PUTAR.

Variations on each of these parts have been built and operated. The gasifier does not employ an air “blow”, but pulse combustor heaters to attain the desired operating temperature. These units have very high heat transfer coefficients, about two orders of magnitude higher than corresponding conventional heat transfer coefficients [13,14,15], which is why the gasification can be done this way. The pulse combustors are based on Rijke tubes [16] and the gasifier is different from the one shown in Fig 4, which is based on Helmholtz pulse combustors [17,18].

The same version of pulse combustor is used for the PUTAR and also the super critical steam boiler. A 0.5MW version of the boiler is shown in Fig 5. The highest efficiency that has been measured for this

boiler is 98% based on the higher calorific value of the fuel. The efficiency figure that has been used in this paper is 95%. Another advantage of this pulse combustion system is the emissions which are very low. NOx is about 1ppm and is mainly NO, SOx is less than 1ppm and similarly with CO.

The heat exchangers that are used to shuffle the "heat" between stream are plate heat exchangers, PHE, [19]. They exist in sizes that are applicable to power station flues. The advantages of PHE are they are low pressure drop devices, they can operate efficiently at low temperature differences and they can be easily opened up if they need to be cleaned.

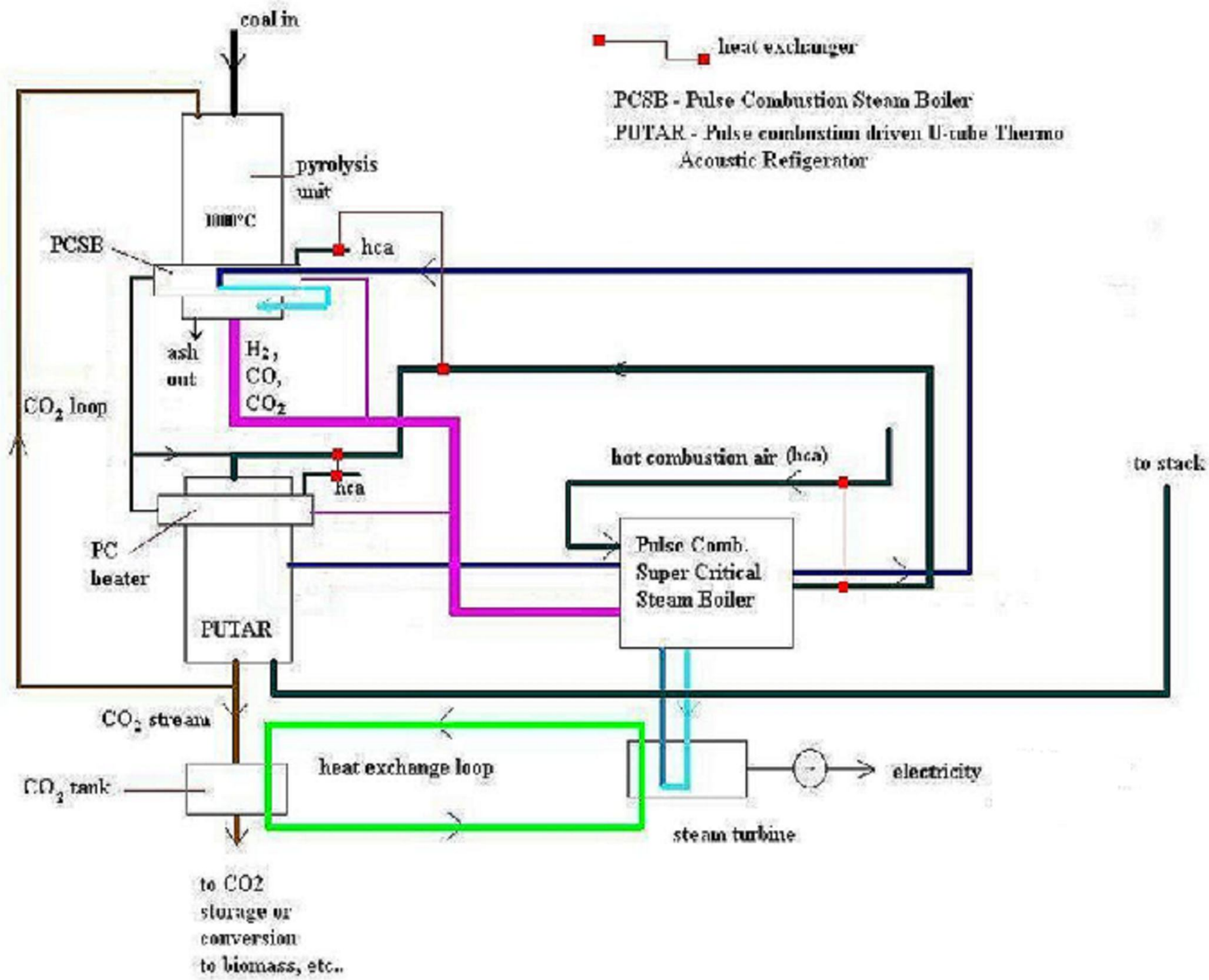

Figure 3. Advanced Power Station

The heat exchange loop between the steam turbine and the CO_2 tank contains ethylene and is used to provide the cold sink for the steam turbine and to condition the CO_2 to a state that is suitable be able to process the CO_2 at the next stage.

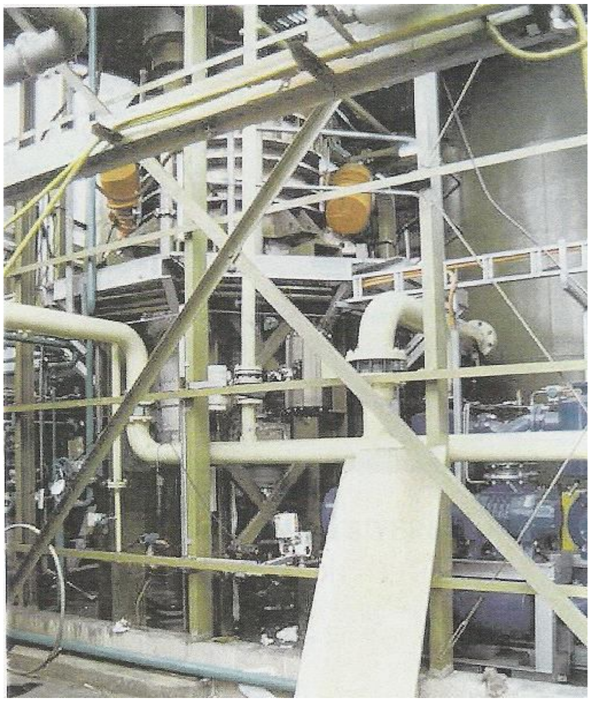

Figure 4. Pulse Combustion Gasifier

Figure 5. 0.5MW Pulse Combustion Steam Boiler

Profit and Loss Statements

The picture changes yet again when the costs of generating electricity with CO_2 removal are included. Here only the amine and condensation PUTAR CO_2 removal process have been considered with different power stations. The cost of selling the electricity from the power stations in Australia is set by AEMO and their figures are available on the web [20]. The average cost for electricity has been taken as $41.40 /MWh based on the last three years and includes the data from NEMMCO [20]. The cost of CO_2 removal has been taken as $80/t CO_2 for the amine scrubbing process [2] and $6/t CO_2 for the PUTAR process, although it is thought that it could drop as low as $3/t CO_2 with mass production of the units. The range of costs for the PUTAR have been calculated at between $3 and $8/t CO_2, the range mainly due to what the maximum size the unit can be made. It has been assumed that AEMO will not change the price of electricity from the power station from the current levels.

The profits and losses are listed in Table 3. It is based on a unit of brown coal producing 1 MWh and 1.44t CO_2 . The same quantity of coal has been used in each of the other electricity generating scenarios. The existing generator is based on Hazelwood Power Station, which is probably among the worst emitters in Australia. The cost of generation has been taken as $30 for the existing power stations and $35 for the new power stations. IGCC has been taken as the most likely candidate for new power station construction [5] because of its “high” thermal efficiency. The advanced power station that is proposed here is based on super critical steam boilers heated by pulse combustors.

In Table 3 it has been assumed that AEMO will not increase the price that the power companies can sell their electricity at to the retailers of electricity. The things that are apparent from Table 2 are:

1. that no matter what the permit price is set at, systems with the PUTAR CO_2 capture will always be profitable
2. systems with the PUTAR CO_2 capture will always be more profitable than the existing brown coal power stations

3. power stations with amine capture will always be in a no win situation because if the costs of amine capture can be reduced the permit cost is going to increase over time and negate any gains that are made.

Electricity Generating System	Relative MWh	Sell at (AU$)	Profit/MWh (AU$)	Profit/MWh with $23/t CO_2 permit(AU$)
existing brown coal	1.00	41.40	11.40	-20.80
existing brown coal with PUTAR CO_2 capture	1.35	55.89	17.49	17.51
existing brown coal with amine CO_2 capture	0.70	28.98	-96.22	-101.05
advanced power station	2.60	107.43	62.03	62.06
IGCC with amine CO_2 capture	1.49	61.48	-70.72	-75.55
IGCC with PUTAR CO_2 capture	2.12	87.56	42.16	42.18

Table 3. Profit/loss for different electricity generating systems.

What To Do With The CO_2?

It is all very well to remove the CO_2 from flue gases, but the big question is what can be done with the captured CO_2? Although the use of the advanced power station for all Australia's electricity could reduce Australia's GHG by about 28%, its still not a total solution to the greenhouse problem. There have been a number of possible solutions put forward:

1. put the CO_2 down into old oil wells or saline aquifers at a cost of just over $10/t CO_2 processed [21],
2. put the CO_2 at below 3000m at the bottom of the ocean under a membrane covered with silt at a cost of $10/t CO_2 processed [22],
3. put the CO_2 encapsulated in a membrane restrained below 1000m in the ocean $10/t CO_2 processed[22],
4. lock the CO_2 in a “carbon sponge” [8] or carbonate at a cost of $20/t CO_2 processed ,
5. convert the CO_2 into formic acid at a cost of $100/t CO_2 processed with the formic acid selling at $1440/t CO_2 processed [23], or
6. convert the CO_2 into bio-fuels via solar energy at a cost of $70/t CO_2 processed with the “crude” oil selling at $230/t CO_2 processed, (the figures for ethanol are $90 and $600), [25, 26].

The first four solutions result in further losses and are only valid options for the PUTAR based processes. The last two make the PUTAR process even more profitable. They may make other removal routes marginally profitable, but as the CO_2 permit to pollute price rises the profits could be wiped out.

Conclusions

There is no need for all the doom and gloom that has said about mitigating the release of CO_2 into the atmosphere. It has been shown here that by looking at things a little differently we can turn the mitigation process to everyone's advantage.

The other point to come out from this CO_2 mitigation process is that even if, and its a big if, global warming turns out not to be due at all from fossil fuels, it makes economic and thermodynamic sense to

install PUTAR systems into power stations.

Can we make a profit out of removing CO_2, NOx and SOx from flue gases – YES WE CAN!

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