

Research Article

Exploring Potential Non-CCUS Pathways for Emissions-Free Energy

Subodh Chandra Gupta* 

Heretech Energy Inc., Calgary, Canada

Abstract

To be effective in addressing the emissions challenge on the global scale, the focus has to be on the processes that are inexpensive to implement and can be applied at a massive scale. CCS satisfies the ‘massive scale’ condition but at present falls short of satisfying the ‘inexpensive’ part. The CCUS approaches (other than CO₂ based EOR) where useful products from CO₂ are hoped to be monetized to offset costs, take the focus even farther away from the desired objective. This is because (a) costs increase due to required energy input, and (b) market value of the products, and hence the desired monetization cannot survive the massive oversupply thus created. A more direct and efficient strategy involves either converting CO₂ into a (non-monetizable) solid or liquid with minimal energy input, or restricting the waste by-product of the fuel oxidation process to be in a liquid or solid state that does not interact with the atmosphere to add to the greenhouse gas effect. The paper presents novel lower REDOX approaches as more energy-efficient and affordable alternatives to provide emissions-free energy. A strong case is made with available information for the techno-economic viability of these methods, and gaps identified for further development.

Keywords

Bio-Sequestration, Thermo-Catalytic and Electro-Chemical Processes, Atmospheric Carbon, CCS-CCUS, Carbon Abatement, Novel Sequestration Method

1. Introduction

Carbon Capture and Storage (CCS) is an established technology for carbon abatement. Moreover, in absence of better alternatives it presents a way forward there is sufficient sequestration capacity world-wide to accommodate emissions for over a century [19]. Currently, approximately 37 million tons per year (Mt/y) of CO₂ worldwide or about 0.1% of our global emissions (37 Bt/y) are effectively sequestered through CCS [31]. The main issue with CCS is its cost, which makes larger scale application of the technology challenging.

1.1. Notional Cost of Carbon-Neutral Energy

In establishing a benchmark for the cost of carbon-free energy, we consider the expense of energy derived from fossil fuels and rendered carbon neutral by employing CCS. Recognizing the cost of CCS varies greatly with geography [2-4, 23, 20] and taking a representative number of \$C 138.5/tCO₂(net) and assuming a long-term average NG price of \$C 2.5/GJ, carbon neutral heat at (e.g. gas fired power plants) can be obtained at \$C10.1/GJ. This doesn't equate to the cost of carbon-neutral energy for retail use, however for point sources of emissions any new technology must compete with this yardstick for successful adoption.

*Corresponding author: subodh.gupta@heretechenergy.com (Subodh Gupta)

Received: 28 February 2024; **Accepted:** 27 March 2024; **Published:** 17 April 2024



Copyright: © The Author(s), 2024. Published by Science Publishing Group. This is an **Open Access** article, distributed under the terms of the Creative Commons Attribution 4.0 License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

1.2. CCUS and Issues

When CCS is accompanied with CO₂ utilization as in CO₂-EOR (or when CO₂ capture is necessary for natural gas purification), it is found to be economically viable. CCS with CO₂-EOR is a specific case of CCUS – Carbon Capture, Utilization, and Storage, and only about 0.5% of global oil production is amenable to CO₂-EOR [24]. If application of this form of CCUS is extended to all potential known suitable reservoirs (containing about 470Bbbl reserves [26], of the total remaining reserves of 1600Bbbl [27]) within reach of CO₂ production sites, its extent could cover about 7% of global emissions by 2040 (IEA SDS report), increasing from its current 0.1%. This is significant but still less than 10% of the challenge.

In its broader sense, CCUS involves capturing CO₂ from waste streams, and utilizing it products that would otherwise incur a cost, such as plastics, cement, food, activated carbon, soap, and fuel, etc. Can the remaining 90% emissions challenge be addressed with the general form of CCUS where useful products from it are expected to offset the high cost of underlying energy intensive processes? It's easy to see if we convert even a fraction of CO₂ to useful products such as cement-substitute, the supply of such products will overwhelm the market, resulting in the loss of much of its market value, and making it impossible to recover costs. With one exception, we do not consume anything globally in that amount, as Table 1 shows. In fact, top 10 commodities the world consumes on annual basis add up to less than 10 Bt. This implies when conversion to useful products is talked about in CCUS context, either the extent of application is assumed to be insignificant, or assessment of product value is unreasonably optimistic. In either case the CCUS approach of making useful products from CO₂ has limitations of application at a significant scale.

Table 1. Annual global production and consumption of various substances.

Products/Substance	Approximate amount, B t/y
CO ₂ emitted	37
Carbon in emitted CO ₂	9.8
Cement use	4
Food consumption	3.6
Steel use	1.8
Plastics (PE, PP, PVC, etc.) use	0.35
Asphalt consumption	0.12
Natural rubber use	0.014
Activated carbon use	0.006

We consume about 12 B t/y of fossil fuel including oil, gas, and coal, overcoming the argument presented above. Arguably then, if all the emissions are converted back to fuel (using solar energy, and assuming technoeconomic feasibility), one can fix all the emissions. Additionally, by burning that fuel and carrying the process in a cyclical manner, carbon addition to atmosphere can be avoided. While it is technically feasible to do this, the cost of such fuel is always going to be more than the carbon-neutralized fossil fuel, as explained in Appendix I. This appendix also explains why converting CO₂ using solar energy to fuel is also less energy efficient for transport purposes than using that solar energy directly to charge batteries to run, for example, the EVs. In summary, even the renewable-fuel route of CCUS is not economically robust.

Against this background the highlights of this paper include:

1. Description of the economic issue with CCS and the general form of CCUS, including the case of renewable fuels, as explained above
2. Identification and dealing with the underlying issue of using carbonaceous fuels (gaseous nature of combustion byproduct - CO₂) directly
3. Presentation of novel lower-energy-investment approaches where the degree of carbon oxidation (oxidation number) can be controlled to yield only non-gaseous byproduct
4. Describing L-ox and L-red approaches which help achieve this by thermo-catalytic or electrochemical means, and providing literature references in support of the proposed chemical reactions
5. Identification of specific gaps for further development, to exploit these approaches

2. The Underlying Issue with the Use of Carbonaceous Fuels

At the heart of the emissions issue is the fact of gaseous nature of the waste byproduct of combustion (necessary for deriving energy from fuel) - CO₂. If it were a liquid or solid, it would not interact with atmosphere to add to any greenhouse effect.

There is a relationship between successive stages of oxidation of fuel and the material state of the resulting (waste) byproducts, the main or desired product being energy. Successive stages of oxidation of fuel are technically described by oxidation states or oxidation numbers of carbon in the fuel. As pointed out in [16], with successive oxidation of carbon in fuel, e.g., in CH₄, the extracted energy progressively increases, and the energy left in the reaction non-water byproduct decreases. A modified version of a table given in [16] is reproduced here as Table 2. It shows almost a linear declining relationship between the state of oxidation of carbon in the byproduct and its energy content. In each stage of oxidation some energy is released.

Table 2. Carbon oxidation states and heating value remaining in the oxidized product.

Step No.	Compound	Common Names	Oxidation Number	GJ/t, Heating Value (HV)	GJ/t-mole, (HV)
0	CH ₄	Methane	-4	50	800
1	CH ₃ OH	Methyl Alcohol	-2	22.7	726
2	HCHO, CH ₂ O	Aldehydes, Carbohydrates	0	17.3	519
3	HCOOH	Formic Acid	+2	5.5	253
4	(COOH) ₂	Oxalic Acid	+3	2.8	252
5	CO ₂	Carbon Di-oxide	+4	0	0

In Table 2, one should take note of two factors: (a) with each successive row, the oxidation number of carbon increases and the energy left in the byproduct is reduced, and (b) the products in all steps numbered 1 to 4 are non-gaseous at NTP. This implies, if the fuel is oxidized to a lower oxidation state of carbon, we end up having a waste byproduct that does not interact with the atmosphere, and yet can exploit some energy from the fuel. Conversely, in the case when oxidation is carried out to the fullest extent and we end up having CO₂ gas, the waste gas can be converted back to products of any of the steps mentioned in steps 1 to 4 with input of slightly more energy than the thermodynamic minimum.

3. The Potential of Electro-Thermo-Chemical Methods in Carbon Abatement

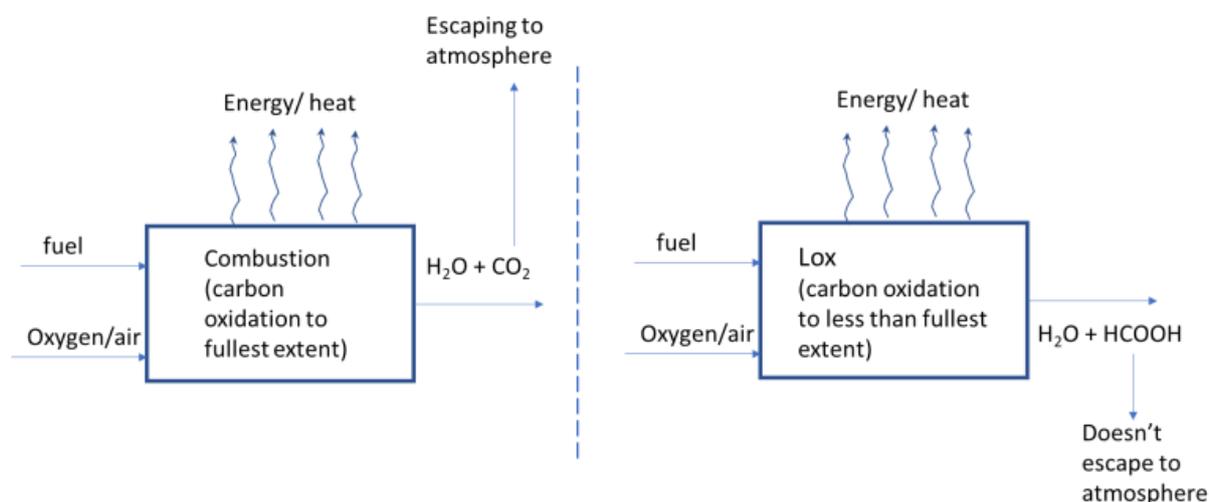
There are two approaches discussed here that promise to be more cost effective than the alternatives on account of lower energy requirements in bypassing formation of gaseous byproduct of combustion – CO₂ or converting it back to non-gaseous products, as well as requiring fewer unit opera-

tions and simpler equipment to carry out the process.

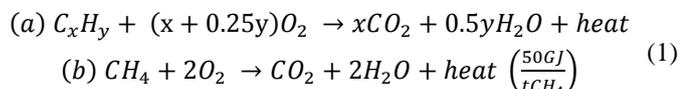
These two approaches broadly fall into the categories of (1) avoiding formation of CO₂ in combustion process by keeping the end waste product in liquid / solid state through lower oxidation or L-ox, and (2) if the combustion is carried to the fullest extent, converting the CO₂ back into a solid or liquid matter through lower reduction or L-red, with least energy input. The ensuing discussion answers if the two approaches are chemically feasible, i.e., if the proposed reaction routes resulting in non-gaseous byproducts of oxidation of fuels are feasible and proven.

3.1. L-ox Processes

The concept of L-ox is also illustrated schematically in Figure 1. In conventional combustion, fuel is combusted to the highest oxidation state of carbon. This results in formation of CO₂ which escapes to atmosphere. In Lower-oxidation (L-ox) the fuel is oxidized only to state of oxidation yielding a liquid or solid waste byproduct. Such waste products do not interact with the atmosphere and can be more easily disposed of.

**Figure 1.** Conventional combustion vs. L-ox.

While a hydrocarbon fuel can be represented chemically as C_xH_y , the simplest of these is CH_4 or methane. On combustion with oxygen, they produce water and CO_2 and yield the desired energy. This can be described by a stoichiometric reaction (1) below:

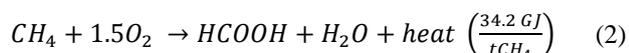


For methane this simplifies to reaction (1b)

For keeping the discussion simple only CH_4 fuel is considered and it is assumed the same applies to other fuels with some modification.

3.1.1. Notional Economics

While a detailed economics of the process is beyond the scope of this work, a quick estimate of the benefit of the presented approach can be had with the following analysis. An observation from Table 2 is that if the fuel is oxidized only to such degree that carbon attains an oxidation number of 2, one will be able to keep the product of oxidation ($HCOOH$) in liquid state and be able to still withdraw approximately 70% of the energy contained in CH_4 and leave a waste byproduct that does not result in emissions. This is shown in the reaction (2).

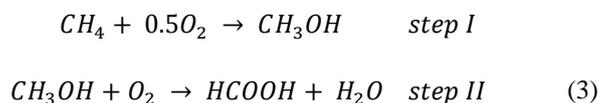


$HCOOH$ is an example of lower oxidation, but any other non-gaseous product having lower oxidation of carbon than CO_2 such as oxalic acid is going to be useful. The cost of carbon-neutral energy, before accounting for Opex and Capex of the process, becomes \$C 3.66/GJ (compared to \$C 2.5 with emissions). The challenge in presenting actual economics is in the estimation of Capex and Opex in absence of an established technology for this process at present. To overcome this predicament, one can make some reasonable assumptions for these two costs based on appropriate analogues. These two together are assumed here to be equivalent to an additional 50% cost of lost energy (per GJ). It can be argued that 50% is too little or too much for this contingency, but a reasonable place holder can be assigned for a preliminary assessment of the opportunity, and revised when more is known about the detailed process equipment.

The implicit cost of carbon abatement in leaving the end oxidation product as $HCOOH$ becomes \$21/t CO_2 [= (3.66-2.5)/0.055]. With the 50% additional assumed, this becomes \$32/GJ. This compared with the CCS cost of \$115/t CO_2 -processed (or \$138/t CO_2 -net) - a difference of \$83+/t CO_2 is thus the incentive for pursuing this route to carbon abatement. Carbon neutral heat with these assumptions is \$4.3/GJ as opposed to \$10.1 estimated above with CCS.

3.1.2. One-Step Conversion vs. Two-Step

Ideally, to replace the simple combustion reaction (1b) by (2), it will be preferable to have a process to do it in one step, such as the one described by Li et al. [25]. It is surmised that the reason why more literature on it is not available, could be the difficulty to control the oxidation from proceeding to completion to make CO_2 . That is why a two-step oxidation process is considered here. In the first step methane is oxidized into methanol. This releases part of the available energy as heat or power. In the second step methanol is oxidized into formic acid, giving up the remaining extent of energy without leaving a gaseous waste product - CO_2 . For the stated purposes these individual steps are not burdened with the requirements of producing pure methanol or other intermediate-oxidation products such as aldehydes and ketones. The objective is to extract energy, not the purity of the product. The two steps are shown in the reaction (3).



Although from energy extraction perspective a one-step process (2) may be more efficient, there are some commercial benefits of carrying out the process in two steps denoted by (3). A significant number of natural gas reservoirs found the world are isolated and too small to be commercially exploited. For commercial exploitation one needs these pools to be either connected to a pipeline network which is expensive, or compressed as CNG or LNG and transported by road/rail, which is also expensive. If the produced gas could be converted to a liquid fuel economically such as CH_3OH , it will greatly enhance the commercial viability of these gas pools. CH_3OH is a commercial product in its own right, and the current commercial process to convert methane to methanol is highly capital and energy intensive. Secondly, methanol being a liquid fuel, it can find use relatively more easily in transport sector either through Direct Alcohol Fuel Cell (DAFC) or through modification of ICEs (MICE), requiring relatively a smaller degree of change in the existing infrastructure. There is a potential (at least thermodynamically) to exploit the thermal energy released in conversion of CH_4 and at the same time make a more valuable product, with least amounts of emissions in step - I, CH_4 to CH_3OH . Similarly, in step-II (CH_3OH to $HCOOH$), there is a potential with a modified version of DAFC (MDAFC) to exploit the energy without emitting CO_2 . However, all currently discussed DAFCs in literature result in CO_2 emissions, just as current ICEs result in complete combustion producing CO_2 . MDAFC or MICE will require innovation to prevent ultimate oxidation of the fuel to CO_2 and only result in liquid (waste) product - $HCOOH$. This concept is illustrated schematically in Figure 2.

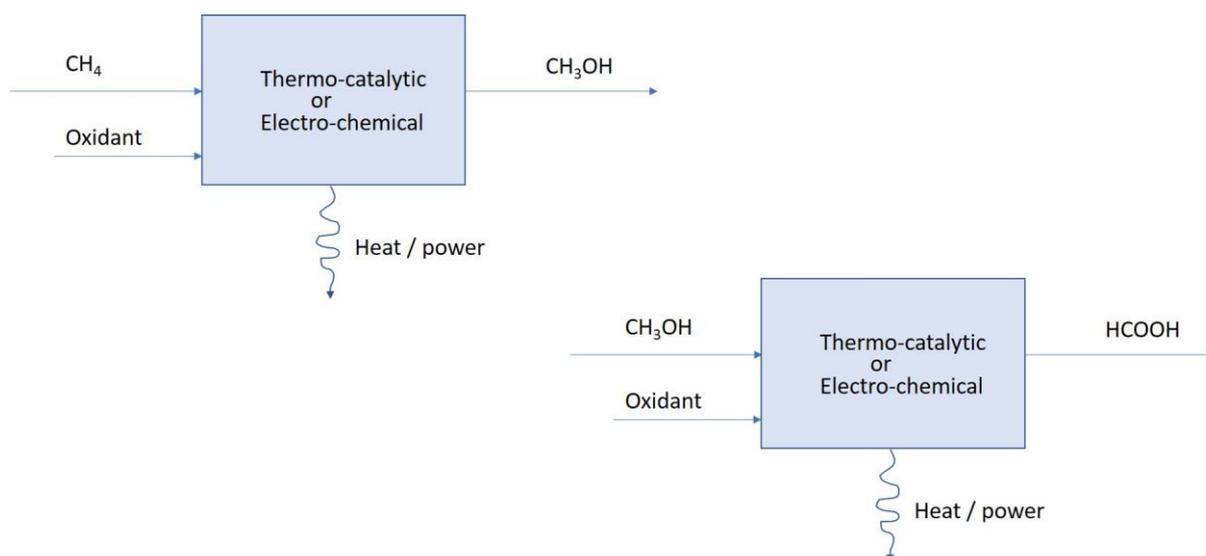


Figure 2. Energy without emissions: two-step process.

As indicated above, these two energy-releasing steps can either be carried out through a process based on thermo-catalysis, or on electro-chemistry. The following discussion is dedicated to substantiate the feasibility of step I and II processes with based on the existing literature, and pointing out the areas where further work is needed to complete the technological gaps.

3.1.3. Thermo-catalytic L-ox

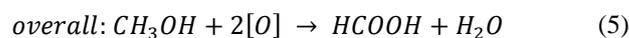
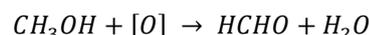
(i). Step-I: CH₄ to CH₃OH

Zuo et al. [36] describe a low temperature reaction at 450K in presence of water, and CeO₂/Cu₂O/Cu(III) catalyst that converts CH₄ to CH₃OH with high selectivity. Li et al. [25] discuss an iridium-based catalyst system (Ir-ZSM-5) in aqueous phase in presence of CO that converts CH₄ either to CH₃OH or to HCOOH depending on the addition of a second metal. With Cu the system selectively produces CH₃OH, and with Pd formic acid (HCOOH) is produced. They report methanol selectivity to be in the range of 80% at 150 C in a IrCuPd-ZSM-5 trimetallic catalyst. The one step conversion from CH₄ to HCOOH mentioned by Li et al. is right along the most favored path stated above in reaction (2).

Although thermodynamically favored exothermicity of these reactions, larger scale experiments need to be carried out to establish availability of usable high-grade heat. This is also true of the step-II described below.

(ii). Step-II: CH₃OH to HCOOH

Many online available texts on chemistry, e.g., [6], or [5] give a catalytic route to conversion of methanol to formic acid in presence of sodium dichromate (Na₂Cr₂O₇) and sulfuric acid (H₂SO₄). However, from these sources do not specify how that heat manifests itself. The two-step reaction is as given by (4) and net reaction as shown in (5).



While in presence of these catalysts the reaction can achieve the desired conversion of methanol to formic acid, methanol can also be oxidized in presence of silver (Ag) catalyst at high temperature (500C) with air [5, 7]. This converts methanol to methanal (HCHO). This is in fact the commercial process for making HCHO from methanol. However not enough in the literature is available to suggest that the process can be extended to further oxidation of HCHO to formic acid releasing full extent of intended heat. This is an area for further investigation. A thermo-catalytic process that converts methanol to HCOOH will look similar in terms of the equipment to the combustion process. The combustion process typically used in fired heaters (or boilers) has air and fuel reacting at the specially designed burners. The outside surface of the tubes provides the heat transfer area. In the L-ox case, burner may be replaced with a mixer, but the heat transfer area will be designed to also provide the catalytic action needed for the reaction to limit the oxidation to just HCOOH.

3.1.4. Electrochemical L-ox

The process of electrochemical conversion of CH₄ to HCOOH is thermodynamically favored to generate electric power in a galvanic cell directly, as is accomplished in fuel cells, bypassing the step of first generating the heat and converting it to power with heat engines. The efficiency of the latter is dependent on the grade (temperature) of the generated

heat as dictated by Carnot's law. The mechanics of the cell operation may additionally provide reaction controls to limit oxidation of the fuel to only a certain oxidation number. Again, the feasibility of conversion of CH_4 to HCOOH and generating useful energy is not completely established but available literature points to the potential of the process with some further development.

(i). Step-I: CH_4 to CH_3OH

Haomin [17], presents a good summary of advances in electro-catalytic conversion of CH_4 to CH_3OH and the challenges in this process. Yanfang Song [34] and Zhikai Guo [37] mention conversion of CH_4 to ethanol with 89% Faradaic efficiency (FE) with NiO/Ni catalyst at ambient temperature and pressure and alkaline electrolyte. While this is a great discovery from the perspective of monetization of isolated gas pools as well as to meaningfully use the otherwise flared associated gas, it is unfavorable from carbon abatement perspective - where the aim is to exploit maximum energy out of the fuel and leaving minimal amount with the waste byproduct. Ethanol does not qualify for doing that. But if ethanol could again be used in the second step as feed to yield HCOOH (or e.g., oxalic acid etc.) and energy, it will be a desirable scenario. With slightly different conditions they also report conversion to CH_3OH with 54% FE. Kim et al. [30] discusses a platinum-based catalyst which at moderate temperature results in continuous CH_3OH production with 70% selectivity. Maria Sarno et al. [22] used a nano catalyst (nanocomposite) based on NiO and V_2O_5 with Rh dispersed (NiO- V_2O_5 /Rh) at 100C temperature, resulting into methanol formation with 91% FE and 97% selectivity.

An important issue to note here is that even if the electro-chemical systems described here have shown higher selectivity to make the desired product, this is not achieved in a galvanic-cell operation. The reason is that the provision of active oxygen here generally comes from splitting water (or another reactant giving active oxygen) at the cathode. This means the reaction at the other electrode will be even more spontaneous with giving more energy. However, to establish that the overall cell results in power generation (rather than some power input and a lot of heat output) still remains to be demonstrated.

(ii). Step-II: CH_3OH to HCOOH

In the context of ethanol, many scientists such as Ye Wang [35] or El Mahdi Halim [8] have described its electro oxidation with Pt or Pd Catalysts follows a dual pathway. Under C1 path results in CO_2 but under C2 path results strictly in CH_3COOH . Formation of CH_3COOH appears to be a dead-end reaction, with acetic acid not reacting further. This encourages a surmise that methanol to HCOOH formation with similar arrangement may be possible, if there were an equivalent C2 path in this system.

Xinfa et al. [33], amongst many other authors, describe

formation of HCOOH from CH_3OH at anode, however at cathode the usable (active) oxygen comes from reduction of CO_2 . This is a similar situation to the one described under the step-I, as for the needed reduction of carbon at cathode to yield [O] electric power needs to be fed into the circuit. Ideal system would be able to use oxygen from air, avoiding needed energy for the CO_2 reduction reaction.

With the current search, there are not too many indications of a lab result about electro-oxidation of CH_3OH to HCOOH in the literature. In absence of missing electrolytic step-II, the possibility still exists to exploit the step-I potential electro-catalytically and carry out the second step with thermo-catalytical methods.

To recap the gaps in the electrochemical route:

1. Ideally there should be a single step conversion of CH_4 to HCOOH yielding energy enabled by use of oxygen from air
2. Step-I while feasible needs to be improved to be able to use oxygen from air
3. Step-II needs discovery of suitable catalysts and electrolyte system for making it feasible

3.2. L-red Processes (Low Energy Reduction of Combustion Byproduct - CO_2)

3.2.1. Preservation of Produced Biomass as a Means of Carbon Sequestration and Challenges

A subclass of L-red process deserves some consideration where CO_2 is converted to biomass naturally using solar energy. The energy required in making the renewable fuels from CO_2 is exactly as much as we took out by burning the fuel, plus some additional amount to carry the process out. This is obviously highly energy intensive as discussed above. But according to Table 2, we have number of other options. If we convert CO_2 back to complex sugars (carbohydrates) mentioned in step 2, we need to supply only one third energy compared to converting it all the way back to being a fuel, and at the same time we have the carbon sequestered in solid form! This is essentially the idea behind enhanced biomass growth as a means of carbon sequestration, or afforestation, or bio-sequestration. Again, the energy needed for converting CO_2 to biomass comes from the sun, and the process occurs naturally all around the globe where temperatures are between 0 and 40° Celsius, and water is not scarce. The issue with this approach is that produced biomass is subject to insect and fungal activity as a result of which carbon stored in biomass is eventually release back to the atmosphere as CO_2 . But with preservation of biomass, this hurdle can be overcome. Appendix II describes several approaches for preservation of biomass for long term carbon sequestration.

3.2.2. Exploring Feasibility of Electro-chemical L-red

One limitation with biomass-preservation as a sequestra-

tion-approach is its dependence on procuring or growing sufficient biomass which can be expensive due to the process being area intensive and slow, even if the technology exists.

If the produced combustion gas after cooling ($\text{CO}_2 + \text{N}_2$) is routed in an electrochemical cell along with water where CO_2

preferentially passes through the semi-permeable barrier, and N_2 acting as an inert, and the other inputs such as electrolyte solution and catalysts are chosen properly, CO_2 can be converted (reduced) to, for example, oxalic acid $[(\text{COOH})_2]$ with relatively small amount of energy. This is illustrated in Figure 3.

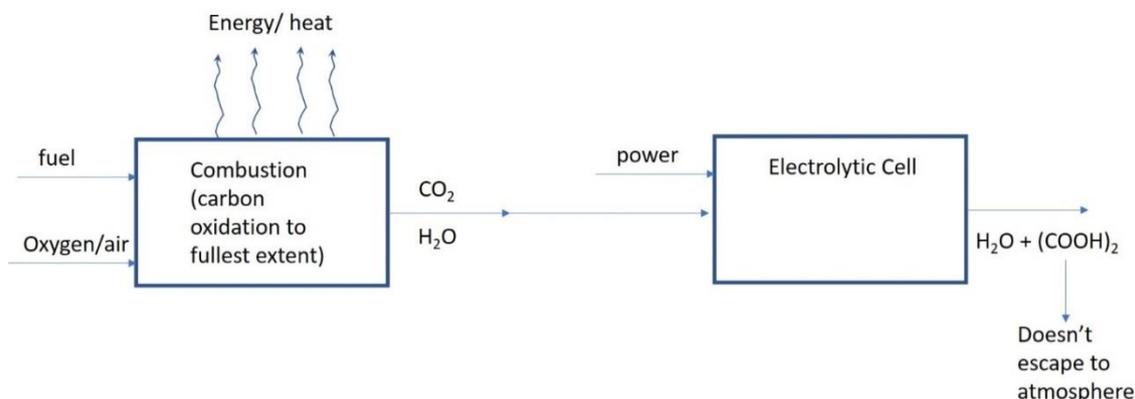


Figure 3. L-red process concept explained.

Heat of combustion of oxalic acid is approximately 2.8 GJ/t or 252 GJ/t-mole, or 2.8GJ/t CO_2 , implying 2.86GJ energy needs to be supplied to reduce 1 t CO_2 to oxalic acid. This energy however is going to be supplied in the form of electric power for the cell to function. The cell will have to operate in a manner that a constant stream of $(\text{COOH})_2$ will have to be withdrawn constantly as waste byproduct to maintain a certain concentration of reactants in the cell. The cost of such process will be on account of power input and capex + opex of the cell. If the energy efficiency of the cell is 80%, cost of power is \$60/MWh, on account of power input alone, the cost of carbon abatement will be $(2.86\text{GJ/t})/(3.6\text{GJ/MWh}) \times 60/0.8 = \$59.6/\text{tCO}_2$. The remaining cost can only be guessed at this juncture and assuming it to contribute to about half of the power cost over the usable life of the cell, the total cost of carbon abatement will be approximately \$90/t CO_2 . Oxalic acid being unmonetizable (even with a few uses) due to its large scale for reasons described above, does not need to incur costs for further transport and sub-surface injection. It can be surface stored.

If one were to convert CO_2 to other substances such as carbon fiber, or plastics, or complex sugars, the cost of input power will be relatively higher. For pure carbon (30GJ/t C) with 80% efficiency, it will be $(12/44) \times (30/0.8) \times (60/3.6) + 30 = \$201/\text{tCO}_2$. If CO_2 were to be converted to biomass (17.3GJ/t) or complex sugars $[(\text{CH}_2\text{O})_x]$ electrochemically with 80% efficiency, the cost will be $(30/44) \times (17.3/0.8) \times (60/3.6) + 30 = \$276/\text{tCO}_2$. All said though, the potential of this alternative needs to be established further with additional research and development.

If L-red cell only accepts pure CO_2 then $\$115 \times 0.75 \sim \$86/\text{tCO}_2$ will be used for capture and $\sim \$90/\text{tCO}_2$ for its conversion to oxalic acid for a total of $\sim \$176/\text{tCO}_2$ seques-

tered. This obviously does not compare favorably with the \$115/t CO_2 cost of CCS. This suggests the cell has to be such that flue gas mixture can enter the unit without needing CO_2 separation. In support of such reactions being technically feasible, Weixin et al. [32] report a combination of lead cathode and a sacrificial Zn anode in 0.1TEAP/AN electrolyte leads to formation of insoluble (and more easily recovered) Zinc Oxalate with 88.7% efficiency at 2.2 to 2.8V. In their experiment CO_2 was bubbled into the cell. Interestingly when N_2 was bubbled there was no reduction wave in the voltammograms, pointing to a potential of introducing a mixture of CO_2 and N_2 without having to separate the two in advance.

Ito et al. [21] describe use of lead cathode at 3V with TEAP/PC non-aqueous electrolyte, oxalic acid was formed with 80% current efficiency, which decreased with increasing voltage. Ikeda et al. [18] describe use of various electrode and electrolyte combinations to reduce CO_2 to formic or oxalic acid with very high current efficiencies. With lead cathode (working also as a catalyst) in aqueous electrolyte TEAP/ H_2O (0.1M tetraethylammonium perchlorate in water), at 2.4V potential formic acid was formed at 78.9% efficiency. With Indium cathode at 2V formic acid was formed with 87.6% efficiency. Similarly, with TEAP in non-aqueous solution comprising propylene carbonate (PC), acetonitrile (AN), and dimethyl sulfoxide (DMSO), the reaction favored formation of oxalic acid. With Pb cathode and 2.6V, oxalic acid formation was with 73.3% current efficiency.

While these results are extremely promising, they do not completely present a workable technology. Further work focused on the following areas is needed:

1. Introduction of N_2/CO_2 mixture in the cell to establish and obviate the need for CO_2 separation
2. Establish impact of NO_x/SO_x on the conversion process

and the equipment

3. Increase conversion efficiency further to 95+% by using specially designed catalysts

As indicated above the energy needed to convert CO₂ to oxalates is going to be the least and that is why it is best to not to attempt making useful products out of CO₂. 'Useless' in this case is of a lot of use as it requires significantly less energy.

4. Conclusions

CCUS (except in CO₂-EOR context), where monetization of the CO₂-conversion products is expected to offset high costs of the process, has a limited scope in massive carbon abatement prompting to explore fresh ideas to economically make fuel use carbon-neutral.

L-ox and L-red described in this paper present alternative routes to CCS for emissions-free energy and promise to be less expensive due to their lower energy requirement.

For L-ox route with thermo-catalytic processes it is possible to convert CH₄ to HCOOH in one step or two steps, both having their commercial advantages. However further (a) larger scale tests are needed to ascertain the usability of the heat that is generated and to ascertain it is available at what temperature, and (b) to explore if lower cost catalysts can be substituted for the relatively more expensive ones. This needs to be established with further work, in addition to establishing the reactions on the cathode should be utilizing oxygen rather than splitting other molecules such as H₂O for the source of active [O].

With the L-red route it is already established that the energy requirement in making non-monetizable products such as oxalic acid are minimal compared to the production of monetizable products, however the improvements in following areas will be useful: (a) established use of flue gas instead of pure CO₂, (b) use of less expensive catalysts, and (c) larger scale tests to establish associated Capex and Opex. A sub-class of these L-red approaches, namely biomass preservation holds a significant promise and does not require development of new technologies.

Author Contributions

Subodh Chandra Gupta is the sole author. The author read and approved the final manuscript.

Funding

No funding was used from any agency in preparation of this paper except investing author's own time.

Conflicts of Interest

The authors declare conflicts of interest.

Appendix

Appendix I: Issue with the Renewable Fuels

In principal CO₂ can be chemically reduced with solar energy to yield liquid or solid fuel, which when used will give away CO₂ again, to run in an endless cycle, and thus restricting any addition to atmospheric carbon. This is spontaneously done by photosynthesis to produce a solid fuel, however the energy efficiency of the process is only around 2% resulting in very small growth rate. To yield more concentrated form of (liquid) fuel from it, one needs additional energy to carry out fermentation, pyrolysis or gasification etc., of the feed. For a commercial process of conversion of solar energy to fuel one needs the process to proceed more quickly, minutes or hours instead of months, and in smaller area instead of being spread over hectares of land. It is because of these requirements that the conversion of CO₂ to renewable fuels by any method other than the natural photo-synthesis requires concentrated energy, typically in the form of electric power e.g., [10], or high grade heat. All this adds to the cost, as a result renewable fuels are significantly more expensive than their natural (fossil) fuels counterpart. [9] puts the cost of renewable fuels to be 0.7 to 1.3 more expensive than fossil fuels. Saysset [28] found the price of renewable fuels to be 1.5 to 2 times the fossil fuels.

Even with advancement of technology the renewable fuels are not expected to be cost-competitive with fossil fuels. This is not surprising. The use of fossil fuel (e.g., fossil oil) is always going to require less energy compared to the renewable fuel in most cases (it can be different when naturally occurring fossil resource is difficult to get at and is energy intensive). The main reason is that to make these renewable fuels one has to supply concentrated energy (electric power or high-grade heat) whereas with the fossil fuels this energy input was already made by solar energy collected over millions of years over vast areas and then acted upon by geothermal energy to cook it under pressure and high temperature to the concentrated crude oil that we have. Even when electric power is used to make the that renewable fuel, use of that electric energy directly for transport is more energy efficient comparatively and first converting it to a liquid fuel will incur significant loss of efficiency. Assuming the conversion can be done with 70% efficiency (For conversion to hydrogen it has been shown to have as high as 75% efficiency), and the conversion of fuel to mechanical power in cars is in the range of 18%, with the effective electric power to mechanical power conversion efficiency of 12.6%. Worth noting here is that the stationary engines are typically more efficient with efficiency in the range of 35%. Even in those cases overall efficiency is only 25%. Compare that with the average battery round trip efficiency of 80% [1] multiplied with electric power to mechanical power efficiency of EVs of 80+%, resulting in an overall electric power to mechanical power efficiency of 64+%

Appendix II: Biomass and Existing Technology Based Alternatives to Address Emissions

Natural photosynthesis and accompanying biomass production is a natural form of bio-sequestration of carbon. This is also the most effective way of DAC – the direct air capture. Falling in the row no. 2 of Table 2, this corresponds to a lower-energy reduction of CO₂ than converting it back to the original fuel. The issue with this approach is that produced biomass is subject to decay due to insect and fungal activity, releasing that carbon back to the atmosphere as CO₂. But with preservation of biomass, this issue can be avoided. The following describe various biomass-preservation based methods with existing technologies:

1. Charcoal sequestration
2. Torrefaction of biomass
3. Biomass harvesting and movement of the biomass to inert locations
4. Increase soil carbon

Charcoal Sequestration

Gupta et al. [11-16] have described in detail the process and economics of a scheme based on converting biomass into charcoal through biomass-pyrolysis to preserve carbon contained in it for centuries, and thus achieve effective sequestration.

Torrefaction of Biomass

Compared to charcoal sequestration, a moderate approach of mild pyrolysis or torrefaction can be employed to buy several decades to deal with the emissions issue. Torrefaction also is beneficial as it preserves more carbon into the converted biomass.

Biomass Harvesting and Movement of the Biomass to Inert Locations

Life on this planet, including for these creatures, thrives in the temperature range of 0 to 40 C, and in presence of moisture. When one of these ingredients are missing, decay is naturally arrested. To preserve the carbon in the produced biomass, it can also be transported to hot or cold deserts where decay activity on account of insects or microbes becomes negligible [16]. In effect this process exchanges conversion costs to transport or hauling costs. The added advantage of this process is preservation of almost all the carbon contained in the biomass.

Increase Soil Carbon

Experts [29] believe by restoring back some of the carbon into the soil a 2 to 5 Gt of carbon can be sequestered every year. When plant residues and roots are acted upon by a melanized endophytic fungi, the complex sugars get converted into a more stable form of carbon called melanin. Melanin is the major component of the soil organic carbon.

References

- [1] Administration, E. I. (2021). *TODAY IN ENERGY*. Retrieved August 20, 2022, from <https://www.eia.gov/todayinenergy/detail.php?id=46756#:~:text=According%20to%20data%20from%20the,%2Dtrip%20efficiency%20of%2079%25>.
- [2] Advisory Council, E. f. (2011). *The Costs of CO₂ Capture, Transport and Storage*. European Technology Platform for Zero Emission Fossil Fuel Power Plants.
- [3] Alexander Zoelle, D. K. (2015). *Cost and Performance Baseline for Fossil Energy Plants*. USDOE NETL.
- [4] Anchondo, C. (2021, March 29). DOE lab unveils technology to slash CCS costs. *Energy and Environment*.
- [5] Chemistry, G. (2020). *Oxidation of Methanol*. Retrieved November 21, 2022, from <http://www.passmyexams.co.uk/GCSE/chemistry/oxidation-of-methanol.html>
- [6] Clark, J. (2022). *Making Carboxylic Acids by Oxidation of Primary Alcohols or Aldehydes*. Retrieved November 21, 2022, from [https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_\(Organic_Chemistry\)/Carboxylic_Acids/Synthesis_of_Carboxylic_Acids/Making_Carboxylic_Acids_by_Oxidation_of_Primary_Alcohols_or_Aldehydes](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Carboxylic_Acids/Synthesis_of_Carboxylic_Acids/Making_Carboxylic_Acids_by_Oxidation_of_Primary_Alcohols_or_Aldehydes)
- [7] Collins, G. J. (2017). Industrial Production of Formaldehyde Using Polycrystalline Silver Catalyst. *Industrial & Engineering Chemistry Research*, 56(33), 9247-9265.
- [8] El Mahdi Halim, S. C. (2022). Recent Advances in Anode Metallic Catalysts Supported on Conducting Polymer-Based Materials for Direct Alcohol Fuel Cells. *Frontiers in Energy Research*, 10(March).
- [9] Environment, T. a. (2022). *Billions wasted on biofuels*. Brussels: Transport and Environment.
- [10] Fei Hu, L. Y. (2021). Ultrastable Cu Catalyst for CO₂ Electroreduction to Multicarbon Liquid Fuels by Tuning C-C Coupling with CuTi Subsurface. *Angewandte Chemie International Edition*, 60(50), 26122-26127.
- [11] Gupta, S. (2007). *What Are Our Options for Sequestration of Atmospheric CO₂--Some Thoughts*. Anaheim: SPE.
- [12] Gupta, S. (2009). *Are there Less Costly Ways to Sequester Carbon than CCS?* New Orleans: SPE.
- [13] Gupta, S. (2010). A Practical Way Out of the GHG Emissions Problem. *Journal of Canadian Petroleum Technology*, 49(8), 33-42.
- [14] Gupta, S. (2010). *Charcoal Sequestration as an Alternate Approach to Carbon Abatement – Working with Nature*. Calgary: Canadian Institute.
- [15] Gupta, S. C. (2011). Carbon Sequestration from Waste Through Conversion to. *Society of Petroleum Engineers*. <https://doi.org/10.2118/136887-PA> (December).
- [16] Gupta, S. C. (2019). *Promising Pathways to Lower Atmospheric Carbon Without Sacrificing the Petroleum Advantage*. Calgary: SPE.
- [17] Haomin Jiang, L. Z. (2022). Direct conversion of methane to methanol by electrochemical methods. *Green Energy & Environment*, 7, 1132-1142.

- [18] Ikeda, S. T. (1987). Selective Formation of Formic Acid, Oxalic Acid, and Carbon Monoxide by Electrochemical Reduction of Carbon Dioxide. *Bull. Chem. Soc. Jpn.*, 60 (July), 2517-2522.
- [19] Institute, G. C. (2020). *GLOBAL CO₂ STORAGE RESOURCE DATABASE A CRITICAL STEP FORWARD FOR THE DEPLOYMENT OF CCS*. Retrieved November 28, 2022, from <https://www.globalccsinstitute.com/news-media/insights/global-co2-storage-resource-database-a-critical-step-forward-for-the-deployment-of-ccs/>
- [20] Irlam, L. (2017). *GLOBAL COSTS OF CARBON CAPTURE AND STORAGE*. Global CCS Institute.
- [21] Ito, K. I. (1985). Electrochemical Reduction Products of Carbon Dioxide at Some Metallic Electrodes in Nonaqueous Electrolytes. *Bull. Chem. Soc. Jpn.*, 58(October), 3027-2028.
- [22] Maria Sarno, E. N. (2020). Methane electrochemical oxidation at low temperature on Rh single atom/NiO/V₂O₅ nanocomposite. *Applied Catalysis A: General*, 603(August).
- [23] Maura Vaccarelli, R. C. (2014). Energy and economic analysis of the CO₂ capture from flue gas of combined cycle power plants. *Energy Procedia* (pp. 1165-1174). Elsevier.
- [24] McGlade, C. (2019). *Can CO₂-EOR really provide carbon-negative oil?* Retrieved November 28, 2022, from <https://www.iea.org/commentaries/can-co2-eor-really-provide-carbon-negative-oil>
- [25] Mengwei Li, J. S.-S. (2021). Single-step selective oxidation of methane to methanol in the aqueous phase on iridium-based catalysts. *Applied Catalysis B: Environmental*, 292 (September).
- [26] Michael Godec, V. K. (2011). CO₂ Storage in Depleted Oil Fields: The Worldwide Potential for Carbon Dioxide Enhanced Oil Recovery. *Energy Procedia*, 2162–2169.
- [27] Rystad Energy. (2023, June 28). *Recoverable oil reserves top 1,600 billion barrels, capable of warming the planet an extra 0.2 °C by 2100*. Retrieved from Rystad Energy: <https://www.rystadenergy.com/news/recoverable-oil-reserves-billion-barrels-warming-planet>
- [28] Saysset, S. H. (2021, February 2). *Biofuels, an alternative that is still too expensive*. Retrieved from Polytechnique insights: <https://www.polytechnique-insights.com/en/braincamps/plane-t/zero-carbon-aviation/biofuels-an-alternative-that-is-still-too-expensive/>
- [29] School of International Service, A. U. (2022). *Fact Sheet: Soil Carbon Sequestration*. Retrieved October 30, 2022, from <https://www.american.edu/sis/centers/carbon-removal/fact-sheet-soil-carbon-sequestration.cfm>
- [30] Soyoung Kim R., and Surendranath, Y. (2019). Electrochemical Reoxidation Enables Continuous Methane-to-Methanol Catalysis with Aqueous Pt Salts. *ACS Central Science*, 5, 1179-1186.
- [31] Statista. (2022). *Capacity of operational large-scale carbon capture and storage (CCS) facilities worldwide from 2012 to 2021*. Retrieved November 28, 2022, from <https://www.statista.com/statistics/726634/large-scale-carbon-capture-and-storage-projects-worldwide-capacity/>
- [32] Weixin Lv, R. Z. (2013). Electrochemical reduction of carbon dioxide with lead cathode and zinc anode in dry acetonitrile solution. *Solid State Electrochem*, 17(July), 2789–2794.
- [33] Xinfa Wei, Y. L. (2020). Formic Acid Electro-Synthesis by Concurrent Cathodic CO₂ Reduction and Anodic CH₃OH Oxidation. *Angewandte Chemie International Edition*, 60(6), 3148-3155.
- [34] Yanfang Song, Y. Z. (2020). Efficient methane electrocatalytic conversion over a Ni-based hollow fiber electrode. *Chinese Journal of Catalysis*, 41(7), 1067-1072.
- [35] Ye Wang, S. Z.-B. (2015). Recent Advances on Electro-Oxidation of Ethanol on Pt- and Pd-Based Catalysts: From Reaction Mechanisms to Catalytic Materials. *Catalysts*, 5, 1507-1534.
- [36] Zhijun Zuo, P. J. (2016). *The Low - Temperature Conversion of Methane to Methanol on Ce - Ox/Cu₂O catalysts: Water Controlled Activation of the C - H Bond*. Brookhaven National Laboratory, USDOE.
- [37] Zhikai Guo, W. C. (2020). Electrocatalytic oxidation of methane to ethanol via NiO/Ni interface. *Applied Catalysis B: Environmental*, 270(August).