

The Low Concentration of CO₂ in the Atmosphere Is an Obstacle to a Sustainable Artificial Photosynthesis Fuel Cycle Based on Carbon

In his Viewpoint, “Advantages of Solar Hydrogen Compared to Direct Carbon Dioxide Reduction for Solar Fuel Production”, Bruce Parkinson from the University of Wyoming argues that it is not advisable from a cost and energy perspective to use renewable energy to directly reduce carbon dioxide produced from burning fossil fuels to reduce CO₂ emissions. He also states that because of the complexity of the chemical conversion, solar energy-driven CO₂ reduction would be several times as expensive as solar energy-driven electricity production. He concludes that fossil fuels should be used for the production of high-value products and not for the production of energy.

As a researcher engaged in solar hydrogen production, I support this view and would like to add the following point: The detrimental effects of carbon dioxide on our climate are very significant at the 400 ppm level, as evidenced by the increase of global temperature over the past decades. It makes little sense to build a renewable fuels technology that prolongs carbon dioxide emissions into the atmosphere because it relies on concentrated CO₂ from coal-fired power plants and cement factories. We need to reduce carbon emissions immediately, not prolong them, to avoid warming beyond the 2 °C goal.

A fuel technology built around carbon (or any fuel) must support a closed loop in order to be sustainable (Figure 1). This means that it must be able to achieve CO₂ sequestration at a rate equal to CO₂ emissions, so that atmospheric CO₂ concentrations are kept at steady state or reduced to the level of preindustrial times. However, the low concentration of CO₂ in

the atmosphere makes it very difficult to build a *closed carbon fuel cycle* that is sustainable.

On the basis of thermodynamics, the *minimum* energy required to concentrate CO₂ from 400 ppmv in the atmosphere to 1 atm requires 19.38 kJ energy per mole of CO₂ ($=RT \ln [1 \text{ atm}/0.0004 \text{ atm}]$). The actual energy expenditure of the best air CO₂ sequestration processes is 20–30 times higher (440–600 kJ of energy per mole of CO₂).^{1,2} This is because of the energy need for regenerating the CO₂ absorbent and because of the need to pump large quantities of air through the CO₂ absorber (3 million cubic meters of air per ton of CO₂ removed). Theoretically, the CO₂ absorbent could be replaced with a CO₂-selective membrane, but that would require costly pressurization of large quantities of air. Another option is CO₂ conversion without preconcentration; however, that would require reactors with large capture areas, also driving up costs for installation, operation, and absorbent cycling in such plants.³ Alternatively, one could capture CO₂ directly at the emission source, for example, at the tail pipe of an automobile. Currently, the energy to separate CO₂ from *coal-fired flue gas* is 200 kWh per ton of CO₂, which is equivalent to 20% of the power output from one ton of CO₂ emissions.⁴ CO₂ removal from hydrocarbon fuel combustion engines will be much harder due to the lower CO₂ content and the presence of water.

No matter how one looks at this problem, the energy penalty of recycling CO₂ is going to significantly reduce the energy efficiency of hydrocarbon fuel combustion.

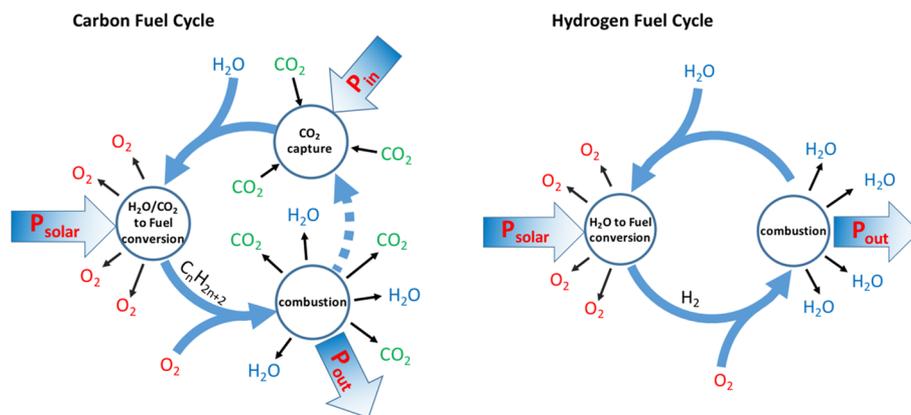


Figure 1. Carbon versus hydrogen fuel cycle, including power inputs and outputs.

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A hydrogen-based fuel cycle (Figure 1) does not suffer from these problems because the products of hydrogen combustion do not have any adverse effects on the environment and because the source of hydrogen, liquid water, is available in concentrated form. Therefore, a completely sustainable, closed fuel cycle can be built more easily. Although advances have been made in the past decade in raising the efficiency of photoelectrochemical and photovoltaic water splitting, further cost reductions are necessary to make this technology competitive with fossil fuels. Particle-based photocatalytic water splitting approaches are less expensive but do not yet reach the efficiency required for commercialization. I am convinced that a workable compromise can be achieved by applying the lessons of photovoltaics and photoelectrochemistry to particle-based water splitting systems.

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Notes

Views expressed in this Viewpoint are those of the author and not necessarily the views of the ACS.

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