

Efficient Production of Solar Fuel Using Existing Large Scale Production Technologies

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Published in Environmental Science & Technology (2011)

ECN-W--11-058 NOVEMBER 2011





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■ INTRODUCTION

Global energy consumption will at least double during this century. Today about 80% of the primary energy used is provided by fossil fuels. To avoid anthropogenic climate change, it is essential that the world's energy system is gradually transformed from fossil energy based to a solar based one. In such a solar world, efficient energy storage is prerequisite to deal with the intermittency of this abundant source. Storage in the form of chemical energy, that is, solar fuels, provides a natural route to deal with this problem. An obvious solar fuel would be hydrogen, which can be produced efficiently from solar energy through direct splitting of water or through combination of solar electricity production with electrolysis of water. Unfortunately, hydrogen has a major disadvantage as its transport and storage is not trivial. No such storage problem exists for alcohols or liquid hydrocarbons. Especially liquid hydrocarbons are preferred solar fuels in view of their unprecedented combination of gravimetric and volumetric energy density and the worldwide existing markets and infrastructure.

SOLUTION

Though hydrogen is not the ideal solar fuel, it is a very attractive intermediate as liquid hydrocarbons can be produced

through hydrogenation of CO_2 . The CO_2 is captured at fossil fuel based power plants or directly from the air. To produce liquid hydrocarbon fuels from solar hydrogen and CO_2 , the reverse water-gas shift reaction (RWGS):

$$H_2 + CO_2 \leftrightarrow CO + H_2O \Delta H_0 = +41 \text{kJ/mol}$$

combined with commercial cobalt based Fischer-Tropsch technology is the obvious route. Figure 1 gives an artist impression of this solar fuels scheme. With the exception of the RWGS process the whole process train is already available on a (sub)commercial scale today. The RWGS is an endothermic equilibrium reaction, and the equilibrium lies on the product side only for temperatures above 800 °C. The conversion at lower temperatures, 150−250 °C can be enhanced greatly, up to 100%, if a reaction product, that is, water, is selectively removed. At laboratory scale Carvill et al.² showed that even pure CO could be produced at 250 °C in a sorbent enhanced RWGS (SERWGS) process. In the current solar fuels process it suffices if the SERWGS step produces a mixture of CO and hydrogen (synthesis gas). The inset in figure 1 shows a typical experimental result. In this case CO₂ and hydrogen are fed to a fixed bed reactor, which contains a mixture of a low temperature WGS catalyst (SüdChemie) and a water sorbent (for our experiments molsieve 4A (Merck)). Initially essentially complete conversion of CO₂ is obtained. After saturation of the sorbent, breakthrough of CO₂ occurs and the conversion converges toward chemical equilibrium.

In practice the SERWGS process is also executed in a fixed bed reactor, which contains a mixture of a watergas shift catalyst and a sorbent. Saturation of the sorbent with water necessitates a number of parallel reactors: one reactor is producing synthesis gas, while the others are in various stages of regeneration. This configuration is similar to that of the sorbent enhanced water-gas shift process, SEWGS, currently under development. No major hurdles are therefore foreseen for further development of the SERWGS process. The heat released by the sorption reaction is sufficient to drive the RWGS reaction. The heat released by the exothermic Fischer—Tropsch process ($-160~{\rm kJ/mol}$) can subsequently be used to fully regenerate the water sorbent ($55~{\rm kJ/mol}$), optimizing the sustainability of the process.

To obtain an estimate of the efficiency from solar energy to liquid fuels one can multiply the efficiency of the various subprocesses. State-of-the-art photovoltaic panels achieve efficiencies of

Received: September 9, 2011 Accepted: September 12, 2011

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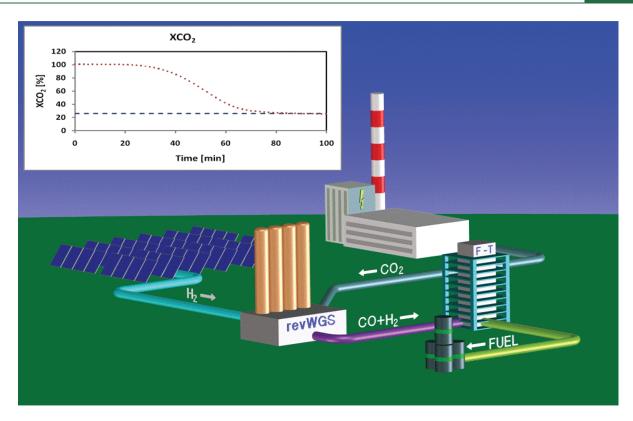


Figure 1. An artist impression of a solar fuels process. Liquid hydrocarbon fuels are produced from solar hydrogen and CO₂. Inset shows experimental conversion of CO₂ as a function of time in the SERWGS reaction (p = 1 bar, T = 300 °C, H_2/CO_2 feed ratio = 4, GHSV= 170 h⁻¹, equilibrium conversion: horizontal dashed line).

19%. The efficiency of high pressure electrolysis is about 85%, which implies that solar hydrogen can be produced with efficiencies around 16%. Including a mismatch between photovoltage and electrolysis potential this number reduces to 13%. The efficiency of the SERWGS and Fischer—Tropsch steps are estimated to be of the order of 90% and 70% respectively. This yields an overall efficiency from solar energy to liquid fuels of about 8.2%. This number is not very sensitive to inclusion of the energy penalty connected with $\rm CO_2$ capture. A realistic energy penalty of 150 kJ/mol of $\rm CO_2$ reduces the efficiency of solar fuel synthesis to 7.7%.

This number compares favorably with efficiencies reported for a number of alternative routes to produce solar fuels including advanced biomass conversion, artificial photosynthesis and thermochemical production.⁴ Many of these technologies, though promising in the long term, are still in a rather early stage of their development and the efficiencies from solar energy to chemical energy are still low, typically below 1%.

SUMMARY

Solar fuels can be produced efficiently already today using existing technologies. Liquid hydrocarbon fuels production from $\rm CO_2$ and water with efficiencies approaching 10%—from solar energy to fuel—is feasible. This is about an order of magnitude higher than alternative technologies currently under development. The main challenge for further research is to reduce costs and further improve efficiency through optimized process schemes. The main challenge for further research is to reduce costs and further improve efficiency through optimized process schemes and PV systems.

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