

# HYDROGEN PRODUCTION VIA THE SOLAR THERMAL DECARBONIZATION OF FOSSIL FUELS

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*Two hybrid solar/fossil-fuel endothermic processes, in which fossil fuels are used exclusively as the chemical source for H<sub>2</sub> production, and solar energy as the source of high-temperature process heat, are considered: 1) the solar thermal decomposition of natural gas; and 2) the solar steam gasification of coal. These processes offer viable and efficient routes for fossil fuel decarbonization and CO<sub>2</sub> avoidance. The advantages of the solar-driven process are three-fold: a) the discharge of pollutants is avoided; b) the gaseous products are not contaminated; and c) the calorific value of the fuel is upgraded.*

## 1 INTRODUCTION

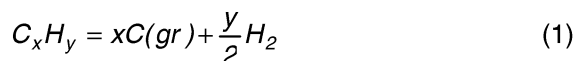
The conversion of solar energy into chemical energy carriers, i.e. *solar fuels* (e.g. solar H<sub>2</sub>), which can be long-term stored and long-range transported, overcomes the major drawbacks of solar energy, namely: being a diluted, intermittent, and unequally distributed energy source [1].

The substitution of fossil fuels with solar fuels is a long-term goal requiring the development of novel technologies. Strategically, it is desirable to consider mid-term goals aiming at the development of hybrid solar/fossil-fuel endothermic processes in which fossil fuels are used exclusively as chemical reactants and solar energy as the source of process heat. The products of such hybrid processes are cleaner fuels whose quality has been solar-upgraded: their calorific value is increased by the solar input in an amount equal to the enthalpy change of the reaction. The mix of fossil fuels and solar energy creates a link between today's fossil-fuel-based technology and tomorrow's solar chemical technology. It also builds bridges between present and future energy economies because of the potential of solar energy to become a viable economic path once the cost of energy will account for the environmental externalities from burning fossil fuels. The transition from fossil fuels to solar fuels can occur smoothly, and the lead-time for transferring important solar technology to industry can be reduced.

## 2 DECARBONIZATION OF FOSSIL FUELS

An important category of thermochemical processes for mixing fossil fuels and solar energy is the decarbonization of fossil fuels, i.e. the removal of carbon from fossil fuels prior to their use for power generation. Two methods are considered: the solar thermal decomposition and the steam-reforming/gasification. Both methods make use of high-temperature solar process heat for driving the endothermic transformations.

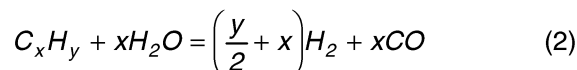
The thermal decomposition of natural gas, oil, coal (pyrolysis), and other hydrocarbons can be represented by the simplified reaction:



Other compounds may also be formed, depending on the reaction kinetics and on the presence of impurities in the raw materials. The thermal decomposition yields a carbon-rich condensed phase and a hydro-

gen-rich gas phase. The carbonaceous solid product can either be sequestered or used as material commodities under less severe CO<sub>2</sub> restraints. They can also be used as reducing agents in metallurgical processes. The hydrogen-rich gas mixture can be further processed to high-purity hydrogen that is not contaminated with carbon oxides and can be used in fuel cells without inhibiting platinum-made electrodes. H<sub>2</sub>-rich mixtures can also be adjusted to yield high-quality syngas.

The steam-reforming/gasification of natural gas, oil, coal, and other hydrocarbons can be represented by the simplified reaction:

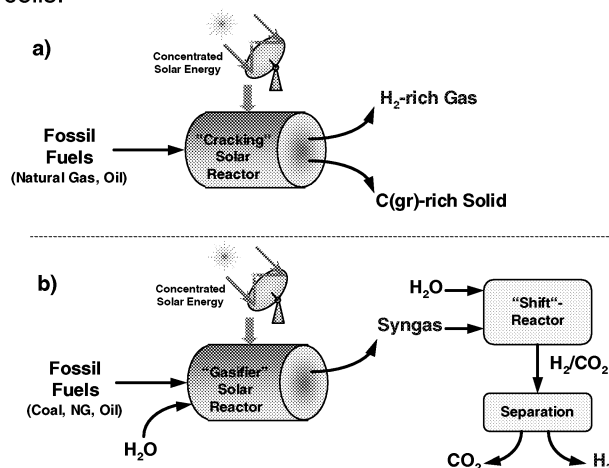


Other compounds may also be formed, especially with coal, but some impurities contained in the raw materials are cleaned out prior to the decarbonization process. The principal product is syngas of different H<sub>2</sub>:CO molar ratios. The CO content in the syngas can be shifted to H<sub>2</sub> via the catalytic water-gas shift reaction, and the product CO<sub>2</sub> can be separated from H<sub>2</sub> using, for example, the pressure swing adsorption technique.

Reactions (1) and (2) proceed endothermically in the 800-1500 K range. Several chemical aspects of these reactions have already been studied [2, and literature cited therein]. Some of these processes are currently practiced at an industrial scale, but the energy required for heating the reactants and for the heat of the reaction is supplied by burning a significant portion of the feedstock. Internal combustion results in the contamination of the gaseous products while external combustion results in a lower thermal efficiency because of the irreversibilities associated with indirect heat transfer. Alternatively, using solar energy for process heat offers several advantages: 1) the discharge of pollutants is avoided; 2) the gaseous products are not contaminated; and 3) the calorific value of the fuel is upgraded by adding solar energy in an amount equal to the ΔH of the reaction. Furthermore, by directly irradiating the reactants, solar energy can be efficiently transferred to the reaction site, bypassing the limitations imposed by heat exchangers.

The two solar thermal decarbonization methods are schematically shown in Figure 1 in the form of simplified process flow diagrams. The two methods have been compared [3], focusing on thermodynamics and

exergy efficiency. From the point of view of carbon sequestration, it is easier to separate, handle, transport and store solid carbon than it is  $\text{CO}_2$ . Also, the steam-reforming/gasification method requires additional steps for shifting CO and for separating  $\text{CO}_2$ , while the thermal decomposition accomplishes the removal and separation of carbon in a single step. In contrast, the major drawback of the thermal decomposition method is the energy lost associated with the sequestration of carbon. The thermal decomposition may be the preferred option for natural gas and other hydrocarbons with high  $\text{H}_2/\text{C}$  ratio. But for coal and other solid carbonaceous materials, the residual of energy upon decarbonization may be too low for an industrial application. Instead, the gasification of coal via reaction (2) has the additional advantage of converting a relatively dirty solid fuel, which is traditionally used to generate electricity in 35%-efficient Rankine cycles, into a cleaner fluid fuel (cleaner only when using solar process heat) that can be used in highly efficient Brayton-Rankine combined cycles and fuel cells.



**Fig. 1:** Simplified process flow diagram for the solar thermal decarbonization of fossil fuels. Two methods are considered: (a) the solar thermal decomposition; (b) the solar thermal steam-reforming/gasification. Omitted is the formation of by-products derived from impurities present in the feedstock.

### 3 EXERGY EFFICIENCY AND $\text{CO}_2$ MITIGATION POTENTIAL

The following routes for  $\text{H}_2$  and power generation are examined:

- The solar thermal decomposition of natural gas followed by carbon sequestration and  $\text{H}_2$  use in a 70%-efficient  $\text{H}_2/\text{O}_2$  fuel cell;
- The steam gasification of coal followed by syngas processing to  $\text{H}_2$  (by water-shift gas reaction and  $\text{H}_2/\text{CO}_2$  separation), which is used to fuel a 70%-efficient fuel cell.

The exergy efficiency for each of these open-cycle routes is defined as the ratio of the work output by the fuel cell to the total thermal energy input by solar and by the heating value of the reactants:

$$\eta_{\text{exergy}} = \frac{\text{Work Output}}{Q_{\text{solar}} + \text{HHV}_{\text{reactant}}} \quad (3)$$

where  $Q_{\text{solar}}$  is the solar energy input and  $\text{HHV}_{\text{reactant}}$  is the high heating value of the fossil fuel being proc-

essed, e.g. about  $890 \text{ kJ}\cdot\text{mole}^{-1}$  for natural gas, and  $35,700 \text{ kJ}\cdot\text{kg}^{-1}$  for anthracite coal. Exergy efficiencies are carried out for a blackbody solar cavity-receiver/reactor operated at 1350-1500 K and subjected to a mean solar flux concentration ratio in the range of 1000-2000.

For route Nr. 1 aimed at  $\text{H}_2$  generation from natural gas, the exergy efficiency amounts to 30%. This route offers zero  $\text{CO}_2$  emissions as a result of carbon sequestration. However, the energy penalty for completely avoiding  $\text{CO}_2$  amounts to 30% of the electrical output, vis-à-vis the direct use of  $\text{CH}_4$  for fuelling a 55%-efficient combined Brayton-Rankine cycle.

Higher exergy efficiencies (exceeding 65%) could be obtained when the carbon is either steam-gasified to syngas in a solar gasification process and the syngas further processed to  $\text{H}_2$ , or used as a reducing agent of ZnO in a solar carbothermal process for producing Zn and CO that are further converted via water-splitting and water-shifting to  $\text{H}_2$ . Any of these two alternative solar processes yield 2 additional moles of  $\text{H}_2$  per mole C(gr) and offer a net gain of 40% in the electrical output (and, consequently, an equal percent reduction in the corresponding specific  $\text{CO}_2$  emissions), as compared to the conventional combined cycle power generation.

For route Nr. 2 aimed at  $\text{H}_2$  generation from coal, the exergy efficiency amounts to 56%. This route offers a net gain in the electrical output by a factor varying in the range 1.8-2.2 (depending on the coal type), vis-à-vis the direct use of coal for fuelling a 35%-efficient Rankine cycle. Specific  $\text{CO}_2$  emissions amount to 0.44-0.52  $\text{kg CO}_2/\text{kWh}_e$ , about half as much as the specific emissions discharged by conventional coal-fired power plants.

## 4 CONCLUSION

There is a pressing need to develop greenhouse gas mitigation options that can be applied to fossil fuels in the mid-term. The proposed solar/fossil fuel hybrid chemical processes conserve fossil fuels and reduce emissions. It further converts solar energy into a storable and transportable chemical fuel. The fossil and solar energy mix could substantially reduce  $\text{CO}_2$  emissions and become an important intermediate solution towards a sustainable energy supply system.

## 5 ACKNOWLEDGEMENTS

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