# Solar Thermal Chemistry

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## 1. Introduction

The advantages of solar energy versus all conventional or planned energy sources are as follows: solar energy can provide a renewable supply of process heat at different temperatures ranging from room temperature up to approximately 2000 K; in addition, all atmospheric pollutions such as $CO_2$ (greenhouse effect), $NO_x$ (destruction of the ozone layer), and $SO_2$ (acid rain) are strictly avoided and full renewability is guaranteed.

The process heat so obtained can be used as cheap and clean energy for nearly all chemical processes. It can be transported in the form of steam, and – in some cases – as molten salts or molten metals.

The following chemical reactions can be performed by using solar process heat:

### *1.1. Production of Light Hydrocarbons*

The production of simple hydrocarbons and derivatives thereof such as methanol, ethene, ethanol, or acetylene can supply basic chemicals in organic industrial chemistry and as transportable and storable fuels. As parent carbon compound, $CO_2$ can be used (ideal case). This group of processes avoids the extensive and wasteful

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use of fossil resources as well as any increase of atmospheric $CO_2$. Their relevance for post-fossil energy scenarios is obvious.

Fundamental processes for the reduction of $CO_2$:

$$CO_2 \rightarrow CO + \tfrac{1}{2}O_2$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
$$CO + 2H_2 \rightarrow CH_3OH$$

There are many more known catalyzed processes leading to various light hydrocarbons.

$CO_2$, as the parent compound, may be obtained from many different sources (cement production, metal carbonates, and fossil-fuel byproducts for example). Hydrogen, as another major parent compound, can be obtained from the solar-driven processes described below.

The theoretical and practical basis for such solar-driven $CO_2$ reduction processes must be further studied. Due attention has to be paid to the development of suitable reactor / converter/ transport facilities.

### *1.2. Production of Hydrogen*

Solar process heat can be used for the splitting of water, i.e. the production of molecular hydrogen and oxygen.

Hydrogen represents an important compound as an energy storage material and fuel as well as a major chemical feedstock. The direct thermal splitting of water requires extremely high temperatures. Furthermore, the products $H_2$ and $O_2$ are formed simultaneously (requiring conventional separation and purification). Consequently the following multi-step process is preferable to direct splitting:

$$H_2O + MO \rightarrow H_2 + MO_2$$
$$H_2O + 2MO \rightarrow H_2 + M_2O_3$$
$$H_2O + 3MO \rightarrow H_2 + M_3O_4 \text{ etc.}$$

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Water is one of the cheapest and most abundant chemicals. The solar-driven conversion into a high-value compound such as $H_2$ is very promising. No pollution effects result from this process. Research on appropriate metal-oxide systems for facilitating or catalyzing the splitting of water is needed. Metal oxides, which can be thermally reduced (e.g. $M_2O_3 \rightarrow 2MO + \tfrac{1}{2}O_2$) are preferable.

### *1.3. Reversible Redox Processes in Metal Oxides*

Thermal reduction of metal oxides to metals or low-oxidation-state metal oxides can be performed using solar process heat. The products are important with respect to applications as reactants (see forgoing topic) or as battery materials, etc. The thermal reduction of metal oxides usually takes place at high temperatures (> 1200 K). It can be performed in windowless reactor systems under atmospheric conditions. In the case of reversible redox systems, such metal oxides represent catalysts (for heterogeneous reactions) and/or reactants for stochiometric conversions.

Apart from the well-known binary transition metal oxides undergoing reversible reduction-reoxidation processes at different temperature levels, ternary oxides such as spinels, perovskites, etc. are of importance. Metal oxide processes are:

$$M_3O_4 \rightleftarrows 3MO + \tfrac{1}{2}O_2 \ (M = Mn, Fe, Co)$$
$$2MO \rightleftarrows M_2O + \tfrac{1}{2}O_2 \ (M = Cu)$$
$$ABO_3 \rightleftarrows ABO_{3-x} + \tfrac{x}{2}O_2 \ (A, B = \text{metals})$$

The above mentioned materials and processes are well suited for future investigation of the interdependence of thermal energy $\Omega$ and chemical potential $\mu$.

### *1.4. Metal Hydride Systems*

Metal hydrides can be obtained by the reduction of selected metals with molecular hydrogen at low temperatures. They act as hydrogen storage systems, hydrogen purification devices, etc. The fact that metals such as magnesium react with molecular hydrogen and thermally release molecular hydrogen renders these materials important with respect to hydrogen storage as well as to chemical storage systems. Exothermal hydride formation occurs at low temperature and thermal degradation of the hydride into metal and hydrogen is solar driven at elevated temperature.

The fundamental process for the use of metal hydride chemistry is reversible:

$$M + \tfrac{x}{2}H_2 \rightleftarrows MH_x$$

The reaction is carried out in cycles using regenerative beds contained in pressure vessels.

At present, metal hydride systems are produced on a semi-commercial level (magnesium-based). Research work on the optimization of the reversibility as well as on new metal compounds should be emphasized.

### *1.5. Selection of Further Possible Processes*

Solar process heat at different temperatures can be used for numerous reactions leading to high-value products, replacing the use of conventional (fossil) heat sources. Processes of importance:

Carbothermal reductions

$$Al_2O_3 + 3C \rightarrow 2Al + 3CO$$
$$CaO + 3C \rightarrow CaC_2 + CO$$

Formation of inorganic solids

$$Si + C \rightarrow SiC$$
$$M_mO_3 + M^*_nO \rightarrow M_mM^*_nO_{x+y} \text{ etc.}$$

Calcination (cement production)

$$MCO_3 \rightarrow MO + CO_2$$
$$MCO_3 \rightarrow MO_2 + CO \text{ (formal!)}$$

Formation of ammonia (multi-step process)

$$N_2 + 3H_2O \rightarrow 2NH_3 + \tfrac{3}{2}O_2$$

(as mediating materials: iron oxide or metallic lithium)

This selection of processes is arbitrary and can be extended almost without limits. The potential of such conversions can only be estimated by economic evaluations.

## 2. Solar Equipment

The equipment needed to carry out solar thermal chemistry is not fully available. Much research is needed to provide the basis for its design. There appear to be no unsolvable problems, no «show stoppers». Practical solar thermal chemical systems generally need concentrators, solar receiver-reactors, and thermal storage devices.

Research and development is required for solar energy collection primarily in the area of secondary concentrators. These devices increase the concentration that is needed for high-temperature (> $10^3$ K) thermochemical processes. Since the secondary concentrator receives flux from the primary concentrator, it is itself subjected to high fluxes (1 to 10 $MW/m^2$) and thermal and materials problems must be investigated.

Solar receiver-reactors have attracted almost no research attention, thus many research efforts have to be initiated. The solar receiver-reactor contains the chemical reactants and, often, heat-transfer equipment. They may be classified first into direct or indirect receiver-reactor systems. A direct system receives the highly concentrated solar energy directly upon the reactants or upon a catalytic surface simultaneous with its exposure to the reactants. An indirect reactor-receiver receives the solar flux on an intermediate heat-transfer medium that subsequently transfers heat to the reactants.

The absorber can also be classified as surface or volumetric. Volumetric absorption may be enhanced by the use of partic-

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ulates (perhaps catalyst particles), wires, or fabrics of ceramic fibres. To our knowledge only one volumetric receiver concept has been tested, but with promising results. Research needs to be performed to explore and develop the reactor-receiver technology. The high pressures to be sustained simultaneously with high fluxes transmitted by the window must be accommodated by design studies.

The advantages of direct absorption are obvious: no walls or windows need to be exposed to high fluxes, thermal stress problems are reduced, high absorptivities can be achieved, no temperature drop need be taken for indirect heat transfer, and loss of available energy (exergy) is avoided. Gases loaded with particulates, liquid films, and falling catalyst pellets can be used in direct absorption. The technology to be developed can be applied to photothermochemical reactions and may advance heat-transfer technology in general.

Research is needed in the absorption and scattering of radiant energy by the specific particulates to be used. Investigations on gas two-phase fluid dynamics should be carried out. Clearly materials research is needed to develop catalyst carriers and other media involved.

Not to be overlooked is the need for the development of measurement concepts and instruments based on these new concepts.

Transparent windows subject to high fluxes and several atmospheres of pressure difference are to be developed and demonstrated.

Some of the research required is not especially process specific and should be initiated at once. The process specific research should be phased in as simultaneous research on the specific chemical processes develops.

Thermal storage is almost certainly needed (even with direct reactors) to maintain process control, high overall effiency, reduction of startup-shutdown losses, and to meet peak demands. Promising new techniques involve sensible and/or latent heat storage in pebble beds or composite materials as well as chemical storage. Research specifically dedicated to high temperature levels should be promoted.

*This paper is also supported by: B. Qvale (DK), H. Larsen (DK), A.J. Nozik (USA), J.C. Courvoisier (CH).*