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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 2: Hydrogen Production Technologies – Part 1
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-2
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-652-1

Methanol from CO_2 and Solar Energy – A Literature Review

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1 Background and Motivation

In the future generation of methanol, hydrogen produced by solar energy will be one major source of primary energy. Different technologies are currently under investigation. Among these, high-temperature thermochemical cycles are considered very promising. Prerequisite for converting water with one or more chemical steps into hydrogen and oxygen is the concentration of solar energy to high flux levels.

At the solar tower facility at Jülich, a heliostat field of about 18000 m² focuses the sunlight onto an absorber surface of just 22 m² - a concentration high enough to reach temperatures beyond 1000°C, which is necessary to drive the endothermic steps of many thermochemical cycles.

The Solar-Institute Jülich, with its partners Ferrostaal and DLR, is now investigating in the project SolMethCO_2 the use of solar hydrogen for the reduction of CO_2 to methanol, addressing the issues of transportability of hydrogen and the exploitation of fossil resources for the methanol production.

The impending changes in the world climate are related to an accumulation of CO_2 in the atmosphere. One approach to counteract is by binding CO_2 in different chemical form like methanol. Concerning the high amount of energy, which is necessary for this process and generally derived from fossil energy sources, the implementation of solar technologies could be a key solution for delivering clean, carbon-free energy. The chemical and physical ways from solar energy and CO_2 to methanol are manifold and hard to compare with respect to their economical and ecological potentials due to different degrees of maturity of sub-processes. To make a comparison of the sub-processes possible, all established procedures have to be recorded and analysed systematically. Based on the results of literature research, practical experiences, experimental results and simulations, the aim of this project will be a final assessment of all CO_2-to-methanol processes.

2 Methods of Methanol Synthesis

Besides its technical use as a chemical feedstock, as e.g. for the production of acetic acid, formaldehyde or MTBE, methanol is a high potential energy carrier. Due to this, it is either used as a basis for the transformation into other fuels like dimethylether (DME), or it can be used pure or as a mixture with petrol or diesel fuels directly in combustion engines. Direct methanol fuel cells (DMFCs) directly convert the liquid fuel methanol into CO_2 while producing electric energy. This seems to be an attractive alternative to fuel cell systems operation with hydrogen, because of the higher volume-specific energy density of methanol.

Nowadays methanol is mainly produced by natural gas, which provides on the one hand carbon and hydrogen and on the other hand thermal energy during combustion.

The classical approach for the synthesis of methanol is via the transformation of synthesis gas, which is generally produced by the reformation or gasification of fossil energy carriers, as for example methane, at high temperatures (700-1100°C):

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

In the next step, the synthesis gas reacts catalytically at 250°C and 50 to 100 bars to methanol:

$$CO + 2H_2 \rightarrow CH_3OH$$

Other carbon sources for the gasification process are coal or biomass.

Another promising approach for methanol synthesis is the direct or indirect use of carbon dioxide with hydrogen:

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$
$$CO_2 \rightarrow CO + \frac{1}{2}\ O_2$$
$$CO + 2H_2 \rightarrow CH_3OH$$

Besides methanol production from CO_2 and hydrogen it is also possible to generate methanol biotechnologically from biomass reformation or microbiological fermentation.

2.1 CO_2-capturing

In general there are three possible sources for the accumulation of CO_2: from the air, from sea- or other surface-waters and from industrial point sources.

On the one hand the adsorption of CO_2 from natural sources, especially from the atmosphere, depicts a promising method for lowering the concentrations of the harmful greenhouse gas but on the other hand, the comparatively low CO_2 content (currently ca. 380 ppm in atmospheric air as annual mean) makes an effective adsorption very difficult. [1] A higher CO_2-output can be reached with the more established methods of CO_2-capturing from industrial sources. These methods are restricted to a local application at fossil fuel combustion plants, however, most of which are far from places with optimal solar irradiation. All processes have in common that high energy amounts are necessary for the concentration of CO_2. **Fehler! Verweisquelle konnte nicht gefunden werden.** gives an overview of the most common techniques for CO_2 capturing, including artificial trees and carbon capture and storage (CCS) techniques.

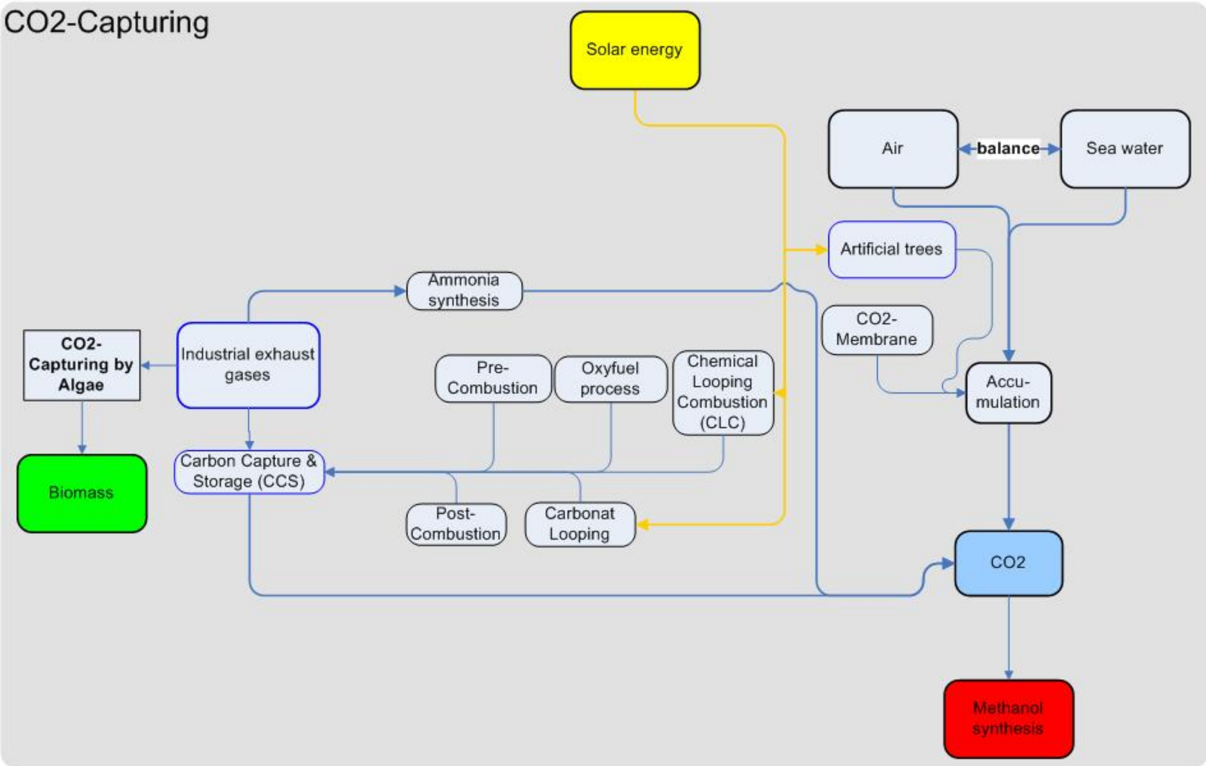

Figure 1: CO_2-Capturing.

2.2 H_2 / synthesis gas

In most processes for the conversion of CO_2 to methanol that are currently under investigation, hydrogen is used as a reactant. To provide hydrogen, according to the projects agenda, by use of solar energy, in principle three possible reaction pathways exist in which water is dissociated into oxygen and hydrogen: solar thermolysis, solar electrolysis and thermochemical cycles, using metal oxides or sulfuric acid. [2]

It is also possible to convert and energetically upgrade carbonaceous fossil fuels by means of solar energy to hydrogen or synthesis gas, accordingly. This can be achieved for example by reformation of methane, which is actually an intermediate step for the production of products like methanol or ammonia. [3] In solar reformation we distinguish between steam reformation and dry reformation, using CO_2 as reactant. Other “fossil” techniques for hydrogen/syngas production are solarthermal cracking of methane or solar degasification of solid fossil sources, like e.g. biomass or charcoal. [4]

2.3 Biotechnological techniques for methanol synthesis

As already mentioned in Chapter 2.2, an alternative route on the way solar methanol synthesis is using solid carbonaceous sources like biomass. The most classical approaches would be the processes of syngas production (gasification, pyrolysis) mentioned above.

Furthermore, biomass, in particular algae, can also be used for CO_2-capturing. In a newly developed technique, industrial exhaust gas is fed into large biomass production tanks, filled with a microalgae-suspension, where the CO_2 is utilized by the algae as carbon source. The so produced biomass can be further processed for the production of biofuels. [5], [6]

By the use of special microorganisms it is also possible to generate methanol directly from biomass. Classical fermentation of biomass or the newly developed Helioculture process appear to be promising alternatives, but still demand further research. [7]

An overview of the biotechnological processes is given in Figure 2.

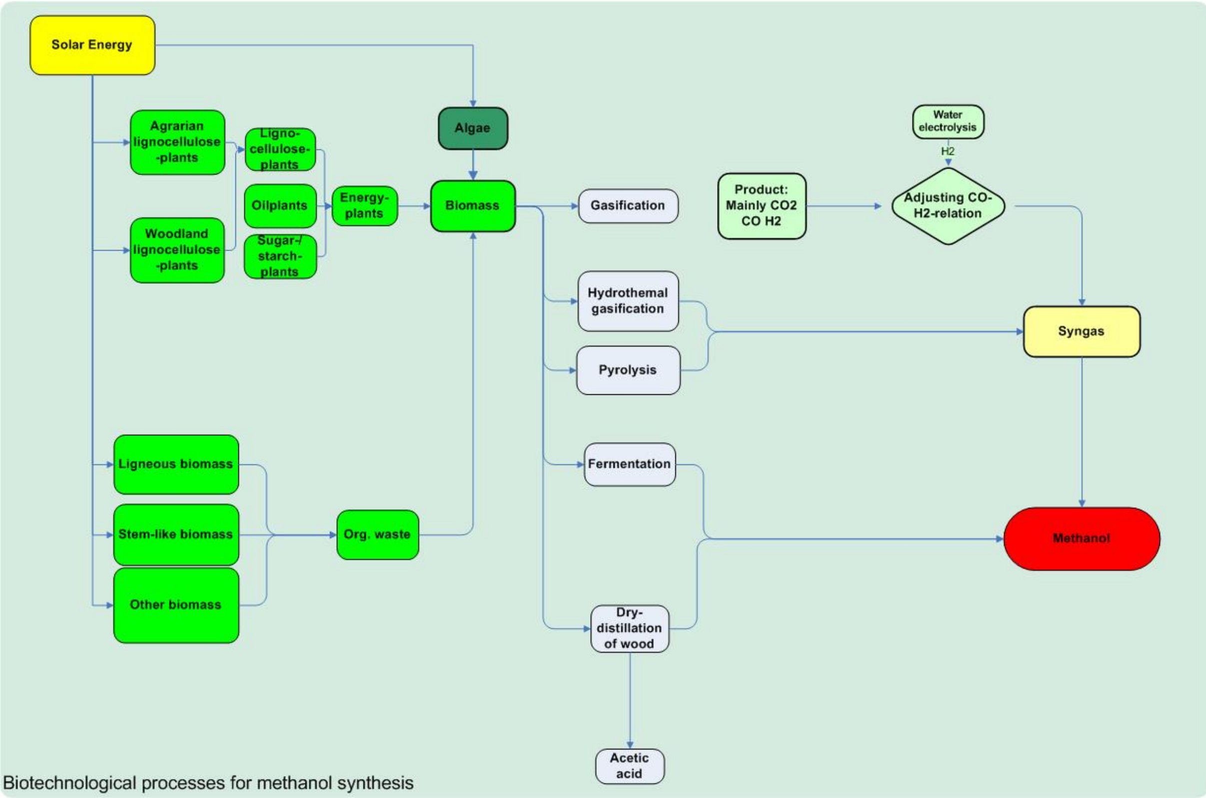

Figure 2: Biotechnological processes for methanol synthesis.

2.4 Integration of solar energy

Many of the processes presented in the previous chapters allow for the integration of solar energy. For example, in CO_2-capturing, the endothermic regeneration of absorption solution from artificial trees could be performed by solar technology. Most of the processes for hydrogen synthesis are already designed for solar operation. During the last years, many solar reactors for hydrogen and syngas production, using direct or indirect concentrated solar irradiation, have been developed, like e.g. vortex reactors, volumetric reactors or tubular reactors.

A completely different approach of solar methanol synthesis that is also accounted in our project is the use of special spectra of the visible sunlight in low-temperature processes like photochemical catalysis.

3 Further Steps

The first part of our project was a general literature research about all possible processes and sub-process involved in solar methanol synthesis from CO_2.

The upcoming steps include detailed analysis about the possibilities of solarisation of different process steps, the conduction of small and technical scale experiments for the analysis of photochemical and thermochemical reaction pathways, as well as the modelling of economic scenarios for a feasible solar methanol production based on information about possible location sites, meteorological influences and capital and operating costs. A list of several criteria will be generated to compare and evaluate different processes. Such criteria are capital and operational costs, cost effectiveness, resource productivity, technical maturity and scalability.

Acknowledgement

SolMethCO2 is a Ziel-2 project of the EU co-funded by the Ministry of Innovation of Northrhine Westphalia.

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