

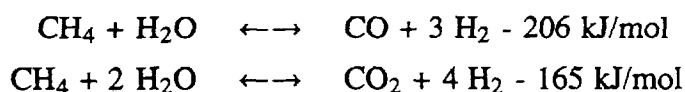
Appendix B

CHEMICAL ENERGY TRANSMISSION SYSTEMS

B.1. STEAM REFORMING SYSTEM (EVA/ADAM)

Within the project "Nukleare Fernenergie" (NFE) (= "Nuclear Long-Distance Energy"), the energy transport system by **natural gas steam reforming / methanation** was theoretically and experimentally investigated at the Research Center Jülich in Germany. Its goal was to demonstrate the operation of a complete helium-heated system for steam reforming of methane on a representative scale and to demonstrate the technical performance and efficiency of a thermochemical pipeline system [5]. Fig. B-1 shows a schematic of this long-distance energy transportation system. The heat source was an electric heater simulating HTGR conditions.

In 1972, the first experimental setup, the so-called EVA ("Einzelspaltrohr-Versuchs-Anlage" = "Single Tube Test Facility") was established to account for the endothermal reforming reactions:



The tube with a variable length of 10 - 15 m and a variable inner diameter of 100 - 150 mm was entered at the bottom by helium of 950 °C which flowed upwards in an annulus at the outside providing heat to the reformer tube inside. The feed gas methane was heated up in a counter current flow and reached a temperature of 825 °C at the tube bottom. The resulting product gas was then cooled down by flowing upwards again through return pipes inside the reformer tube (internal pigtails). The temperature profiles in the EVA system are shown in Fig. B-2, left hand side.

The construction of a follow-up reformer test stand, EVA-II, was started in 1980. EVA-II consisted of a bundle of 30 reforming tubes based on the baffle plate design with an inner/outer diameter of 100/120 mm and a length of 11.4 m. Helium throughput was 4 kg/s. The other components of this helium loop besides the 10 MW electric heater were a hot gas duct, steam generator, and helium circulator. Methane input was 0.6 kg/s. The product gas was generated at a rate of 4400 kg/h.

The reverse process of methanation was realized in 1979 in the test facility ADAM ("Anlage mit drei adiabaten Methanisierungsreaktoren" = "Facility with three adiabatic methanation reactors"). A three-stage methanation reaction including a dilution of the product gas by feedback of already retransformed gas was chosen to mitigate the large heat release, to minimize soot formation, and to maximize CH₄ output. The feed gas was synthesis gas at a rate of 600 Nm³/h in ADAM-I and 9600 Nm³/h in ADAM-II [6].

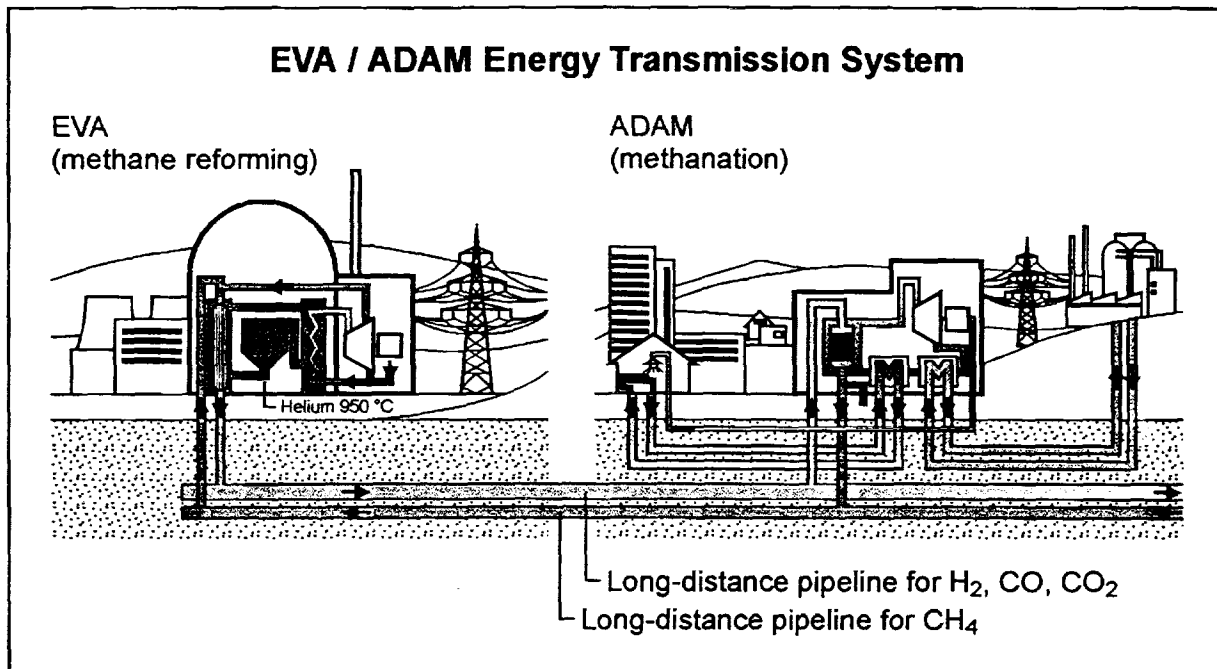


Fig. B-1: Schematic of long-distance energy transportation in the EVA/ADAM facility, from [1]

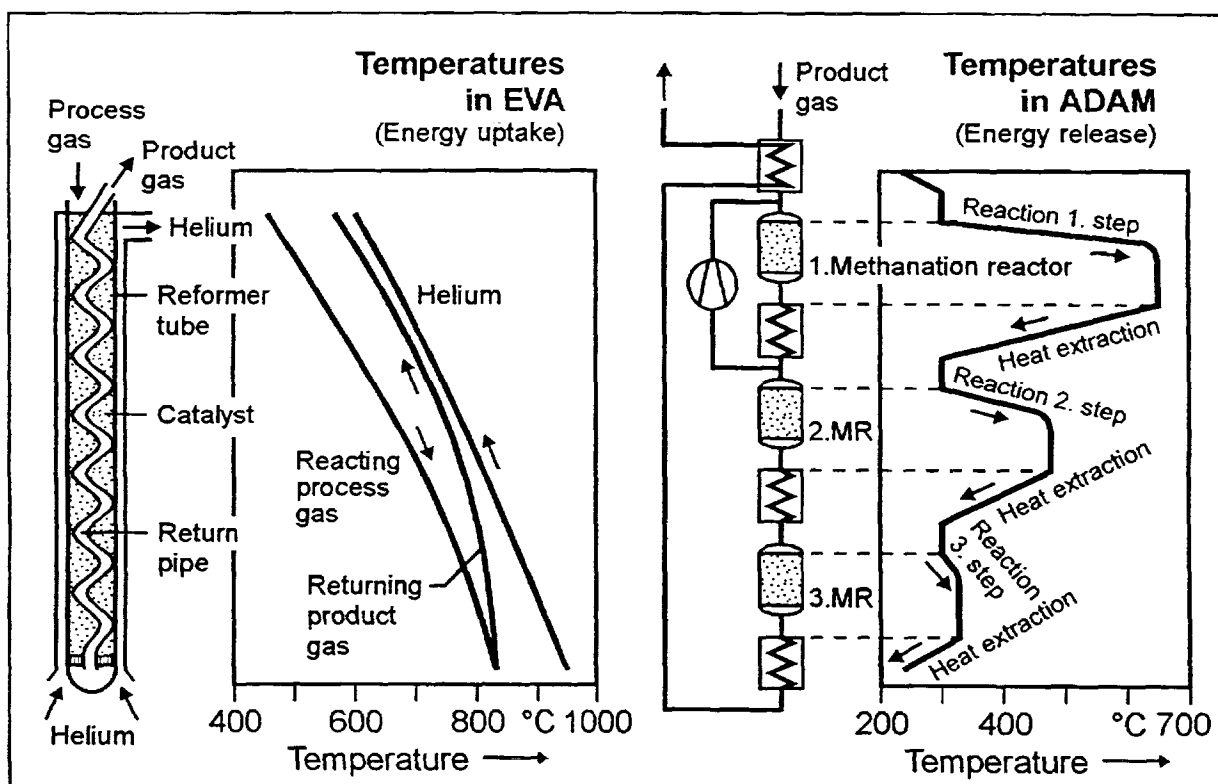


Fig. B-2: Temperature behavior in the methane reformer EVA (left) and in the methanation system ADAM (right), from [1]

The two significant features of the ADAM plant were the complete reconversion to methane, thus releasing the complete reaction enthalpy again and the realization of a 650 °C gas mixture after the first methanation step which allowed for the generation of

superheated high-pressure steam for further use (here added to the heating system of the Research Center Jülich). The temperature profiles in the ADAM system are shown in Fig. B-2, right hand side [1].

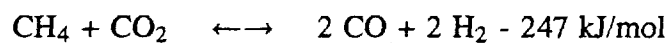
The complete EVA-II / ADAM-II system was operated in Jülich for a total time of 10,150 hours. It has demonstrated for the first time the chemical cycle process under the realistic conditions of industrial application with a transported power of 300 kW (EVA / ADAM) and of 5.4 MW (EVA-II / ADAM-II), respectively. The test facilities, however, were not operated for the sake of maximizing the energy efficiency, they were rather used to examine the components' behavior under various load conditions including fast transients [1, 5, 6].

The CH₄ - H₂O system needs a second return pipe from ADAM to EVA for the liquid water, if a cleanup of the water and the loss of unconverted hydrocarbons are to be avoided [4].

The EVA / ADAM system has been established, besides in Germany, also in the USA and the Russian Federation [9].

B.2. CO₂ REFORMING SYSTEM

The CO₂ reforming process of methane



has been studied as a chemical heat pipe system since 1980 as an alternative in order to overcome some of the potential difficulties. In contrast to the CH₄ - H₂O system, a third pipe is not required since it is not necessary to clean the water. Thus an open cycle system could be adopted [4].

At the Weizmann Institute in Israel, the closed-cycle CO₂ reforming process of natural gas has been adapted and modified to solar energy as the primary heat input. The use of gaseous CO₂ eases the daily startup / shutdown cycles. A lab-scale facility with 5 - 10 kW power was successfully operated. A scale-up plant designed for 480 kW heat input to the reforming reaction and 250 kW heat output in the methanation step is being tested since 1994. Catalysts are rhodium and ruthenium. So far 150 cycles have been completed [3]. The solar power absorbed was 97 kW, a methane conversion rate of 70 % maximum was achieved. A computer code has been developed for loop design and optimization purposes [9].

B.3. METHANOL SYSTEM

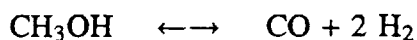
The production of energy alcohol on the basis of biomass plus CO₂-free primary energy features a CO₂-neutral system since the CO₂ release upon combustion of methanol has been formerly extracted from the atmosphere for the biomass production.

The methanol-carbon dioxide system is described by

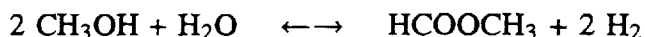


The heat released during the methanol synthesis corresponds to not more than 15 % of the energy stored in the hydrogen. If, however, this heat can be fed into the reforming process, a high storage efficiency could be gained. No additional CO₂ is emitted, if atmospheric CO₂ is used as the carbon source.

The nuclear variant of using CH₃OH as the energy carrier taking the HTGR as the primary source for the required process heat is being described in section 4.3.2.3. Congenial systems are the methanol-carbon monoxide system



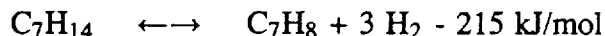
and the methanol-methyl formate (= formic acid salt) system:



B.4. METHYLCYCLOHEXANE - TOLUENE SYSTEM

Among the many candidates of hydrogen transportation or seasonal storage methods, the H₂ evolution from cyclohexanes at the demand site and the reverse reaction, the hydrogenation of benzene, at the supply site offers the advantages of safe and commonly used transport at ambient temperature in chemical tank ships or trucks and mild reaction conditions. Cyclohexanes have a hydrogen density and content comparable with metal hydrides [8]. Methylcyclohexane is the choice of preference, since unlike benzene, toluene is not carcinogenic.

The **methylcyclohexane (MCH) cycle** is described by:



The hydrogen storage capacity of MCH is 6.2 wt%. Dehydrogenation at 1 MPa is an endothermal catalytic reforming step with a high yield of toluene (98 %) at elevated temperatures (> 400 °C). A critical point is the initial conditioning and regeneration of the catalyst. The process conditions of the hydrogenation of the toluene are 2 MPa at 220 °C achieving a yield of 99 % [2]. A comparison of the MCH vector with the LH₂ vector has been made within the frame of the Euro-Quebec project. Characteristics of the LH₂ and the MCH vectors are listed in Table B-1.

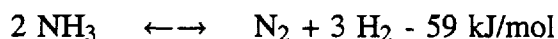
Table B-1: Characteristics of the two vectors investigated in the EQHHPP, from [10]

Liquid Hydrogen	Methylcyclohexane / Toluene
No hydrocarbons involved during production and utilization	Hydrocarbons involved due to conversion limitations
Low environmental impact upon inadvertant release	High environmental impact upon inadvertant release
Use as liquid or gaseous fuel	Use as gaseous fuel only
Sophisticated transport technology not yet commercially available	Conventional transport in chemical tank ships
Limited storage period	Unlimited storage period
Part of liquefaction energy can be recovered	Energy needed for dehydrogenation

Long-term storage of energy by means of MCH is reasonable in cases where the energy structure results in a large cost difference of seasonal electricity production (e.g., hydro, solar).

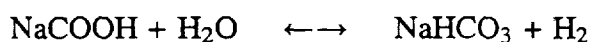
B.5. NH₃ SYSTEM

The ammonia dissociation reaction as a closed-cycle liquid hydride energy storage system has been investigated primarily by Australian researchers in connection with solar primary energy [7]:



The advantage of the above process is the complete absence of any side reactions. The relatively low exothermal reaction rates can be raised, if higher pressures are applied. The fact that ammonia condenses at around room temperature and separates from the reactant mixture allows storage of feedstock for both endothermal and exothermal reaction in the same vessel. Experience with a pilot plant operating at pressures up to 16 MPa and temperatures up to 720 °C indicate a 1 kW closed-loop system to be feasible [7].

A hydrogen storage system using formates seems to be promising. The reversible catalytic reaction with sodium formate to decompose to bicarbonate and hydrogen is



The hydrogen capacity is 2.9 wt%. Its advantages are cheap raw materials and the potential of storing H₂ in solid form [11].

REFERENCES TO APPENDIX B

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