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16. Abstract (Limit: 200 Words)

The performance of a solar chemical heat pipe was studied using CO_2 reforming of methane as the vehicle for storage and transport of solar energy. The endothermic reforming reaction was carried out in an Inconel reactor , packed with a Rh catalyst. The reactor was suspended in an insulated box receiver which was placed in the focal plane of the Schaeffer Solar Furnace of the Weizmann Institute of Science. The exothermic methanation reaction was run in a 6-stage adiabatic reactor filled with the same Rh catalyst. Conversions of over 80% were achieved for both reactions. In the closed loop mode the products from the reformer and from the methanator were compressed into separate storage tanks. The two reactions were run either separately or "on-line". The complete process was repeated for over 60 cycles. The overall performance of the closed loop was quite satisfactory and scale-up work is in progress in the Solar Tower.

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SOLAR CHEMICAL HEAT PIPE

STORAGE AND TRANSPORT OF SOLAR ENERGY.

by

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1. Introduction.

The main problem with wide spread use of solar energy is that it is intermittent in nature and it is not evenly distributed around the world. Therefore, a method has to be developed for the efficient storage and transport of solar energy. Such a method can be the solar chemical heat pipe.

The basic principle behind the chemical heat pipe concept is demonstrated in Figure 1. The method is based on carrying out a highly endothermic reaction, at the site where energy is available, cooling the products to ambient temperatures, for storage and transport, and releasing the heat at the consumer site by the reverse exothermic reaction. The original products are recovered and transferred back to the energy site for recycling. The whole process is carried out in a closed loop, and therefore it is environmentally clean as no CO_2 or any other polluting gases are discharged into the atmosphere.

The process originated in KFA, Julich (Ref.14), for transport of nuclear energy. It was scaled up to a size of 10 MW and the necessary technical and economical information is available for erection of industrial plants receiving their energy from a high temperature nuclear reactor.

The DLR and the Spanish groups (ref.15) are using the same method in the solar tower in Almeria, only instead of an HTGR they are using concentrated solar energy. Air is heated by the sun to 1000° C and this air is used to heat up the reformer. The process is backed up by fossil fuel, so that in fact only a fraction of the total energy is from the sun. In this way they circumvented the problem of the intermittency and variability of the available solar energy.

However, if we want to use the sun as our only source of energy we have to change our working system so that it can operate under non-steay state conditions and can be stopped at night and restarted in the morning. We therefore, began our work with laboratory studies in order to find a catalyst that can withstand such conditions.

2. Laboratory studies.

The reaction used by KFA was the steam reforming of methane:

$$CH_4 + H_2O = 3H_2 + CO \qquad \Delta H = 205 \text{ KJ/mole}$$

A three molar excess of water has to be used in this process in order to avoid carbon deposition. This means that the heat of vaporization of this water has to be supplied and this lowers the total energy efficiency. Moreover, as the water gas shift reaction is always present at equilibrium, CO_2 is always present in large quantities.

We therefore chose to work with CO_2 reforming of methane:

$$CH_4 + CO_2 = 2H_2 + 2CO \qquad \Delta H = 250 \text{ KJ/mole}$$

with only a small excess of CO_2 present and therefore the amount of water formed by the water gas shift reaction, remains in the gas phase. A detailed discussions of the reasons is given in Ref. 1 and App. 1.

Normally, in industrial catalytic processes, working conditions have to be very well controlled and maintained constant during the process. However, when using an intermittent energy source such as the sun, it is obvious that the conditions change during the day and the process has to be started in the morning and stopped at night. We had, therefore, to find a catalyst that can be operated under such non steady-state conditions. We carried out a thorough study in the laboratory and after screening a large number of possible catalysts we chose Rh on alumina, produced by the Engelhard Corporation, as the best candidate (Ref 1,2 App. 1,2). The kinetics of the catalyst for both the reforming and the methanation reactions was studied under a variety of conditions and kinetic equations were derived (App. 14). A 500 w laboratory unit was built for the study of the the long term performance of the catalyst. In this system the reforming and the methanation reactions were first studied separately. Then the reforming products were introduced into the methanator and finally the loop was closed and the same gases were repeatedly cycled in the two reactors. As many as 1100 cycles were performed in one of the series of runs, with the same initial gas mixture. This is equivalent to daily working cycles for a period of three years (Ref. 5 and App. 5). Following the laboratory work it was possible to proceed with experiments under real conditions using the concentrated solar beam from the solar furnace.

3. Solar Reforming.

As stated above, the solar reforming under study in Almeria, uses an indirect approach whereby the heat is transferred to the reactor by air which is heated in the solar tower. In this way the receiver is decoupled from the reactor and each part can be designed separately. This concept has some advantage. However, in order to increase the overall efficiency of the process we have decided to integrate both parts of the system into one unit, and use sodium as the heat transfer agent instead of air. This experiment was then followed by work on a tubular reactor directly heated by the concentrated solar beam and the a reactor where the catalyst was directly irradiated.

3A. Integrated sodium reflux heat pipe receiver/reactor.

The integrated receiver/reactor uses a sodium pipe for absorbing the solar energy and transferring it to the reactor tubes. The main advantage of this method is that sodium metal has excellent heat transfer characteristics and it can supply as much heat as required, to every part of the reactor, while maintaining a uniform temperature on the reactor walls. The reactor was built in SANDIA, Albuquerque, as part of a joint project with J.D. Fish and R.B. Diver from the U.S. Department of Energy and J.T. Richardson, from the University of Houston. It performed well and as much as 8 KW power were absorbed into the reactor. This was the first time that a sodium reflux receiver/reactor was ever operated under solar conditions. A full description of the experiments are given in Ref. 4,8 and in App. 4,8.

3B. Directly heated tubular reactor.

We then tried to eliminate the heat transfer agent by heating the reactor tubes directly. The first reactor studied was an Inconel U-tube placed in the center of a horizontal tubular receiver. The results of the experimental work and the theoretical modelling can be found in Refs. 2,3,6 and App. 2,3,6. The disadvantage of the above set up was that the temperature of the part of the reactor tube facing the solar beam was too high for the Inconel metal. We therefore built a vertical reactor suspended in an insulated receiver. With this reactor we could get a fairly good temperature profile and we could reach absorption of over 8 KW power. The conversions were between 80 and 90% when proper conditions were maintained. An improved simulation model was developed. The experimental and calculated results showed fairly good agreement (Ref. 9,12 and App. 9,12). This reactor was used in the closed loop experiments to be discussed below.

3C. Direct solar irradiation of the catalyst.

A third mode of energy transfer studied is the direct illumination of the catalyst through a transparent quartz window, thus eliminating heat transfer through the wall of the reactor. As in a catalytic process the reaction takes place on the surface of the catalyst, it is reasonable to assume that direct illumination by the concentrated solar beam will result in higher overall efficiency of the system. We have done some preliminary work in this direction. The first such volumetric reactor was built with a sapphire window. The results of these experiments were reported in Ref. 7 and App. 7. A theoretical approach can be seen in Ref. 6 and App. 6,15. We have since then tested a number of other reactors, using a quartz window to protect the reactants from the environment. We have used ceramic foams as well as ceramic honeycombs as supports for the Rh catalyst. So far we have reached absorption of as much as 6.5 KW power and reaction rates higher than those measured with the Inconnel reactor by a factor of almost 10. These high rates are probably due to the high temperature at the reaction site. However, part of this may be attributed to photochemical enhancement, if the species adsorbed on the catalyst surface have different light absorption characteristics. The results are summarized in Ref. 13 and App. 13.

4. Methanation.

The exothermic part of the SCHP is the methanation where synthesis gas is transformed back into CH_4 and CO_2, and the heat released is delivered to the consumer.

As discussed above, laboratory experiments have shown that the rhodium catalyst can be used for both the reforming and the methanation. It was also shown that it can withstand the high temperatures reached in the first step of the methanation. There was some difficulty with possible carbon deposition at the early stages and it was realized that small amounts of water can stabilize the system and also help in the heat transfer avoiding development of very high temperatures locally. The water does not change the final product composition of the circulating mixture,when operating in a closed loop, as the excess water is condensed.

Three experimental methanators were constructed:
1. A single stage variable temperature methanator,
2. A 4-stage methanator,
3. A 6-stage adiabatic methanator.

The performance of each one was evaluated and they were all used in the closed loop operation. A detailed description of the systems and their operation is given in Appendix 17.

A computer model was written for the calculation of the temperatures and compositions of the product gases in the multistage methanator. This was done assuming enough catalyst is present in each stage in order to arrive at equilibrium concentrations. This assumptions will generally be correct as it is desirable to arrive at equilibrium concentrations in order not to recirculate inactive gases. The computer model is described in detail in Appendix 16. Comparison with actual experiments in the 6-stage methanator show fairly good agreement (Appendix 17).

5. Closed loop operation of the SCHP.

For the closed loop operation we chose to work with the vertical Inconel reactor. All three methanators described above were tested at different stages. The combined system with the flow controllers, the compressor and the storage cylinders is shown schematically in Figure 2. Two procedures were followed, one was separate reforming and methanation and the other was on line operation of both. In the first, solar reforming was carried out for a number of hours, while compressing the products into the storage cylinders. The stored synthesis gas was then used for the methanation. The products of the methanation, mainly methane and carbon dioxide, were compressed and stored in different cylinders and then used in the next reforming cycle. In most cases the conversions were kept at a level of 80-90%. In order to maintain a constant composition of the reforming products under changing insolation conditions, the flow of reactants was automatically controlled. In the second mode of operation, the products of the reformer were directly fed into the methanator and the products of the latter were compressed and stored. They were later used as feed for the reformer in the next loop. This is an accelerated mode of operation, where 5-6 loops can be carried out in a single day.

The closed loop was operated, so far, for over 60 cycles with the same initial gas mixture, giving very satisfactory results and no signs of changes in composition or carbon deposition. To the best of our knowledge, this is the first time that such a closed loop was operated under real conditions in a solar environment. The complete system underwent rigorous tests for start-up and shut-down regimes as well as for short and long cloud periods, in order to supply all the information needed for the scale-up work.

Part of the work is included in Ref. 10,11 and App. 10,11 and a complete report is presented in Appendix 18. A complete list of interim group reports, summarizing all the experimental data and giving extended discussions of the results, is given in Appendix 20. All the data, tables and graphs are also saved on computer diskettes.

6. A 100 KW modular dish reformer.

The scale up plans at the Institute are for a 400 KW unit to be operated at the solar tower. The methanator was already constructed and tested. The reformer will be a tubular reformer in an insulated receiver, similar to the one tried successfully in the solar furnace. It is expected to be operational within a year and it will supply the technical data for an economic evaluation of an industrial size SCHP.

Another possible scale up approach is the gradual build-up of an array of parabolic dishes according to needs and availability of funds. A preliminary design of a 100 KW tubular reformer to be mounted on a 150 KW parabolic dish is shown in Appendix 19. It consists of 8 inconel tubes arranged in a symmetrical array, and filled with Rh catalyst. The computer model developed is based on the results obtained with the single vertical tube. It shows that conversions of over 80% can be reached while still maintaining the inconel wall temperatures below 1000° C. Such a dish reformer is modular. It can be connected to a large methanator and a number of dishes can be hooked up to the same methanator according to the desired expansion.

It is believed that such a closed loop solar chemical heat pipe should be erected in the Negev desert, for example in the demonstration site in Sde Boker. If reliable and efficient performance can be demonstrated, it will convince potential users that solar energy can be considered as a real possible alternative to fossil fuels.

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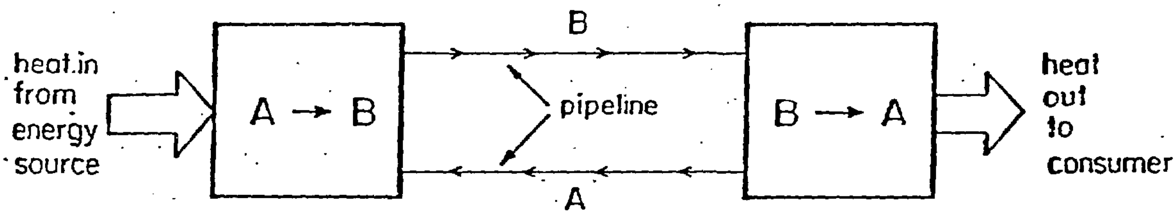

Figure 1. Diagram of the chemical heat pipe concept.

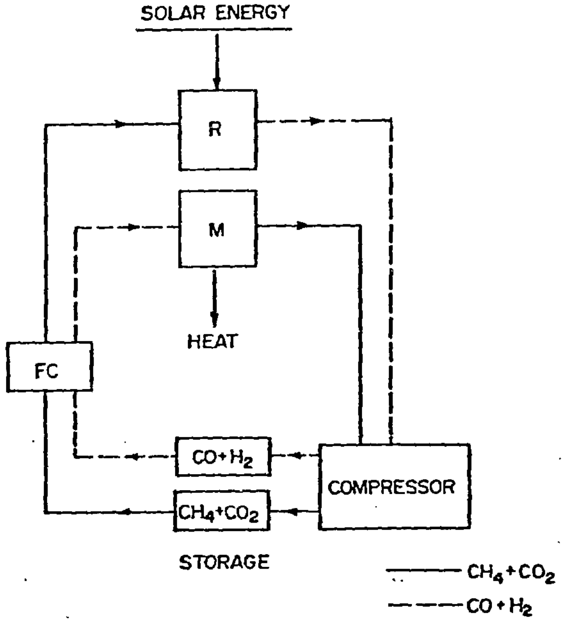

Figure 2. Diagram of the closed loop solar chemical heat pipe.