22
10/3/77
25 copy to WDS

MASTER

UCID- 17590

Lawrence Livermore Laboratory

A Proposal To Utilize Fusion Reactor Energy Sources
For Chemical Process Applications

Oscar H. Krikorian

September 22, 1977

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the laboratory.

Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A Proposal To Utilize Fusion Reactor Energy Sources
For Chemical Process Applications

Oscar H. Krikorian

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ABSTRACT

We propose to study the utilization of high temperature (~ 2000 - 2500 K) process heat from fusion reactors for large-scale chemical process applications. Of particular interest is the decomposition reaction, $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$, which at 2500 K should yield $\sim 60\%$ conversion to CO if O_2 is partially removed through an oxide membrane. Hydrogen can be derived from CO at lower temperatures by reacting CO with steam, and C can also be derived from CO by a disproportionation into C and CO_2 at ~ 1000 K. These chemicals, CO, H_2 , and C, form the basis for a multitude of non-electrical energy applications in the areas of transportation, industrial processes, and residential and commercial uses. In addition to the CO_2 decomposition process, we propose to explore a variety of ideas and evaluate them for scientific and economic merit. A follow-on research and development program will be proposed if the ideas prove promising.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED EB

INTRODUCTION

Only about 25% of the Nation's energy is used for electrical power generation. The balance is utilized mainly for transportation, industrial processes, and for the non-electrical part of residential and commercial uses (e.g., space heating). In view of these large energy needs in the non-electrical area, we propose to undertake exploratory studies to examine the potential applications of MFE to this area, using as a specific example a mirror reactor with its cylindrical blanket. If the studies prove to be sufficiently promising, we expect to subsequently propose a development program.

Briefly, some non-electrical energy options that might be derived from MFE, options that are essentially chemical processing in nature, are as follows: First, in the transportation area, we can consider: (1) production of alternate fuels such as hydrogen or methanol; (2) the economic upgrading of gasoline production by using neutron radiation to catalyze hydrogenation of petroleum, coal, and oil shale; and (3) large-scale production of metals (e.g., Li or Ca) to be used in batteries for electric vehicle transportation. Second, in the industrial area, the production of metals and chemicals are of major concern. Large quantities of carbon (coke) and hydrogen are needed for such processes as reduction of iron ore, production of ammonia, etc. Finally, in the residential and commercial area, space heating and cooling are major energy consumers. Chemical means for energy transport (e.g., chemical heat pipe) and methods for energy storage also need to be considered for this area.

We can expect to attain the best performance for chemical applications of MFE by emphasizing the unique features of MFE reactors that present special advantages for the needed applications. Thus, the two features of mirror reactors that are particularly advantageous as compared to other energy sources are: (1) the accessibility of a substantial volume in the blanket region for chemical processing, and (2) the potential for generating high temperature (~ 2000 - 2500 K) process heat. The availability of process heat at such high temperatures indeed opens up vast new vistas! We can now consider utilizing a much broader range of chemical processes for attaining higher process efficiencies. Higher temperatures are not without problems, however, especially in the areas of materials for construction, containment and insulation. A greater use will need to be made of ceramic type materials, and designs that emphasize compressive rather than tensile loadings will need to be introduced.

The potential areas of chemical applications will be discussed next. Chemical production will be discussed first, with an emphasis on hydrogen production. Brief discussions of energy transport and energy storage will then follow.

Chemical Production

The most obvious non-electrical application of MFE is the production of hydrogen from water for use in a "hydrogen economy". Such an approach could eventually provide hydrogen as a pollution-free and renewable resource that could make us independent of fossil fuels. If hydrogen can be produced at sufficiently low cost, the multitude and flexibility of its uses in meeting the Nation's energy needs, even in the near future, can hardly be overemphasized: chemical feedstocks for producing NH_3 , CH_3OH , CH_4 and other chemicals or fuels, iron ore reduction, hydrogenation of fossil fuels such as petroleum, coal, and oil shale; for energy storage (e.g., as Fe-Ti hydride); for energy transport by pipeline; and even for electrical power generation in fuel cells.

We believe that the best potential for efficient and economical production of hydrogen from water lies in utilizing high temperature thermochemical cycles. Of course, new specific cycles would have to be developed to match the available temperatures and heat source designs. Development studies on thermochemical cycles at our Laboratory,⁽¹⁾ as well as at General Atomics⁽²⁾ and Westinghouse⁽³⁾ have shown that overall thermal efficiencies of 40-50% (for conversion of heat to chemical energy in the form of hydrogen) can be achieved using HTGR or VHTR heat sources at $\sim 1200\text{K}$. Cycle efficiencies are expected to increase with increasing temperature, both because of higher Carnot efficiencies and because fewer and simpler process steps are expected at higher temperatures. Although explicit efficiency figures can not be stated until specific cycles are developed and analysed, we believe that it is reasonable to expect cycle efficiencies of 60-70% for heat source temperatures of $\sim 2000\text{K}$.

From an economics standpoint, some rough comparisons can be made between thermochemical cycles based on HTGR and MFE heat sources. Assuming basic heat costs of about $\$1.25/\text{GJ}$ for an HTGR at 1200K and $\$4/\text{GJ}$ for an MFE reactor at 2000K , and assuming 45% and 70% overall thermal efficiencies, respectively, for the cycles, gives total heat source costs of about $\$2.80$ and $\$5.70/\text{GJ}$, respectively, for heating value of the hydrogen produced. To these costs must be added the cost of the chemical plants. For the HTGR cycles, chemical plant costs add about $8-10\$/\text{GJ}$ for a total cost of about $11-13\$/\text{GJ}$ for hydrogen. For MFE cycles, due to the simpler nature of the cycles and the higher efficiencies, chemical plant costs should be substantially reduced. A cost of $\sim \$3/\text{GJ}$ for a chemical plant may not be unreasonable, leading to a hydrogen production cost of about $8-9\$/\text{GJ}$. Although absolute values of these costs are not accurate, the indicated trends are significant; and we expect that the trade off in lower chemical plant costs for an MFE cycle should more than compensate for its higher energy costs.

In addition to hydrogen production, production of CO and C are needed to provide basic chemical feedstocks for the large-scale production of industrially important chemicals. For example. CO may be reacted with

H₂ to produce methane (a fuel) or methanol (an important commercial solvent). Further, methanol may be oxidized to form formaldehyde, an important starting material for many plastics. Carbon would have application in production of metals from ores, or in production of CaC₂ and, hence, acetylene. Carbon can also be used as a sulfur-free coal substitute. Considering the Nation's trend toward large-scale conversion to coal utilization, this may provide an economic option to industrial firms with coal oriented facilities.

Catalysis of chemical reactions by MFE neutrons may be important in certain chemical processes, and we would like to take an exploratory look at possible applications. Other forms of radiation induced by neutrons may provide radiation that is even more specific to particular reactions and also needs to be considered. We feel that the major area for application would be for catalysis of the hydrogenation of fossil fuels; i.e., coal liquification, coal conversion to methane, and cracking of petroleum. Considering the large quantities of hydrocarbons that we use, even small gains here in yields or kinetics may have a significant impact on the Nation's economy.

Energy Transport

For energy transport, in addition to the more conventional approach of pipelining of gases and liquids, we need to consider: (1) chemical heat pipes, and (2) pipeline transport of solids (e.g., carbon slurries).

The EVA-ADAM chemical heat pipe has been under study in West Germany in conjunction with an HTR heat source.⁽⁴⁾ This concept involves energy pickup at the reactor using the endothermic reaction of CH₄ with H₂O to produce CO and H₂. The CO/H₂ gas mixture is then transported by pipeline to the region of use and combined in an exothermic reaction in the presence of a catalyst to form CH₄ and H₂O and provide heat for process applications. The product gases are then returned through a separate pipeline to the reactor. The EVA-ADAM process can also be considered for an MFE heat source. The decomposition of SO₃ to SO₂ presents yet another alternative.

These are both relatively low temperature decomposition processes, however (~ 1100K), and higher temperature processes need to be explored to increase the energy density of transport. A CO₂ decomposition carried out at ~ 2000-2500K, where O₂ is removed at temperature through an oxide filter, presents an opportunity for an improved process. The CO can be transported by pipeline and oxidized at the other end for process heat. The CO₂ can then be returned to the MFE reactor. A variation on this approach may be to convert CO to carbon black and CO₂ at ~ 1000K; i.e., $2\text{CO} \rightarrow \text{C(s)} + \text{CO}_2$. The carbon black can then be transported by pipeline as a slurry. It seems worthwhile to consider yet other chemical systems for a chemical heat pipe approach.

Energy Storage

In non-electrical energy storage, we need to consider: (1) basic chemical feedstocks that can be stored in high energy density forms, and (2) storage of heat at high temperatures. For the former case, the production and storage of hydrogen as hydrides (e.g., Fe-Ti hydride) and of carbon as carbon black are examples that can be mentioned. For the latter, we will need to examine eutectics of salts or other substances that are convenient to melt and contain, and have desirable heat transfer properties. Perhaps below ground storage may present advantages in inexpensive containment of such melts.

OBJECTIVES

Our general objective during the first year of study is to conduct exploratory paper studies to evaluate in a very preliminary way the scientific and economic potential of MFE as a heat source for non-electrical applications. The evaluation would include a delineation of those areas that show the best scientific and economic potential and would indicate the critical technical problems that will need to be resolved.

More specifically, we plan to conduct:

- Conceptual design studies of methods for extraction and utilization of high temperature process heat (preferably $T = 2000\text{-}2500\text{K}$) from a Tandem Mirror Reactor blanket.
- Chemical and chemical engineering concept development studies of processes for production of H_2 , CO, and C as chemical feedstocks.
- Development and evaluation of ideas for production of other chemicals, chemical reaction catalysis by neutrons, energy transport, and energy storage.

We anticipate that the initial year of study will result in promising areas for further study. We would therefore propose to follow up during the second and succeeding years with a program of experimentation, process design studies, and process development in the most promising areas.

TECHNICAL APPROACH

The technical approach as described here will be concerned with the first year of study. The approach is to conduct paper studies except possibly for occasional quick experiments designed to help define or clarify problem areas. Principal contributors are expected to be a high

temperature chemist and a chemical engineer working as a team, with some consulting from materials scientists, mechanical engineers, etc.

The general sequence of development of the study is expected to proceed as follows:

1. MFE Process Heat Generation
 - (a) in-situ
 - (b) out of reactor
2. Development of Ideas for Applications
3. Screening of Ideas
 - (a) scientific feasibility
 - (b) economic potential
4. Detailed Analysis of Best Ideas

We plan to issue a report summarizing our findings at the end of the fiscal year.

MFE Process Heat Generation

Our main goal here will be to see if process temperatures of 2000-2500K can be attained, since these temperatures offer the best potential for efficiently and cheaply producing hydrogen by thermochemical cycles or for producing CO by decomposition of CO_2 . We also plan to explore the lower temperature regime of $\sim 1200\text{-}2000\text{K}$. Both in-situ and out of reactor concepts will be considered in heat utilization. In-situ processes probably offer the best economic option if suitable processes (e.g., decomposition of CO_2) can be found. For out-of-reactor processes, heat will need to be removed in a high energy density form, since a high pressure circulating gas may not provide an adequate approach. Use of a pebble bed ($C_p\Delta T$), heat pipe (ΔH_{vap}), or chemical heat pipe (ΔH_{reac}) approaches may provide better alternatives.

Development of Ideas for Applications

We plan to systematically develop a number of ideas for applications. Some of the ideas that we will consider are: decomposition of water by thermochemical or high temperature electrolysis methods; decomposition of CO_2 ; production of chemicals and fuels such as C (substitute coal), CH_4 , CH_3OH , CH_2O , NH_3 , C_2H_2 , Fe, Li, and Ca; the neutron catalysed hydrogenation of coal liquification, methane formation from coal, gasoline from petroleum, etc.; use of chemical heat pipes for energy transport; and use of hydrides, carbon, etc., for energy storage.

Screening of Ideas

Ideas that appear promising will be further evaluated using simplified process design concepts. Scientific feasibility will be evaluated on the basis of calculated energy efficiencies, equilibrium constants, reaction rates, reaction yields, phase diagram information, solid state properties, etc. Estimates will be made where data is lacking. Engineering and process cost assessments will be concerned with such items as materials requirements and costs, difficulty of chemical separations, unusual power requirements, heat exchanger needs, large capital requirements, etc. Because of the brief nature of this initial analysis, most of the engineering evaluations will be qualitative in nature. Ideas will be ranked into general categories of priority of interest according to the above evaluations.

Detailed Analysis of Best Ideas

For the best ideas, scientific, engineering, and cost analyses will be carried out further. In particular, we plan to define the key issues or problem areas. As time permits, we will begin an evaluation of solutions to these problems, and may conduct some selected experiments to better define the problem areas.

The idea that we feel at the present time is the best idea is the in-situ process for decomposition of CO_2 in a Tandem Mirror Reactor. Some additional discussion may therefore be appropriate for this process.

Thermodynamic calculations show that the equilibrium constant for the reaction,

ranges from $10^{-2.8}$ to $10^{-1.4} (\text{atm})^{\frac{1}{2}}$ from 2000 to 2500K. If we assume a total gas pressure of 1 atm and further that the O_2 pressure can be lowered to 10^{-3} atm by diffusion through an oxide membrane, the CO yield is found to range from 5% at 2000K to 57% at 2500K. These are attractive yields for a CO recovery process.

As a tentative design for an in-situ process, we can assume that heat for the reaction is provided by a CaO stabilized ZrO_2 moderator in the form of a honeycomb-type stack of parallel tubes and heated to ~ 2000 -2500K. A CO_2 feed gas would be passed through certain of the passages and O_2 would be allowed to diffuse through the ZrO_2 walls into separate passages containing a sweep gas. The product mixture of CO_2 and CO with some residual O_2 would be removed from the reactor for further processing.

The CO can now be used in a number of optional ways. It can be reacted with steam by the Shift Process to produce hydrogen and CO_2 ,

thus, in essence, completing a thermochemical cycle for H_2O decomposition. Alternatively, CO can be separated from CO_2 by absorbing the CO_2 onto K_2CO_3 (or other commercial CO_2 absorbers). The CO can then be used as a feedstock for making various chemicals, or as a pipeline gas for a chemical heatpipe. Yet another approach is to disproportionate CO at $\sim 1000K$ to form carbon black as a product along with CO_2 .

A key problem in the in-situ process for CO_2 decomposition is the possible slowness of the permeation rate of O_2 through ceramic oxide membranes. This means that large permeation areas must be made available in the system design. Improvement of this situation may be achieved by: (1) improvement in the ceramic diffusion membrane to give higher permeation coefficients (i.e., materials with higher diffusion coefficients, or greater concentrations of the mobile species dissolved in the material), (2) fabrication techniques that can conveniently provide arrays of capillary tubes which increase the available surface area, and (3) improved strength or support schemes (e.g., thin ceramic layers on porous backings) that will allow thinner membranes or higher gas pressures to be used. It is clear in this key problem area that early experimentation will need to be conducted to evaluate the potential for solving this problem, and to define the best directions to take in pursuing a solution.

REFERENCES

1. Otsuki, H. H., Pearson, R. K., and Krikorian, O. H., "Recent Developments in the Engineering and Chemistry of the ZnSe Thermochemical Hydrogen Cycle", in Proceedings of the 12th Intersociety Energy Conversion Conference, August 28 - September 2, 1977, Washington, D.C., American Nuclear Soc., 1977
2. Schuster, J. R., et al., "Development of a Sulfur-Iodine Thermochemical Water-Splitting Cycle for Hydrogen Production", *ibid.*
3. Farbman, G. H., et al., "Development Progress on the Sulfur Cycle Water Decomposition System", *ibid.*
4. Harth, R. E. and Hoehlein, B., "Hydrogen Production Process by Means of Nuclear Energy", in Conference Proceedings - 1st World Hydrogen Energy Conference, 1-3 March 1976, Miami Beach, Florida University of Miami, 1976

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

NOTICE

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

Printed in the United States of America

Available from

National Technical Information Service

U.S. Department of Commerce

5285 Port Royal Road

Springfield, VA 22161

Price: Printed Copy \$: Microfiche \$3.00

Page Range	Domestic Price	Page Range	Domestic Price
001-025	\$ 3.50	326-350	10.00
026-050	4.00	351-375	10.50
051-075	4.50	376-400	10.75
076-100	5.00	401-425	11.00
101-125	5.50	426-450	11.75
126-150	6.00	451-475	12.00
151-175	6.75	476-500	12.50
176-200	7.50	501-525	12.75
201-225	7.75	526-550	13.00
226-250	8.00	551-575	13.50
251-275	9.00	576-600	13.75
276-300	9.25	601-up	*
301-325	9.75		

*Add \$2.50 for each additional 100 page increment from 601 to 1,000 pages; add \$4.50 for each additional 100 page increment over 1,000 pages.

Technical Information Department

LAWRENCE LIVERMORE LABORATORY

University of California | Livermore, California | 94550