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**PERFORMANCE AND COST OF ENERGY TRANSPORT AND STORAGE
SYSTEMS FOR DISH APPLICATIONS USING REVERSIBLE CHEMICAL
REACTIONS**

By
J. M. Schredder

October 15, 1984

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Jet Propulsion Laboratory
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Pasadena, California

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Performance and Cost of Energy Transport and Storage Systems for Dish Applications Using Reversible Chemical Reactions

J.M. Schredder

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ABSTRACT

The use of reversible chemical reactions for energy transport and storage for parabolic dish networks is considered. Performance and cost characteristics are estimated for systems using three reactions (sulfur-trioxide decomposition, steam reforming of methane, and carbon-dioxide reforming of methane). Systems are considered with and without storage, and in several energy-delivery configurations that give different profiles of energy delivered versus temperature. Cost estimates are derived assuming the use of metal components and of advanced ceramics. (The latter reduces the costs by three- to five-fold.) The process that led to the selection of the three reactions is described, and the effects of varying temperatures, pressures, and heat exchanger sizes are addressed.

A state-of-the-art survey was performed as part of this study. As a result of this survey, it appears that formidable technical risks exist for any attempt to implement the systems analyzed in this study, especially in the area of reactor design and performance. The behavior of all components and complete systems under thermal energy transients is very poorly understood. This study indicates that thermochemical storage systems that store reactants as liquids have efficiencies below 60%, which is in agreement with the findings of earlier investigators. The cost estimates for transport systems have been compared with estimates reported elsewhere for steam and molten-salt thermal energy transport. Based on this comparison, it appears unlikely that reversible-reaction transport will have a compelling advantage in the 427 to 510°C range. This study includes a reactor/heat-exchanger configuration that may, at increased cost, increase the delivery temperature to 790°C or above. In this temperature range, little data exist on thermal (sensible or latent heat) energy transport.

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FOREWORD

This report presents the results of a study undertaken during 1979-80 by the Jet Propulsion Laboratory to assess the feasibility of using reversible chemical reactions to transport thermal energy from a field of paraboloidal dish solar collectors to a central usage site. The use of reversible reactions for energy storage was also considered.

The results of the study have been recently reviewed and are considered currently applicable. Cost estimates, state-of-the-art assessments, and organizational affiliations of referenced authors are current as of 1980.

Prior to this study, other organizations had published several reports dealing with reversible-reaction energy transport from a central heat source (such as a high-temperature nuclear reactor or a solar tower) and with storage of energy from such a source. Most of the end-to-end studies predicted many technical risks for both transport and storage, no compelling cost advantage for chemical energy transport, and low efficiency for storage. One goal of this work was to determine whether low efficiency is inherent in such systems (due to fundamental constraints) or if efficiency could be substantially improved by use of energy-recovery techniques or different system parameters. Another area of concern was the large temperature drop between the input and output energy flows, which reduces the "second-law" efficiency of a system. This study considers two methods of reducing this temperature change.

Quantitative end-to-end studies had not yet been done for dish-specific systems; hence, another objective was to perform such a study and identify factors specific to dishes. Another objective was to generate cost estimates for equipment at each end for use in comparing chemical energy transport with other forms of transport. The final objective was to see if any promising reactions had been overlooked in earlier work.

NOMENCLATURE

kW_e, MW_e	kilowatt or megawatt electric
kW_s, MW_s	kilowatt or megawatt shaft
kW_t, MW_t	kilowatt or megawatt thermal
Q_0	thermal energy output
Q_s	solar energy input
Q_{waste}	waste heat from gas cooling/condensation for storage; some can be used in organic Rankine-cycle power generation
P_{endo}	pressure of endothermic reaction
P_{exo}	pressure of exothermic reaction
T_{endo}	temperature of endothermic reaction
T_{exo}	temperature of exothermic reaction
T_{input}	temperature of working fluid at entrance to exothermic reactor module
T_{output}	temperature of working fluid at exit of exothermic reactor module
W_{max}	maximum work output of expander
W_{min}	minimum work required to run compressor

CONTENTS

I.	INTRODUCTION.....	1-1
	A. BACKGROUND	1-1
	B. OBJECTIVES.....	1-4
	C. APPROACH AND SCOPE.....	1-4
	D. SUMMARY OF RESULTS.....	1-5
II.	FUNDAMENTALS OF REVERSIBLE-REACTION TRANSPORT AND STORAGE SYSTEMS	2-1
III.	REACTION SCREENING.....	3-1
IV.	COST AND PERFORMANCE OF SELECTED SYSTEMS.....	4-1
	A. TRANSPORT-ONLY SYSTEMS.....	4-1
	B. SYSTEMS INCLUDING STORAGE	4-9
V.	DESIGN CONSIDERATIONS	5-1
	A. SELECTION OF BASELINE SYSTEM PARAMETERS.....	5-1
	B. HEAT EXCHANGERS	5-1
	C. REACTORS	5-2
	D. PIPING NETWORKS	5-3
	E. SOME SYSTEM TRADE-OFFS	5-7
	1. Recuperator Effectiveness	5-7
	2. Endothermic Temperature	5-7
	3. Varying Pressure	5-7
VI.	CONCLUSIONS	6-1

VII.	RECOMMENDATIONS FOR FURTHER WORK.....	7-1
A.	STORAGE SYSTEMS	7-1
B.	TRANSPORT-ONLY SYSTEMS	7-1

VIII.	REFERENCES	8-1
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APPENDIXES:

A.	THERMODYNAMIC CALCULATIONS	A-1
B.	COST ANALYSIS	B-1

Figures

2-1.	General Thermochemical Transport/Storage System	2-3
3-1.	Schematic Representation of Reaction Screening Process ..	3-3
4-1.	Low-Temperature SO ₃ -SO ₂ System	4-2
4-2.	High-Temperature SO ₃ -SO ₂ System	4-3
4-3.	CH ₄ -H ₂ O Thermochemical System	4-4
4-4.	CH ₄ -CO ₂ Thermochemical System	4-5
4-5.	SO ₃ Storage System	4-11
4-6.	CH ₄ -H ₂ O Storage System	4-12
4-7.	CH ₄ -CO ₂ Storage System	4-13
4-8.	Energy Balances for Two Chemical Storage Systems	4-15
4-9.	Cost Breakdown for SO ₃ Storage System	4-16
5-1.	Exothermic Reactor Bed	5-4
5-2.	Exothermic Reactor Configuration, SO ₃ System, Output Temperature Near T _{exo}	5-5
5-3.	Exothermic Reactor Configuration, SO ₃ System, Maximized Output Temperature	5-6
5-4.	Varying-Pressure SO ₃ System	5-9

Tables

1-1.	Survey of Work on Reversible-Reaction Systems	1-3
1-2.	Summary of Cost Estimates	1-7
3-1.	Deferred or Rejected Candidate Reactions	3-4
4-1.	Base Cost Breakdown for Case 1 System, Metal Components..	4-6
4-2.	Base Cost Breakdown for Case 1 System, Ceramic Components	4-7
4-3.	Base Cost Breakdown for Case 2 System, SO ₃	4-8
4-4.	Case 3 Systems, Cost Estimates and Output Temperatures ..	4-10
4-5.	Systems with Storage All at T _{exo} = 427°C	4-14
5-1.	SO ₃ Dissociation System with T _{exo} = 627°C	5-8
5-2.	SO ₃ Dissociation System, T _{exo} = 627°C, Uniform versus Varying Pressure	5-10

SECTION I

INTRODUCTION

A. BACKGROUND

As part of the national effort to develop solar energy, the use of reversible chemical reactions to transport or store thermal energy has been investigated. Such reactions can be run in either of two directions, and will either absorb or release energy as heat. The high-energy reaction mixture generated when the reaction is run in the "endothermic" direction can be cooled and transported in low-temperature pipes to a remote usage site.

In the present study, the concept is applied to a field of parabolic dish solar collectors, carrying energy from the receivers at each dish to a central energy user. The high-energy mixture can also be fed into storage tanks for use during periods of little or no insolation.

On initial inspection, reversible-chemical transport and storage appear to have considerable advantages over "brute force" thermal transport and storage techniques. Direct transport of thermal energy at high temperatures from paraboloidal dish solar collectors has many problems and uncertainties. Among them are high cost and thermal cycling and expansion problems associated with high-temperature piping systems, high insulation costs, lack of development of flexible hoses suitable for high-temperature use, and large thermal losses even in optimized systems.

Large-scale thermal energy storage itself does not have the above-mentioned problems but has several of its own. Liquid-phase thermal storage media are the easiest to use but for temperatures much higher than about 560°C they are few in number and not much is known about their behavior. As operating temperatures rise, costs for container and insulation materials increase rapidly. A large thermal storage system can have small percentage energy losses over short periods of time, i.e., if used for diurnal storage. But if seasonal or even weekly storage is attempted, thermal losses become intolerable.

Reversible-chemical transport and storage concepts would seem to have the potential to overcome all of these difficulties. Transport-line and storage temperatures are expected to be ambient or near-ambient, thus eliminating most thermal losses, as well as greatly reducing piping material, insulation, and tankage costs. The problem of high-temperature flexible hoses is avoided. Finally, chemical energy storage systems may feature higher energy storage densities than thermal storage systems.

The next step is to find out if these potential advantages can be realized in practice. Several investigators have performed system analyses and have designed, sized, and costed components. Table 1-1 shows the various investigators and systems they have studied.

Owen Williams at Australian National University has studied a transport and storage system, based on the reversible decomposition of ammonia, for a field of distributed dish solar collectors (Reference 1). The system would operate at pressures of 20 to 30 MPa, the normal pressure range for commercial ammonia synthesis. Tank storage of gaseous reactants is said to be excessively costly, so it is postulated that these reactants will be stored in underground porous rock formations.

Williams and his colleagues have designed and built decomposition reactors and have arrived at some approximate cost estimates.

A comprehensive study by Rocket Research Co. (Ref. 2) screened 85 chemical reactions on the basis of cost, reversibility, corrosiveness, toxicity, and ease of handling of reactants. Twenty-four reactions still seemed attractive after the screening process. Process flowsheets were prepared for these reactions and efficiencies were estimated.

Gilbert Associates performed a study for the Electric Power Research Institute (Reference 3). Four reaction systems were analyzed. Sulfur-trioxide decomposition and sulfuric-acid reconcentration were studied for energy storage applications. Reversible steam reforming of methane and dehydrogenation of cyclohexane were studied for transport without storage. The conclusions were that efficiencies would be low and costs high.

A study was performed for the U.S. Department of Energy by General Electric Corporate Research and Development (Reference 4). This dealt with reversible steam reforming of methane and dehydrogenation of cyclohexane for transport-only applications. The heat source was postulated as a large nuclear reactor or coal furnace, and integration of the chemical energy-absorbing equipment with a power plant located at the energy source was a key feature in these systems. Costs would be much higher and efficiencies much lower if the input module were a "stand-alone" installation as would be the case for use with a solar dish collector.

Wentworth, et al (Reference 5), at the University of Houston, spent several years investigating the reversible decomposition of ammonium bisulfate. The intended application was for a storage system.

Bhakta (Reference 6) did a system analysis of a storage system based on SO_3 decomposition. The analysis showed that efficiency would be low, which is in agreement with the results of other studies.

T. A. Chubb at the Naval Research Laboratory (References 7 through 10) has studied transport systems of dish collectors, based on the decomposition of sulfur trioxide and the carbon-dioxide reforming of methane. He has postulated the need for low-cost ceramic reactor and heat exchanger components.

Table 1-1. Survey of Work on Reversible-Reaction Systems

Investigator	Study	System Characteristics	Principal Results
Williams and Carden	NH ₃ -decomposition transport system, thermodynamic studies, and endothermic reactor design.	P = 20-30 MPa T _{endo} = 749°C T _{exo} = 327°C	Thermal decomposer has been built and operated successfully; it is not, however, a prototype for a commercial reactor. Authors acknowledge much more development is needed. Studies to date have focused on thermodynamics of charging reaction only, not on analysis of entire system.
Rocket Research Corporation	Large-scale reaction screening; more detailed design and cost estimation for SO ₃ storage.	P _{endo} = 100 kPa T _{endo} = 1027°C P _{exo} = 1 MPa T _{exo} = 593°C	Low efficiency and high cost predicted for most systems.
Gilbert Associates	Reaction screening for applicants, systems design performed for four reactions.		Markets exist for temperature profiles of many reactions, but efficiencies low and costs high.
General Electric	Transport system based on steam reforming of methane.	P = 4 MPa T _{endo} = 827°C T _{exo} = 427°C	Many technical risks. System may be cost effective if endothermic end can be integrated with a power plant. Thermal cycling of thick-walled reactor tubes may prevent use in solar applications.
Wentworth, et al	System analysis and experimental study of ammonium-bisulfate decomposition.	T _{endo} = 999°C T _{exo} = 554°C	System design accomplished; many reaction problems uncovered in experimental work but authors believe these problems can be solved.
Bhakta	System analysis and component design for SO ₃ storage system.	T _{endo} = 799°C T _{exo} = 399°C P _{endo} = 100 kPa P _{exo} = 1 MPa	Low efficiency predicted.
Chubb	System study and component design for SO ₃ and CH ₄ -CO ₂ transport systems. Ceramic components.	(SO ₃) T _{endo} = 799-899°C T _{exo} = 499°C (CH ₄ -CO ₂) T _{endo} = 704°C T _{exo} = 427°C	Ceramic reactor has been built and tested. Dr. Chubb is very optimistic about the prospects for a cost-effective system.

B. OBJECTIVES

This study was undertaken to assess the feasibility of using reversible chemical reactions to transport thermal energy from a field of paraboloidal dish solar collectors to a central usage site and for storage of that energy. The end use was postulated to be industrial process heat at temperatures equal to or greater than 427°C. An attempt was made to consider each of the problem areas identified in the Foreword:

- (1) Can the first-law efficiency of storage systems be improved over the values reported in the literature?
- (2) Can the second-law efficiency of transport and storage systems be improved by reducing the temperature drop between input and output energy flows?
- (3) What factors are different in distributed dish solar collector systems as opposed to the central-energy-source systems reported in most of the literature?
- (4) What are the cost and performance estimates for thermochemical transport systems? How are the estimates for storage systems affected by the use of energy-recovery equipment?
- (5) Is it likely that reactions not yet reported in the literature will be found that will give better performance than has been predicted in previous studies?

C. APPROACH AND SCOPE

The approach used was as follows: In a study reported elsewhere (Reference 11), reactions were screened by Drs. H. E. Marsh and S. H. Kalfayan of JPL; ten reactions were selected for inclusion in their report. In the present report, these ten reactions, in addition to one that was taken from a concept paper by Dr. T. A. Chubb of the Naval Research Laboratory, were then screened according to chemical engineering principles. Process flowsheets were drawn up for both transport-only and storage systems, and mass and energy flows and system efficiencies were calculated. Three reactions were judged to be the most promising on the basis of feasibility, efficiency, and cost: SO₃ decomposition, steam reforming of methane, and carbon-dioxide reforming of methane. These reactions were then subjected to a somewhat more detailed analysis, including cost estimation. Only systems based on the chosen reactions are described in this report.

When considering the selected reactions in transport-only systems, a variety of delivery configurations was considered.

- (1) Heating a working fluid from 200 or 260°C to the delivery temperature. This type of system would be similar in performance to a high-pressure steam system.

- (2) Nearly isothermal delivery of heat. This would interface with applications such as phase changes or driving another endothermic reaction.
- (3) Taking each increment of exothermic conversion at decreasing temperatures. This method yields the highest possible delivery temperatures.

For each of the three selected reactions, a "baseline" system was designed. These baseline systems were transport-only, delivered heat as in configuration (1) above at a nominal temperature of 427°C, and were implemented in metals that could withstand the temperatures of the reactant streams. Then various departures from the baseline were analyzed to assess the effect of the inclusion of storage, the use of ceramic technology, and various system trade-offs.

D. SUMMARY OF RESULTS

Principal results were the following:

- (1) Reactions involving solids do not look promising for thermochemical transport systems. In addition to difficulties in transporting the solid reactants themselves over the distances in a field of dish collectors, problems associated with product separation and recovery of heat from solid reactants within cost constraints will be formidable for a distributed collector system.
- (2) Several attractive high-temperature reactions, including ones with solid reactants, face basic reaction problems such as product separation. Until these problems are resolved, it is impossible to produce flowsheets for these reactions; therefore, they were not analyzed or costed in this report. They are deferred for future study.
- (3) If the output heat is required essentially isothermally (small temperature change in a heat transfer fluid), then reactions that can deliver this heat at temperatures above 729°C have not been found. Some reactions with exothermic temperatures this high are known, but they all have fundamental cycle problems that prevented their being analyzed in this study. Based on the extensive lists of candidate reactions that have been surveyed, it is considered unlikely that reactions will be found that can deliver such high-temperature heat isothermally, while not being plagued with insurmountable reaction problems. If the heat is not required isothermally, then reactions exist that may be able to heat a working fluid from lower temperatures to 677-788°C. Such systems were analyzed in this study.
- (4) The baseline transport-only systems have cost estimates in 1980 dollars of 152 to 185 \$/kW_t for SO₃ decomposition, 168 to 215 \$/kW_t for steam reforming, and 166 to 200 \$/kW_t for CO₂ reforming of methane. The cost is increased by about 40% to raise the nominal delivery temperature of an SO₃ system from 427 to 621°C. A three- to five-fold reduction in costs is estimated if advanced ceramics are used instead of metals to build the reactors and heat exchangers. Compared with the baseline SO₃ system, a "case 2" system, delivering heat nearly isothermally, results in about a two-fold increase in cost in metal construction and about

a 50% increase for ceramics as shown in Table 1-2. Maximizing the output temperature (as in "case 3" systems) increases the cost over baseline systems by factors of about 2.4 for SO₃ systems in metals, 2.1 for SO₃ in ceramics, 1.7 for CH₄-H₂O systems in metals, and 1.4 for CH₄-H₂O systems in ceramics. These results are also shown in Table 1-2.

- (5) The results for energy storage are not encouraging. The most cost-effective performance is given by reactions in which the reactants are condensable; unfortunately, predicted thermal efficiencies are 60% or less in spite of the inclusion of energy-recovery equipment wherever feasible.
- (6) Pipeline temperatures, while much lower than heat delivery temperatures, would still be substantially higher than ambient. The systems described in this report have "hot" side pipeline temperatures of 177 to 260°C. In order to maintain even these temperatures, at an acceptable cost for heat exchangers and without wasting heat, organic or steam Rankine heat-recovery equipment must be used. Typically 5 to 15% of the output energy must be taken as electricity rather than as high-temperature process heat.
- (7) The end-to-end temperature drop can be reduced by recycling more material or varying the system pressure. The effect on costs is a pronounced increase. Furthermore, varying the pressure significantly reduces first-law efficiency.

Table 1-2. Summary of Cost Estimates

Reaction	Cost, \$/kW _t Metals	Cost, \$/kW _t Ceramics	T _{endo} , °C	T _{exo} , °C
Case 1				
SO ₃	152 to 185	39 to 72	1027	427
SO ₃	213 to 261	50 to 94	1027	621
CH ₄ -H ₂ O	168 to 215	46 to 85	827	427
CH ₄ -CO ₂	166 to 200	44 to 77	727	427
Case 2				
SO ₃	291 to 339	52 to 104	Working fluid heated from 427 to 482	
Case 3				
SO ₃	377 to 425	81 to 145	788	} Output temperatures
CH ₄ -H ₂ O	310 to 358	62 to 117	677	

SECTION II
FUNDAMENTALS OF REVERSIBLE-
REACTION TRANSPORT AND STORAGE SYSTEMS

The essential major components of a reversible-reaction chemical energy transport system for a field of dish solar collectors are the following: "endothermic" reactors and recuperators at each solar receiver, at least one "exothermic" reactor and recuperator, and a piping network. The systems considered in this study also include a waste-heat boiler coupled with a Rankine engine to reduce the required recuperator sizes.

Figure 2-1 shows a generalized chemical transport system. Given a mixture of substances that can react reversibly, the equilibrium composition will generally be a function of temperature. In accordance with Le Chatelier's principle, as the temperature is increased, the composition will change so as to have additional chemical energy. In this way, heat energy can be stored in a reacting mixture. This occurs at the endothermic reactor. In the exothermic reactor, the mixture gives up its stored energy at a lower temperature. The purpose of the recuperators is to recycle heat from the high-temperature gas streams exiting the reactors to the low-temperature streams entering. This enables the transport pipes to be at lower temperatures. Heat recovery equipment following the exothermic recuperator will reduce its required size. Implementation of such a heat transfer process is very difficult if solid reactants are involved; this problem is exacerbated by the distributed nature of a dish system.

The chief motivation for developing chemical transport systems lies in the low-temperature transport lines that can be used. The "high-energy" composition of the reaction mixture, which thermodynamically exists only at high temperatures, must be kept as such in the low-temperature transport lines. There are two ways this may be accomplished. If the reaction is dependent upon a catalyst, reverse-reaction rates in the transport lines will be negligible. If a catalyst is not used, then endothermic reaction products must be separated before the temperature of the mixture is lowered. Separation equipment is likely to require complex instrumentation, control, and possibly operator intervention, all of which probably rule out the use of non-catalytic reactions in distributed dish systems.

Conversion to high-energy reactants is favored by a high temperature, and conversion to the low-energy reactants is favored by a low temperature. An important design trade-off is balancing the end-to-end temperature drop against the amount of material that has to be circulated through the system. Typically, the endothermic and exothermic reaction temperatures are quite far apart if substantially complete conversions are to be achieved in each reactor. Operation at these conditions reduces costs for transport lines and heat exchangers. The systems analyzed in this study had nominal heat absorption temperatures of 704 to 1027°C and delivery temperatures of 427 to 627°C.

The delivery temperature that can be achieved depends upon the industrial application. If the energy is required all at one temperature, as in effecting a phase change or driving another endothermic reaction, then the exothermic temperature shown in the flowsheets in Section IV is the actual delivery temperature.

If, on the other hand, the delivered energy can be used as approximately equal increments of heat in increments of temperature, i.e., as sensible heat in some other fluid medium, then the delivery temperature can be much higher than the exothermic temperature shown. The exothermic reactor will be run in a "cascaded" fashion, with increments of conversion occurring at successively lower temperatures. Because the nominal exothermic temperature is one at which the exothermic reaction is substantially complete, this is the lowest temperature existing in the cascaded reactor and the working fluid can reach a much higher temperature.

Because the reactions analyzed here involve an increase in the number of moles of gas as energy is absorbed, an increased pressure results in lower conversion at the endothermic end for a given temperature and an increase in delivery temperature.

Finally, reactants can be diverted from the transport lines into storage tanks to enable the system to deliver heat when there is no insolation. In general, separate storage tanks are required for endothermic and exothermic reaction products. In studies done previously, it was assumed that condensable reactants would be stored as liquids to reduce tankage costs. This requires equipment to separate the reactants.

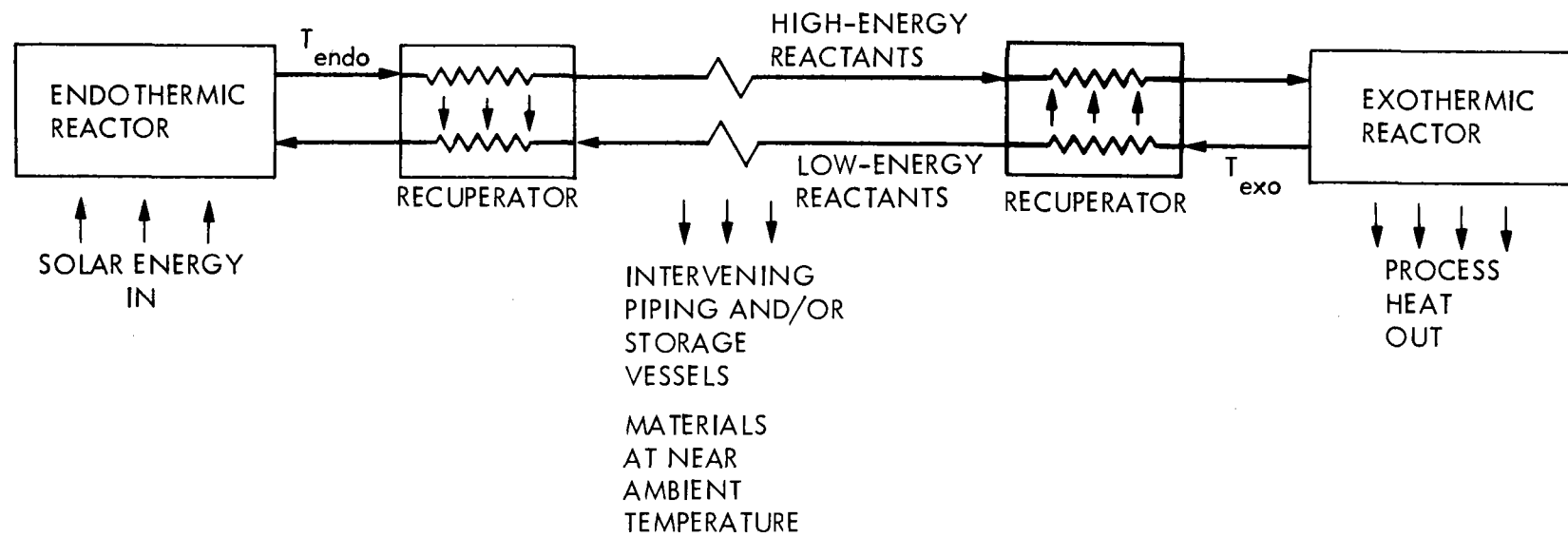


Figure 2-1. General Thermochemical Transport/Storage System

SECTION III

REACTION SCREENING

A list of candidate reactions was prepared by Drs. S. H. Kalfayan and H. E. Marsh of JPL. Their work is described in detail in a separate report (Reference 11). Drs. Kalfayan and Marsh began with a long list of reactions from Reference 2, "Reversible Chemical Reactions for Electrical Utility Energy Applications" published by the Rocket Research Company. To this list they added a number of reactions of their own choosing. They then began a screening process that assigned a relative rank to each reaction based on a composite determination of desirability. The criteria included reversibility (absence of side reactions), materials handling problems (i.e., reactions involving more than one solid were heavily penalized), toxicity, and corrosiveness. They finally arrived at a list of ten candidate reactions.

The Kalfayan-Marsh study was undertaken to identify candidate reactions for a range of purposes. These purposes might include chemical energy transport, transport-with-storage or storage-only applications. Another reaction (from References 7 through 10 by Talbot A. Chubb of NRL) was added to the Kalfayan-Marsh list of ten reactions. A further screening process to identify reactions suitable for energy transport in dish systems was then initiated. Process flow-sheets were drawn up for most of the reactions, and thermal analyses (assuming equilibrium conversion at each reactor) were performed. Three reactions looked promising enough to merit more detailed analysis and inclusion in this report.

The reactions involving solids were deferred after a brief analysis. Transporting solids to and from distributed dish collectors did not seem practical. Also, the sensible heat of the products coming out of a reactor is a substantial fraction of the stored energy, and recovery of this heat is an important feature of an efficient chemical energy transport system. This is difficult and complex to do when faced with solid products. To apply these reactions to a distributed-receiver system would require complex heat-recovery equipment at each dish. This was thought to be impractical. The problems are especially severe in the case of the reaction $\text{Ca} + \text{H}_2 \rightleftharpoons \text{CaH}_2$. Two of the three reactants are highly reactive, and air must be rigorously excluded from the entire system. Also, this reaction is non-catalytic, meaning that Ca and H₂ must be separated at each dish. These reactions may be suitable for storage-only applications, but they appear to be poor candidates for energy transport.

The ammonium-hydrogen-sulfate decomposition reaction was not analyzed because there are many unsolved chemical reaction problems.¹ Among them are the lack of a working separation scheme for the products of the endothermic reaction, irreversible destruction of some of the ammonia, decomposition of SO₃ to SO₂ and O₂, and uncertainties in the feasibility of the reconstitution (exothermic) reaction.

¹Wentworth, W.E., personal communication.

While systems that included storage were being investigated, two reactions ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ and $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$) were eliminated due to extremely low predicted efficiency and high cost. For transport-only applications, it does not seem worthwhile to further investigate these two reactions. In the case of the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, the heat of reaction is very low; therefore, large volumes of gases must be transported, resulting in a detrimental effect on costs. The reaction $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2$ will be plagued with corrosion problems. Initially, it was thought that this would not be the case. Anhydrous HCl is not particularly corrosive, but it became evident that the endothermic reaction would not go to completion. In that case, unreacted steam is present in the product stream, and HCl in the presence of H_2O is very corrosive.

The reaction $2\text{Na} + \text{H}_2\text{O} + 1/2 \text{O}_2 \rightleftharpoons 2\text{NaOH}$ was not analyzed for the following reason: The reaction occurs at a temperature above the boiling point of sodium; thus, separating the highly reactive sodium from the other gaseous products represents a problem. Product separation is necessary because the reaction is non-catalytic. Separation schemes have been proposed, but at this time they are strictly conceptual. If a successful, efficient separation scheme can be developed for economic installation at each dish, this reaction will be very attractive; until then, a conceptual design cannot be developed for performance and cost analysis. The ammonia dissociation reaction was not analyzed. The JPL computer equilibrium calculations indicated that the exothermic reaction temperature would be below that specified in the ground rules of this study. Also, this reaction introduces additional technical risk because of the very high pressure involved. To obtain acceptable conversions and reaction rates, pressures of 20 to 30 MPa are commonly used in industrial ammonia synthesis. Reactor walls thick enough to contain such pressures pose severe thermal cycling problems for solar applications. Also, the need to contain such pressures probably rules out the use of ceramic components.

Figure 3-1 gives a schematic representation of the screening process, and Table 3-1 shows the reasons why various reactions were not considered for more detailed analysis.

The remaining two reactions (steam reforming of methane and sulfur-trioxide decomposition) as well as the one proposed by T.A. Chubb (carbon-dioxide reforming of methane) were selected for further analysis.

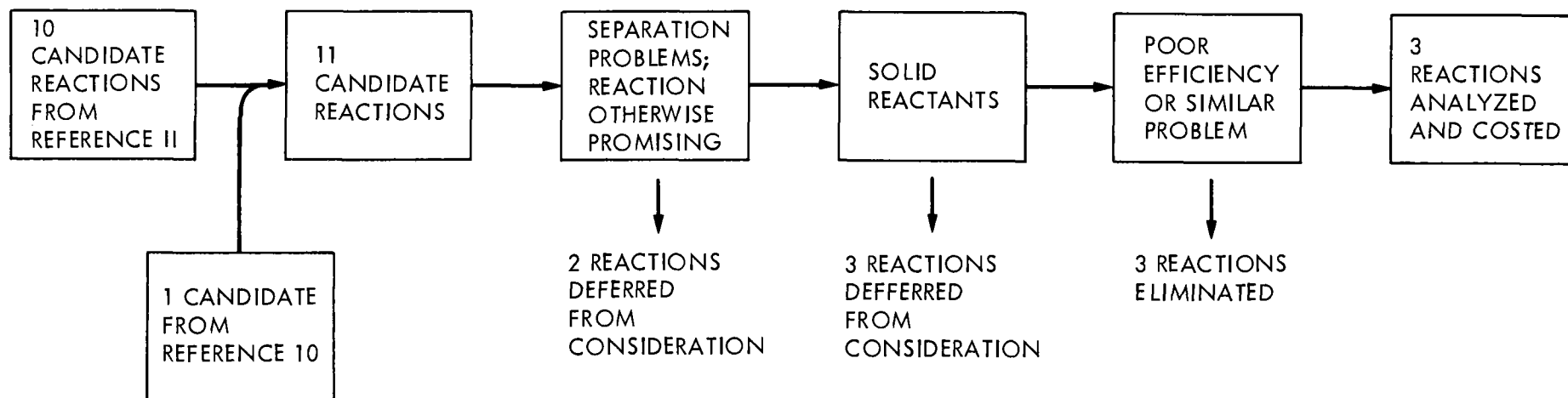


Figure 3-1. Schematic Representation of Reaction Screening Process

Table 3-1. Deferred or Rejected Candidate Reactions

Reaction	Why Deferred or Rejected
$\text{Ca} + \text{H}_2 \rightleftharpoons \text{CaH}_2$	Solids handling problems exacerbated by extreme reactivity of chemicals.
$\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{HSO}_4$	Workable product separation scheme (necessary because reaction is non-catalytic) has not been discovered. Also, workable exothermic reaction scheme not yet worked out; possible irreversible decomposition of ammonia.
$\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$	Heat of reaction very low in relation to mechanical work that probably is required; solids handling problem; separation of solid product from catalyst.
$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	Solids handling problem; difficulty of separating solid product from catalyst.
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	Heat of reaction very low.
$4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$	Reaction very expensive and inefficient for storage; very corrosive.
$2\text{Na} + \text{H}_2\text{O} + 1/2 \text{O}_2 \rightleftharpoons 2\text{NaOH}$	Reaction takes place above the boiling point of sodium; no idea how to separate sodium vapor from other gaseous products with which it will react non-catalytically.
$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2 \text{NH}_3$	T_{exo} too low; very risky and costly due to high pressures involved.

SECTION IV

COST AND PERFORMANCE OF SELECTED SYSTEMS

Three reversible reaction systems were considered: sulfur-trioxide decomposition, carbon-dioxide reforming of methane, and steam reforming of methane. Transport-only systems are discussed first because such discussion establishes sizing for the major power-related components. Later, the effects of including storage are addressed. Criteria for selecting "baseline" design parameters are described in Section V.

A. TRANSPORT-ONLY SYSTEMS

In addition to the three baseline systems, a high-pressure SO_3 -decomposition system, that delivers heat at 627°C , was analyzed.

Three cases were considered, reflecting different performance requirements for the exothermic reactor:

- Case 1: The exothermic reactor heats a working fluid or heat-transfer medium from 204 to 427°C , or, in the case of the high-temperature sulfur-trioxide system, from 260 to 621°C .
- Case 2: The exothermic reactor heats the working fluid from 427 to 482°C . Only the sulfur-trioxide system was considered in this case.
- Case 3: The exothermic reactor is arranged in a "cascade" fashion, with increments of conversion occurring in decreasing increments of temperature. The working fluid flows in an overall counterflow pattern to the reaction mixture. The maximum temperatures are achievable by this method.

Figures 4-1 to 4-4 show the temperatures, pressures, and mass and energy flow rates in the selected systems.

Table 4-1 shows the cost estimates for Case 1 transport systems realized in metals. The total installed cost is the total of component base costs, each multiplied by the appropriate installation factor as explained in Appendix B. The three baseline systems are similar in cost with estimates ranging from 152 to $215\text{\$/kW}_t$. The high-temperature SO_3 system is somewhat higher in cost.

Table 4-2 shows similar estimates for Case 1 systems, this time using ceramic technology. The cost estimates have been reduced by factors of about 3 to 5.

Table 4-3 shows estimates for Case 2 operation, using metal or ceramic components. Delivery of the heat isothermally increases estimated cost by a factor of almost two for metal systems and about 1.5 for ceramics. The higher costs in this case reflect primarily the greater heat-transfer area required for exchanging heat from the hot reactant gases to the working fluid. (The fact that the working fluid enters the reactor module at a higher temperature reduces the mean temperature difference between it and the reaction mixture, which means more heat exchanger area is required.)

4-2

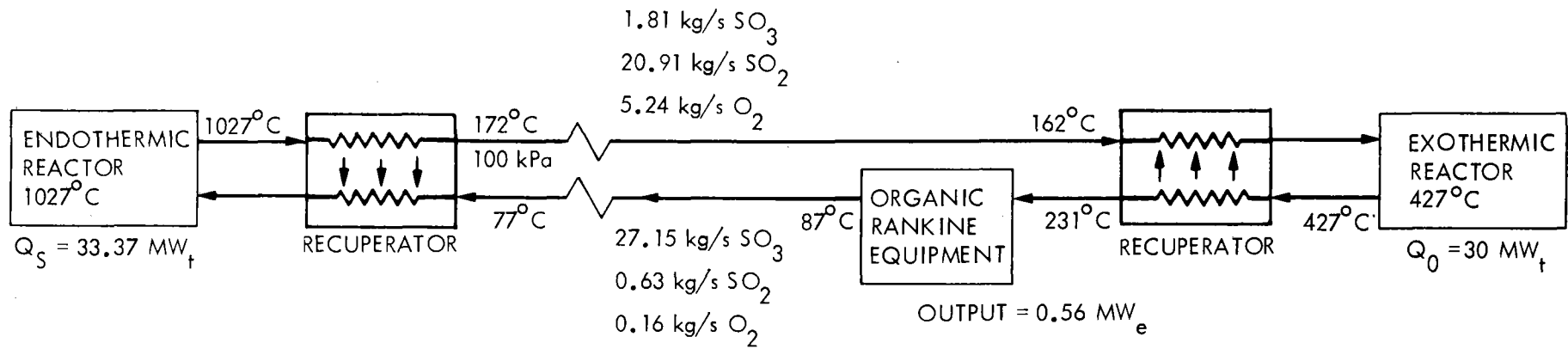
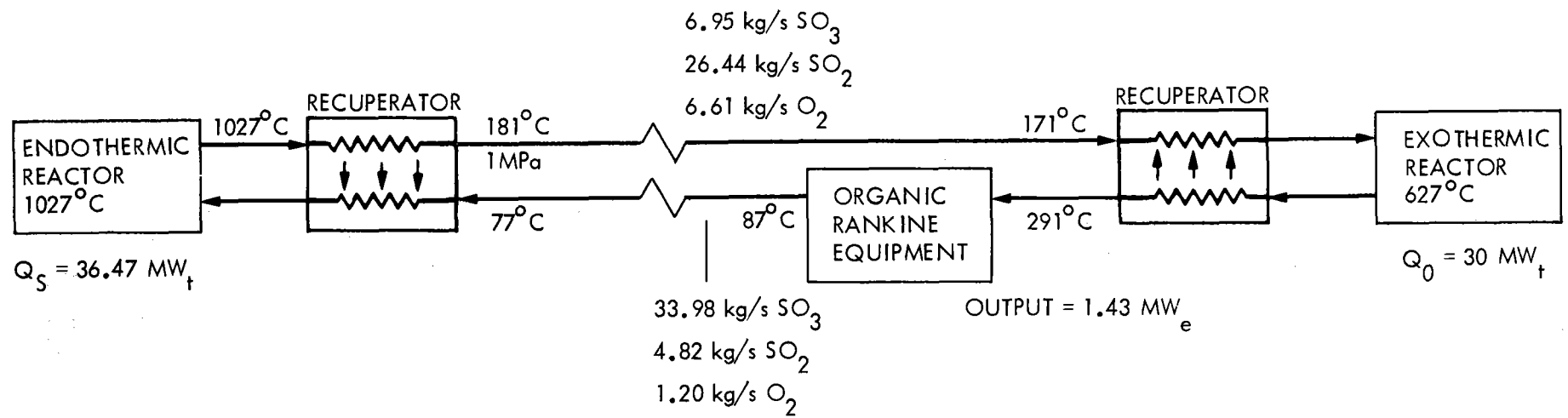


Figure 4-1. Low-Temperature SO₃-SO₂ System

Figure 4-2. High-Temperature SO_3 - SO_2 System

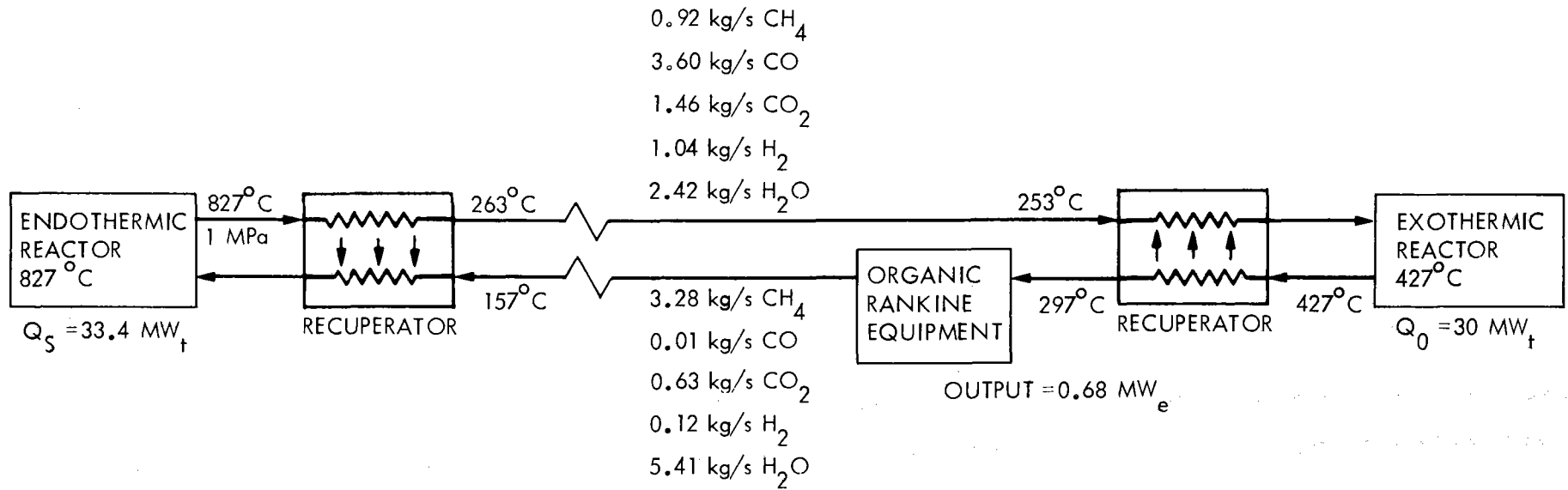


Figure 4-3. CH₄-H₂O Thermochemical System

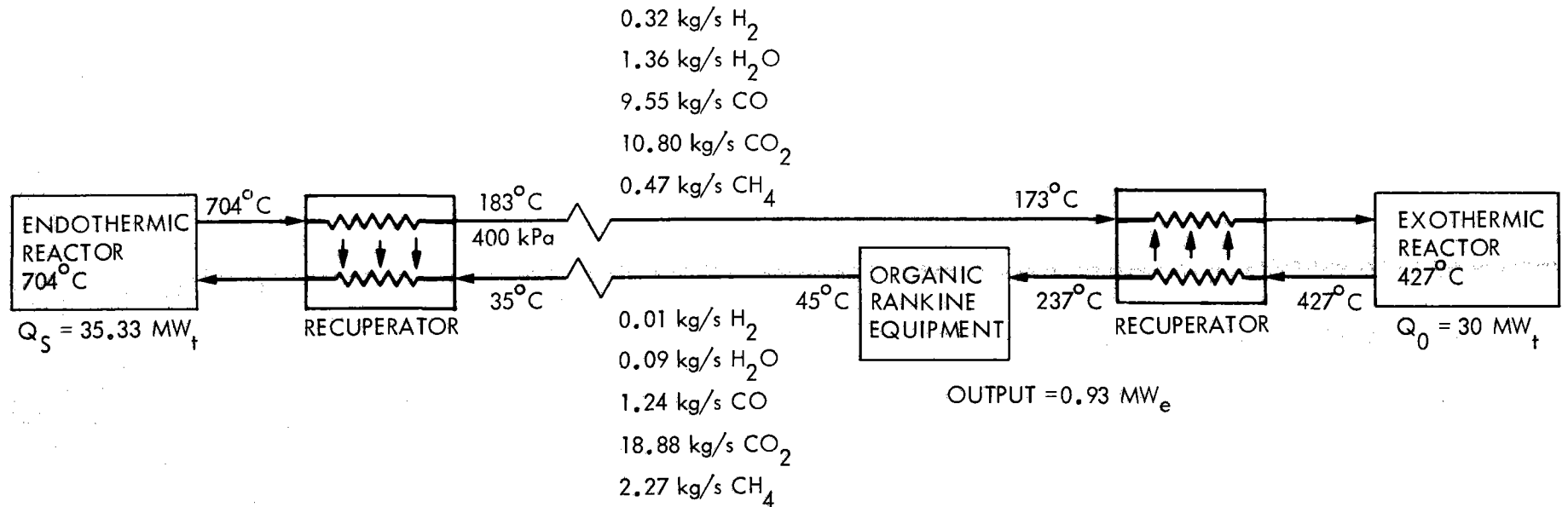
Figure 4-4. CH₄-CO₂ Thermochemical System

Table 4-1. Base Cost Breakdown for Case 1 System, Metal Components

	SO ₃ (100 kPa)	SO ₃ (1 MPa)	CH ₄ - H ₂ O (1 MPa)	CH ₄ - CO ₂ (400 kPa)
T _{endo} , °C	1027	1027	827	727
T _{input} , °C	204	260	204	204
T _{output} , °C	427	621	427	427
Endothermic Reactor, \$/kW _t	7 to 28	10 to 40	10 to 40	7 to 28
Exothermic Reactor, \$/kW _t	16	16	16	16
Endothermic Recuperator, \$/kW _t	29	40	25	32
Exothermic Recuperator, \$/kW _t	8	13	10	10
Heat-Recovery Equipment, \$/kW _t	10	25	17	12
Total Installed Cost, \$/kW _t	152 to 185	213 to 261	168 to 215	166 to 200

Table 4-2. Base Cost Breakdown for Case 1 System, Ceramic Components

	SO ₃ (100 kPa)	SO ₃ (1 MPa)	CH ₄ - H ₂ O (1 MPa)	CH ₄ - CO ₂ (400 kPa)
T _{endo} , °C	1027	1027	827	727
T _{input} , °C	204	260	204	204
T _{output} , °C	427	621	427	427
Endothermic Reactor, \$/kW _t	2.0 to 6.5	2.9 to 9.3	2.9 to 9.3	2.0 to 6.5
Exothermic Reactor, \$/kW _t	4.1 to 6.4	4.1 to 6.4	4.1 to 6.4	4.1 to 6.4
Endothermic Recuperator, \$/kW _t	2.9 to 7.0	3.7 to 9.3	3.3 to 8.0	2.5 to 6.0
Exothermic Recuperator, \$/kW _t	2.6 to 6.4	3.5 to 8.7	2.8 to 7.0	2.6 to 6.3
Heat-Recovery Equipment, \$/kW _t	5.7	9.7	8.9	10.0
Total Installed Cost, \$/kW _t	39 to 72	50 to 94	46 to 85	44 to 77

Table 4-3. Base Cost Breakdown for Case 2 System, SO₃

	Metal (1 MPa), \$/kW _t	Ceramic (1 MPa), \$/kW _t
Endothermic Reactor	10 to 40	2.9 to 9.3
Exothermic Reactor	32	6.0 to 11.3
Endothermic Recuperator	37	3.5 to 8.8
Exothermic Recuperator	27	3.3 to 8.1
Heat-Recovery Equipment	13	7.4
Total Installed Cost	291 to 339	52 to 104

Table 4-4 shows estimates for Case 3 operation, along with output temperatures. Cost increments over Case 2 are due to somewhat higher heat transfer area requirements and higher-temperature operation of the reactor.

The first-law thermal efficiencies of all these systems (with heat-recovery equipment) is 90 to 95%, which does not include parasitic power losses due to pressure drops in piping, reactors, and heat exchangers.

B. SYSTEMS INCLUDING STORAGE

For each of the three selected reactions, a system that includes storage was designed. The systems were sized to put out full power for 20 hours, with 10 hours of insolation at a constant level. Figures 4-5 to 4-7 show the systems.

The reactors and recuperators at each end are required for transport and are not included in the storage cost estimates. Only the additional equipment specifically required for provision of storage capability is included. The storage power-related cost comprises all condensers, evaporators, pumps, compressors, etc., used to move reactants in and out of storage. Energy-recovery equipment (gas expanders and waste-heat boilers driving Rankine engines) is used wherever feasible, and its cost is included in the power-related cost. Energy-related cost comprises tanks and chemicals.

Table 4-5 shows cost and efficiency estimates for systems incorporating storage. Figure 4-8 gives a breakdown of energy losses for two of these systems.

To reduce tankage costs, proposed chemical energy storage systems have usually been based on reactions in which most of the substances can be stored as liquids. Unfortunately, as shown in Figure 4-8, the heats of vaporization of the condensable reactants are a large fraction of the heat of reaction. Furthermore, these substances are condensed at relatively low temperatures, yielding heat that must be considered useless for the purposes of this study. All of these factors place a severe penalty on the efficiency of storage systems. Of the three reactions chosen as suitable for solar dish system energy transport, only the $\text{CH}_4\text{-CO}_2$ reaction does not have massive losses of this type. As shown in Table 4-5, its energy-related storage cost is much higher than the costs of the other two reactions, which reflects the fact that all reactants are stored as gases.

Figure 4-9 gives a breakdown of energy-related costs for the SO_3 system. Costs are dominated by gaseous reactant tanks and chemicals, which in this case are nearly equal in cost. The carbon-hydrogen-oxygen systems should be more completely dominated by gaseous reactant tankage costs.

Methods used for estimating throughput efficiencies for both transport and storage systems are given in Appendix A, and the methods used for cost estimating are given in Appendix B.

Table 4-4. Case 3 Systems, Cost Estimates and Output Temperatures

	SO ₃ (1 MPa), °C		CH ₄ -H ₂ O, °C	
T _{endo}	1027		827	
T _{input}	538		371	
T _{output}	788		677	
	Metal, \$/kW _t	Ceramic, \$/kW _t	Metal, \$/kW _t	Ceramic, \$/kW _t
Endothermic Reactor	10 to 40	2.9 to 9.3	10 to 40	2.9 to 9.3
Exothermic Reactor	51	12.5 to 20.0	46	8.7 to 15.2
Endothermic Recuperator	44	4.1 to 10.3	30	3.4 to 8.5
Exothermic Recuperator	32	3.8 to 9.5	25	2.9 to 7.3
Heat-Recovery Equipment	10.6	10.6	9.2	9.2
Total Installed Cost	377 to 425	81 to 145	310 to 358	62 to 117

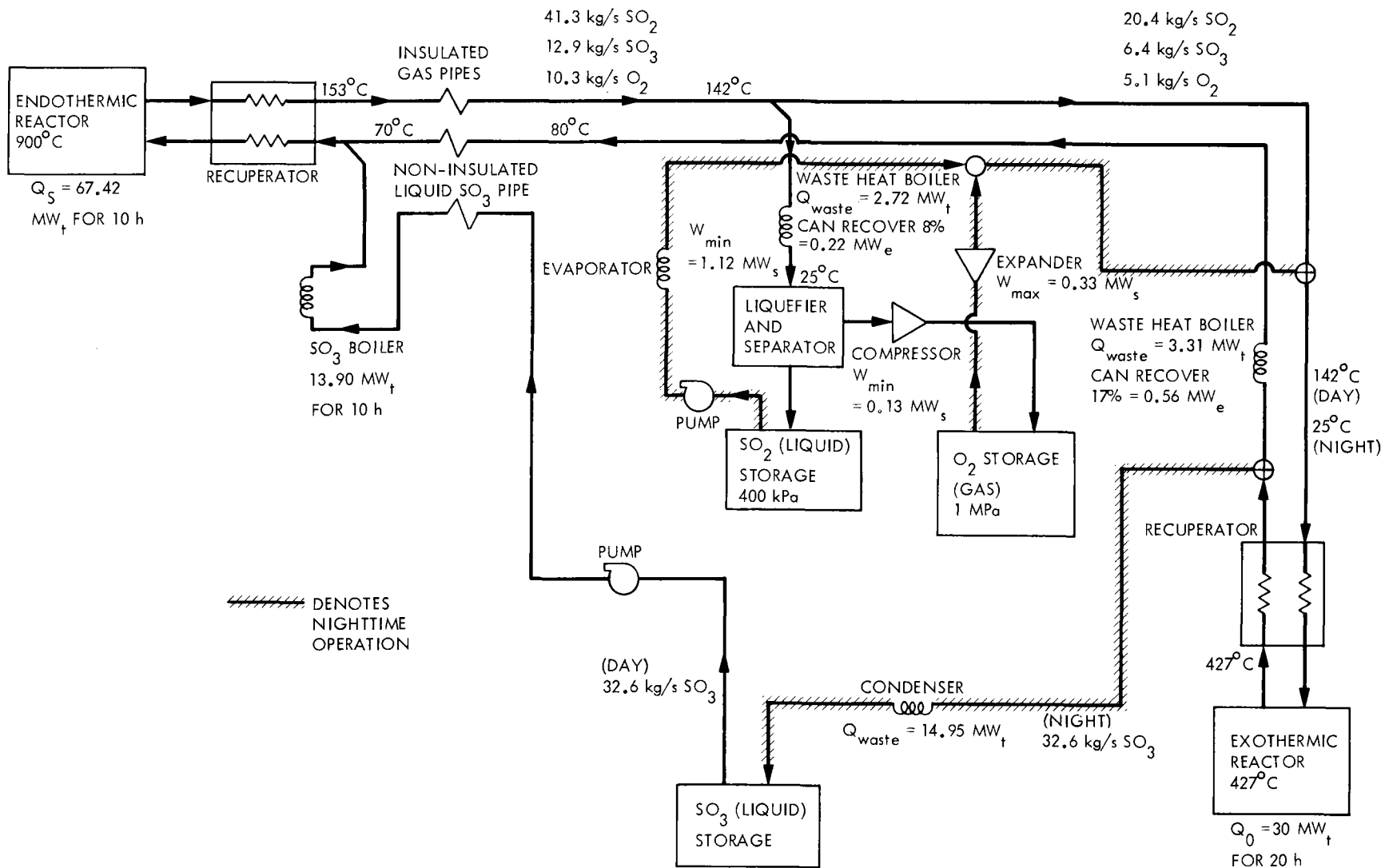
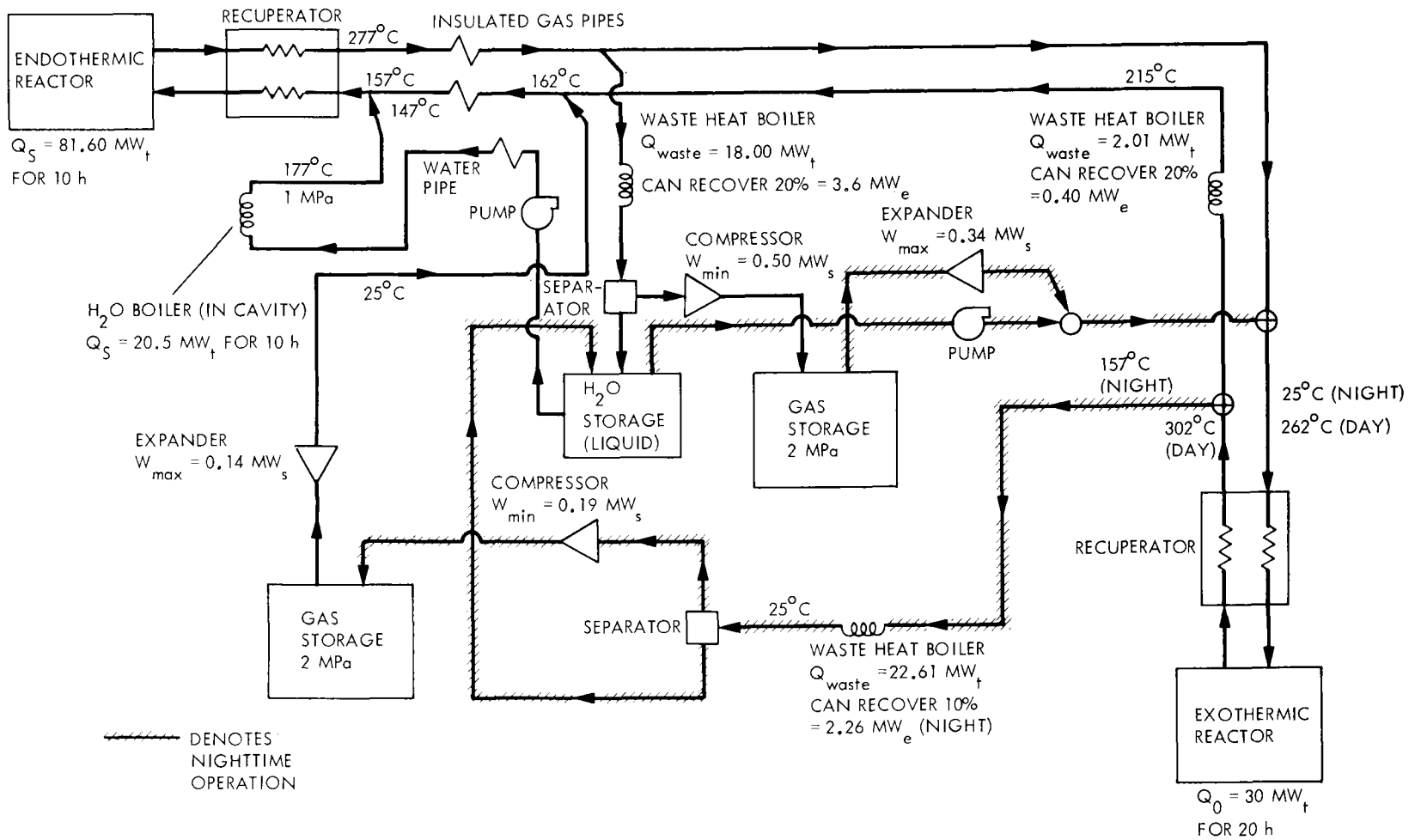


Figure 4-5. SO₃ Storage System

Figure 4-6. $\text{CH}_4\text{-H}_2\text{O}$ Storage System

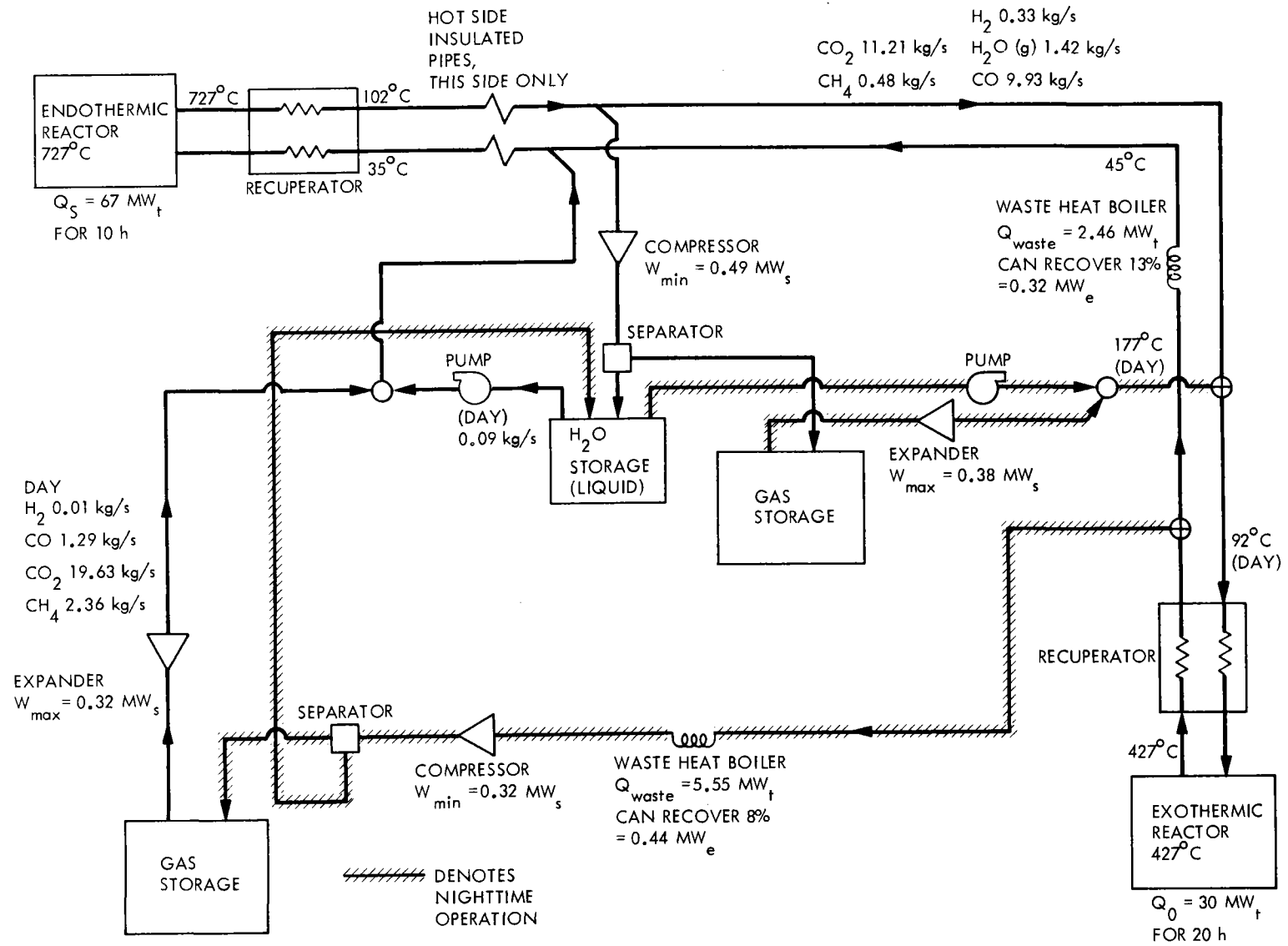
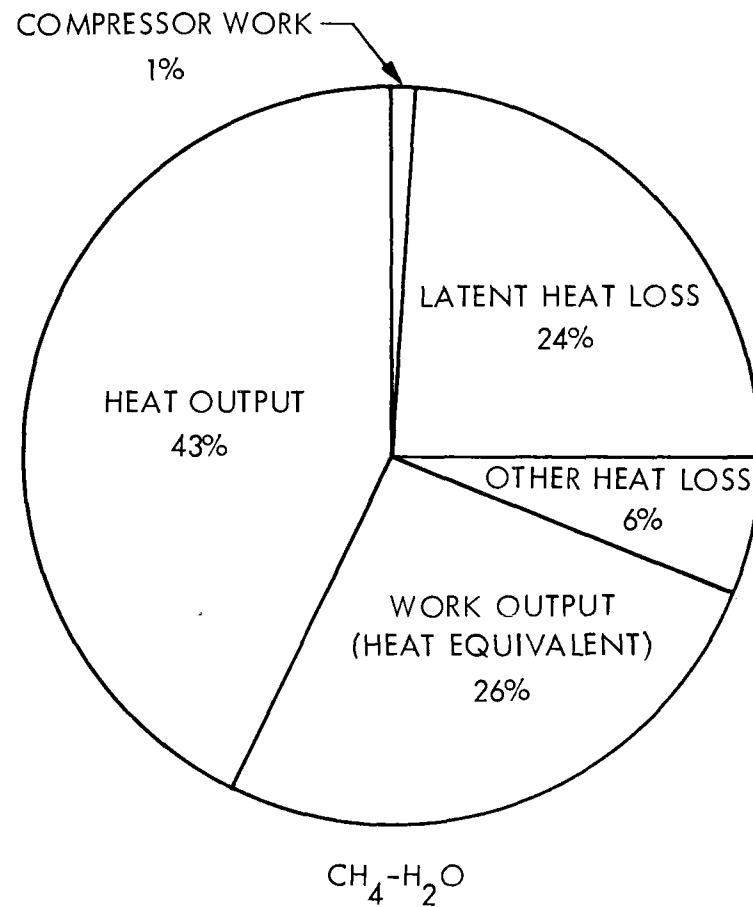
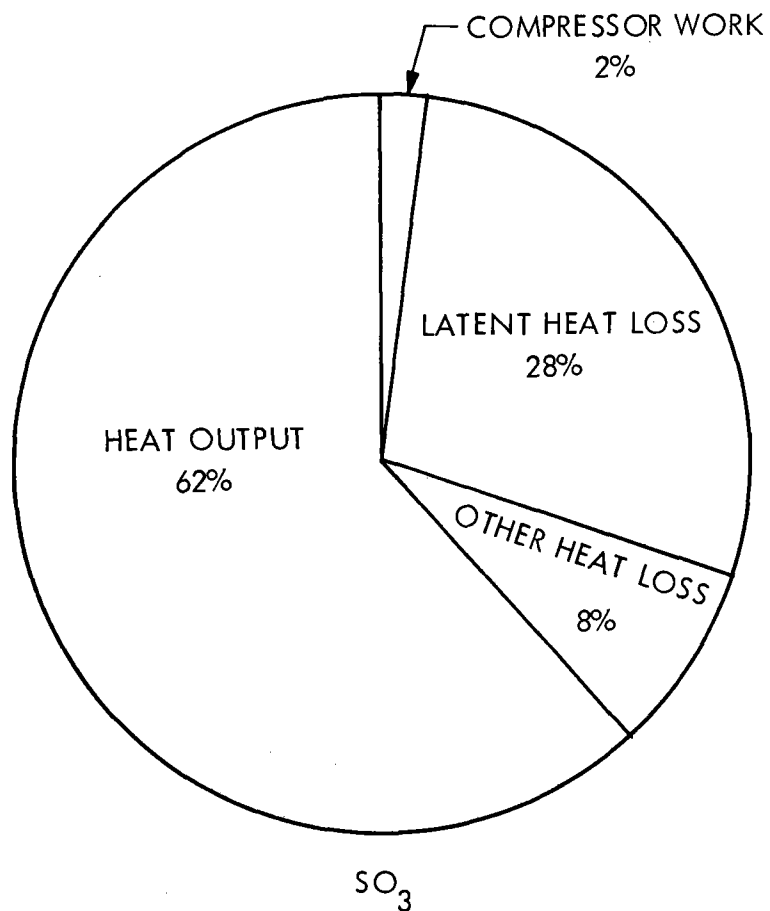
Figure 4-7. CH₄-CO₂ Storage System

Table 4-5. Systems with Storage All at $T_{\text{exo}} = 427^{\circ}\text{C}$

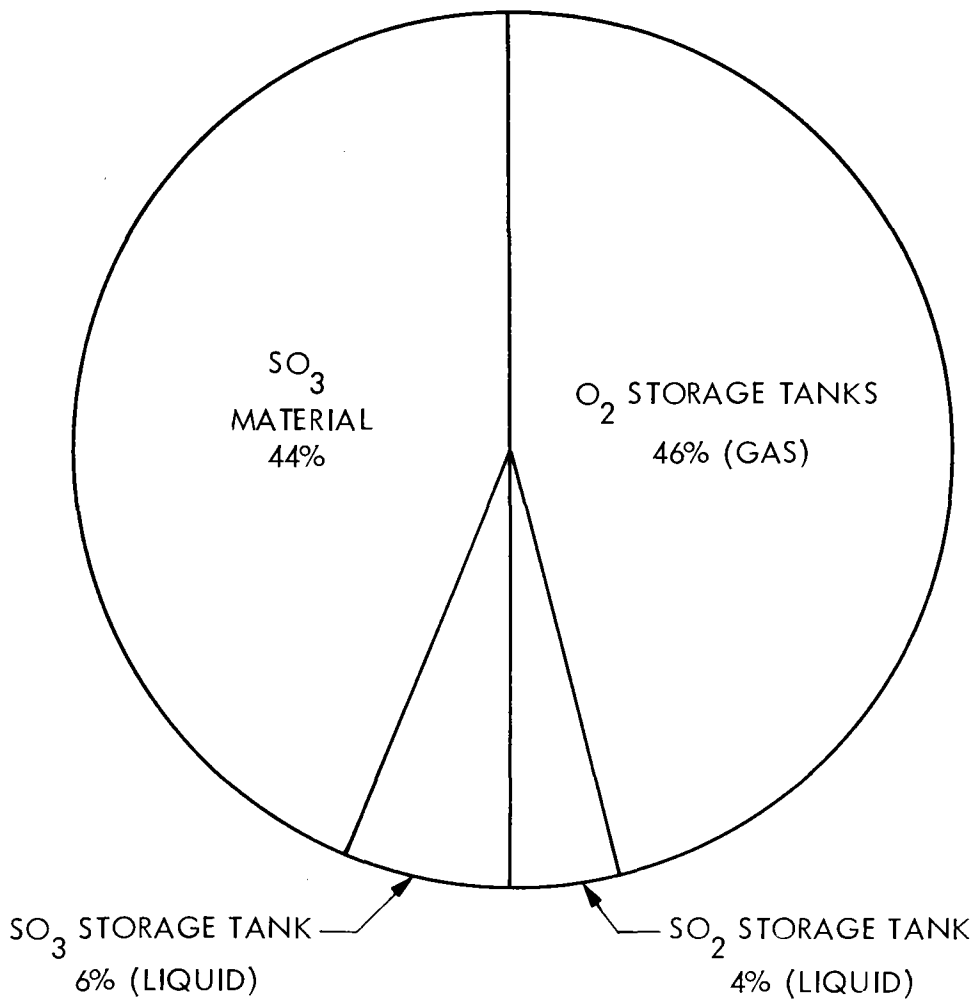
	Power-Related Cost ^a of Storage Capability, \$/kWt	Energy-Related Cost of Storage, \$/kWht	Energy Recovery Efficiency of Storage, %
SO ₃	113	7	59
CH ₄ -CO ₂	64	165	84
CH ₄ -H ₂ O	185	84	57

^aThis is the installed cost of process equipment required for the storage system. Extra endothermic reactors and recuperators required to charge storage are not included.



NOTE: PERCENTAGES SHOWN ARE PERCENT OF TOTAL INPUT ENERGY.
TOTAL INPUT ENERGY = SOLAR HEAT INPUT PLUS ELECTRICAL INPUT
FOR COMPRESSOR WORK.

Figure 4-8. Energy Balances for Two Chemical Storage Systems



NOTE: STORAGE TANKS FOR GASES COMPRISE ESSENTIALLY THE ENTIRE ENERGY-RELATED COST OF THE OTHER TWO SYSTEMS (CH₄-H₂O AND CH₄-CO₂).

Figure 4-9. Cost Breakdown for SO₃ Storage System

SECTION V

DESIGN CONSIDERATIONS

In this section, some of the factors that affect the design of heat exchangers and reactors and the selection of system parameters are identified. Also, some of the major trade-off issues are dealt with.

A. SELECTION OF BASELINE SYSTEM PARAMETERS

With the exothermic reactor temperature fixed by the ground rules of the study, the endothermic reactor temperatures and operating pressures for the systems based on the three reactions were selected by the following method. Using the ratios of elements present in the nominal endothermic or exothermic reaction mixtures, Dr. Hal Marsh ran a computer program that gave equilibrium compositions at a large number of temperatures and pressures. For each reaction, an endothermic temperature and an operating pressure were chosen based on what appeared to be the best compromise between the need to minimize the amount of material circulated and the need to minimize the end-to-end temperature drop. A more quantitative optimization might have yielded somewhat different parameters.

B. HEAT EXCHANGERS

For gas-to-gas recuperators, an overall heat-transfer coefficient of $56.7 \text{ W/m}^2\text{°C}$ ($10 \text{ Btu/h-ft}^2\text{°F}$) was assumed. The effectiveness-NTU method² was used to estimate heat exchanger sizes.

At the endothermic end, the recuperators for a distributed dish system are subject to design constraints that were not considered in previous studies, which dealt with central heat sources. A study performed by General Electric Corporate Research and Development (Reference 4) addressed a chemical transport system attached to a high-temperature gas-cooled nuclear reactor. In this proposed system, the endothermic reactor was integrated with a power plant. Sensible heat in the reactor exit stream can be recovered in such devices as reheaters, boilers, and feedwater heaters in addition to recuperators. Some of these devices have higher heat-transfer coefficients than gas-to-gas recuperators; some juggling of the relative mass flow rates can be done; and, in any case, some of the equipment would be required as part of the power plant and, thus, its cost would not be included in the chemical system cost.

The solar dish system does not have this design flexibility. The maximum amount possible of sensible heat in the endothermic reactor exit stream must be recycled into the reactor in a gas-to-gas recuperator; furthermore, the entering and exit streams have nearly the same product of mass flow rate and heat capacity, thus requiring the maximum heat transfer area. The situation is not so severe at the exothermic end. Here, heat rates are sufficiently large that some of the sensible heat in the reactor exit stream can be recovered in a waste-heat boiler and used to generate power at a reasonable cost or used in some other way. This can greatly reduce the size of the recuperator required.

²NTU = Number of transfer units, a dimensionless heat exchanger size.

The other major heat exchangers required are the intercoolers for the exothermic reactors. (The cost of these is included in the reactor cost estimate.) Reactor configurations will be discussed in some detail later in this section, but at this point it should be said that the probable configuration of the exothermic reactor is a series of adiabatic packed beds with heat exchangers in between. In these exchangers, heat is withdrawn by a working fluid, and the temperature attainable is influenced by the way in which the intercoolers are connected.

For the purpose of sizing the intercoolers, an overall heat-transfer coefficient of $113.6 \text{ W/m}^2\text{°C}$ ($20 \text{ Btu/h-ft}^2\text{°F}$) was assumed. The film coefficient on the working fluid side should be much higher than that on the reactant side, because such efficient heat-transfer media as helium and boiling water can be used.

It is not possible at this time to say what the heat-exchanger configurations will be. The actual design will depend upon heat-transfer surface cost, area required, and acceptable pressure drop, as well as manufacturing considerations for the entire reactor-recuperator module. An example will illustrate this last point. A proposed design for an endothermic reactor involves two concentric metal pipes with the inside surface of the outer pipe coated with catalyst. Manufacturing problems are minimized if this double-pipe configuration is carried beyond the reactor section to serve as a counterflow double-pipe recuperator. However, the overall heat transfer coefficient for this configuration is lower and the cost per square meter of heat-transfer area is higher than in more efficient designs. More cost-effective heat exchanger performance can be achieved if the individual reactor tubes are manifolded into a larger, single heat exchanger of the shell-and-tube or plate-fin type. But now manifold tubing is required, many more welds that can withstand high temperatures are needed, and the question of repeated thermal cycling of more complex shapes arises. To attempt to answer questions such as these is beyond the scope of this report.

However, in the case of ceramics the "welding" problem, at least, can be solved at low cost. Certain ceramic components can be assembled from already-fired pieces, and the whole module re-fired in a reducing atmosphere to effect the "weld." Because ceramic systems showed the greatest potential from a cost standpoint, a plate-and-fin design rather than a double-pipe was assumed for all recuperators and intercoolers along with counterflow operation. This is the lowest-cost design, and yields the most favorable cost estimates for all systems.

C. REACTORS

Endothermic reactor configurations and cost estimates were taken from several sources. The range of cost estimates for metal systems reflects two design options for the endothermic reactors: packed-bed or wall-coated catalyst. It is not clear at this time which configuration will be selected. The tubular packed-bed reactor is less costly than the wall-coated, but may suffer from heat-transfer problems. Packed-bed reactor size and cost estimates were adapted from those given in References 2 and 4. A wall-coated reactor size estimate

was derived by Yong S. Won of JPL. This was adapted to the systems considered here.

Because ceramic tubing should be inexpensive, the ceramic system cost estimates were based on a wall-coated reactor.

In all cases, the exothermic reactor is a series of adiabatic packed beds, with intercoolers transferring the heat of reaction to a working fluid. The design and construction of the reactor beds is the same for both the metal and ceramic systems, due to the relatively large size of these beds. The difference in cost is due to the difference in estimates for metal and ceramic intercoolers.

Figures 5-1 to 5-3 give more information about the exothermic reactor. The adiabatic beds will consist of a ceramic or cast-iron liner (to resist corrosion) surrounded by a steel or Inconel shell that absorbs the stress due to reactor pressure. Each intercooler is a counterflow plate-and-fin heat exchanger. If the working-fluid streams through the intercoolers are connected in parallel, then the system delivers heat at the nominal T_{exo} . Alternatively, the intercoolers (with respect to the working fluid stream) can be connected in series with the working fluid flowing counter to the reactant stream. Then higher temperatures can be achieved.

Reactor sizing calculations were performed for the sulfur-trioxide system with interesting results: Given the catalyst activities available commercially, the minimum size of the reactor is determined by pressure drop rather than reaction-rate considerations. That is, the minimum diameter of each bed is such that the mass flux is low enough to yield an acceptable pressure drop across the bed. The bed length is chosen as 12 times the catalyst particle diameter. Quick calculations for the methane-reforming systems indicated that approximately the same reactor vessel diameter would be required as for the SO_3 system. It was further assumed that the exothermic reactor would be constructed in modules with a capacity of 1 MW per module, and that the catalyst cost would be negligible compared with the reactor vessel and intercooler costs.

D. PIPING NETWORKS

Design of a piping network for a thermochemical transport system requires a system optimization that considers the material and installation costs of piping and insulation, energy losses due to fluid friction in the pipes, and thermal energy losses through the insulation. Algorithms for such an analysis are given by Turner (Reference 12) and Fujita, et al (Reference 13). The effects of various piping arrangements also must be considered, as shown by Biddle, et al (Reference 14).

In a thermochemical system, inputs to the piping optimization will include the endothermic and exothermic pressures and temperatures and the sizes of the recuperators at both ends and of any heat-recovery equipment (these influence the transport-line temperature). Also important are the reactor sizes, which determine the actual--as opposed to equilibrium--extent of reaction at each end of the system. (The extents of reaction, which are also a function of temperature and pressure, determine how much material must circulate through the pipes to transport a given amount of energy.)

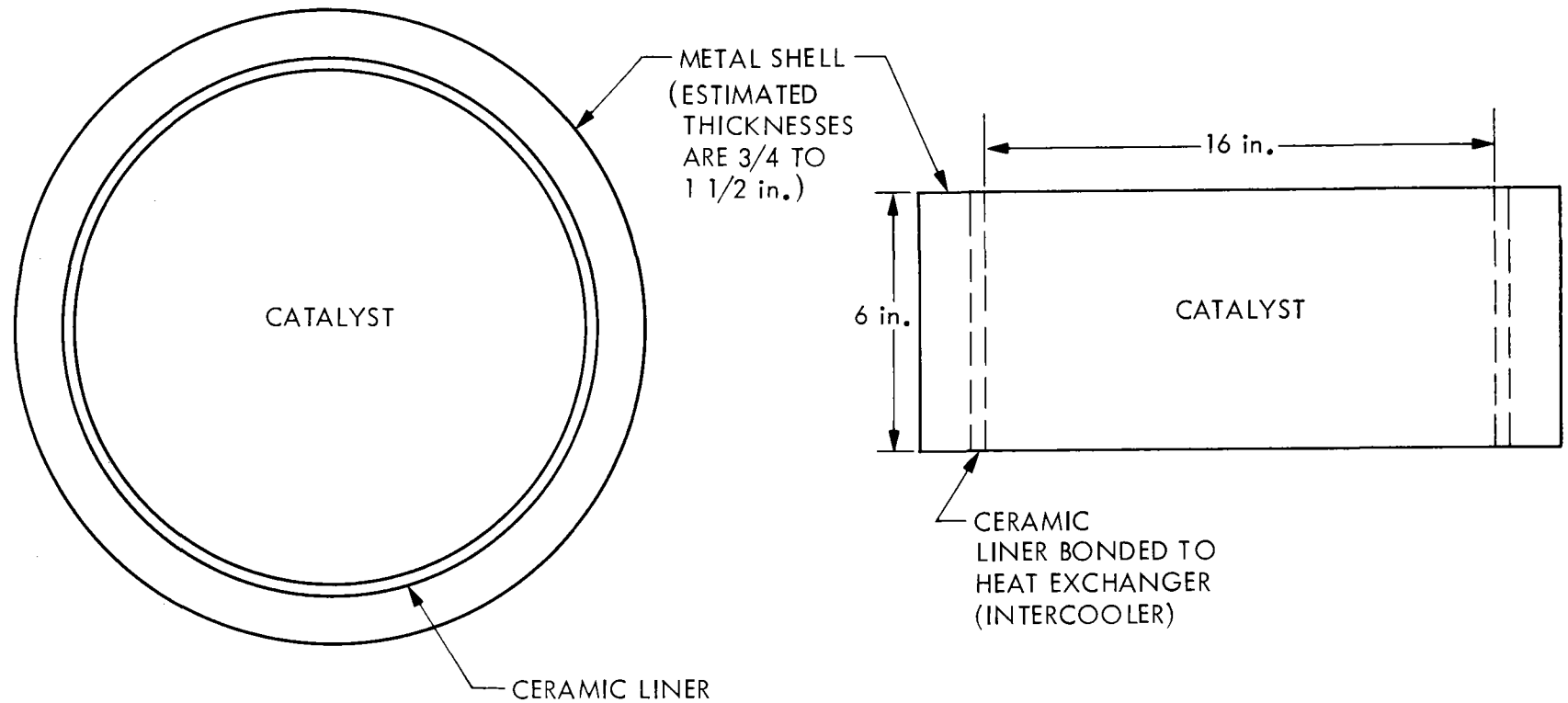


Figure 5-1. Exothermic Reactor Bed

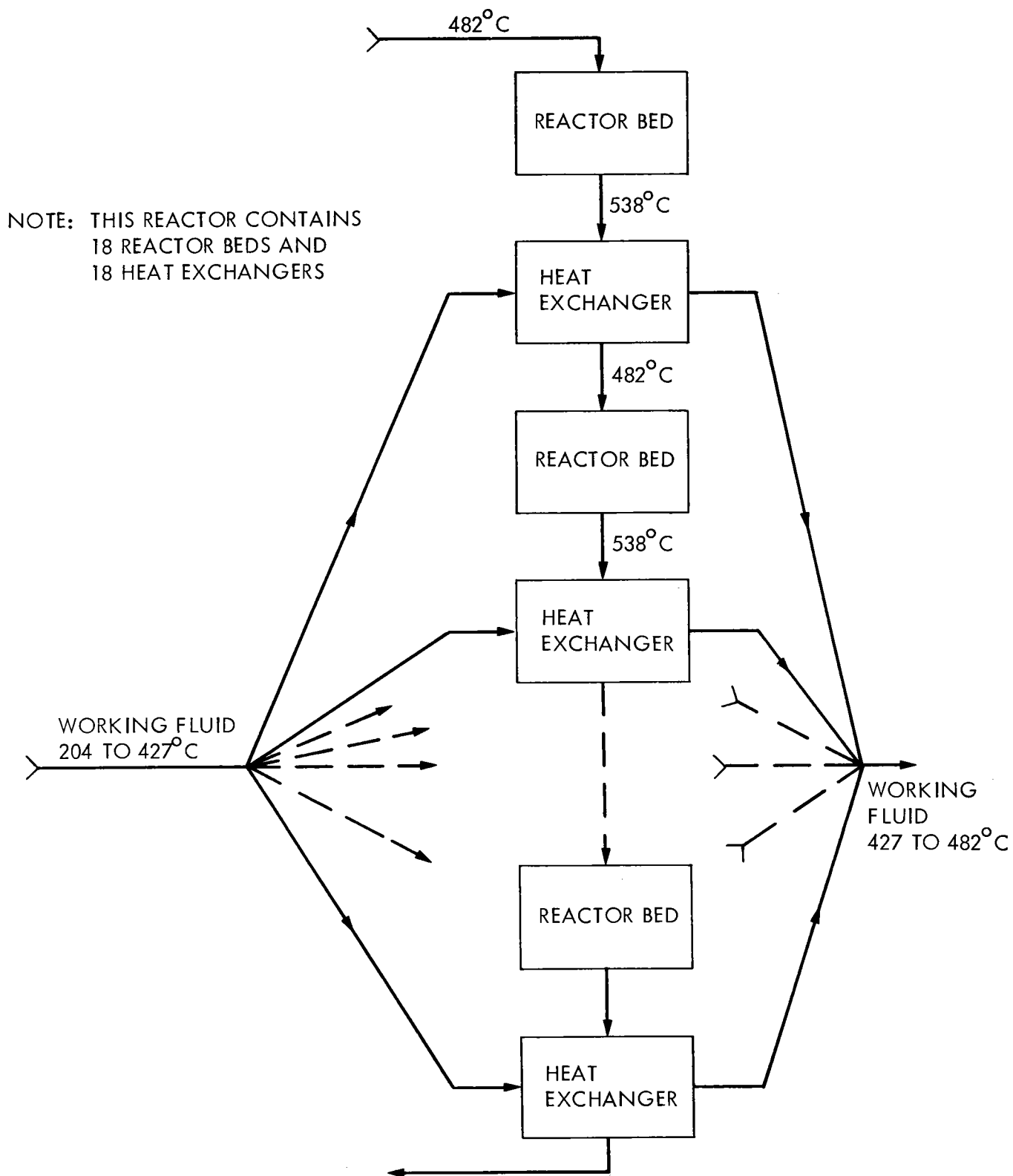


Figure 5-2. Exothermic Reactor Configuration, SO_3 System, Output Temperature Near T_{exo}

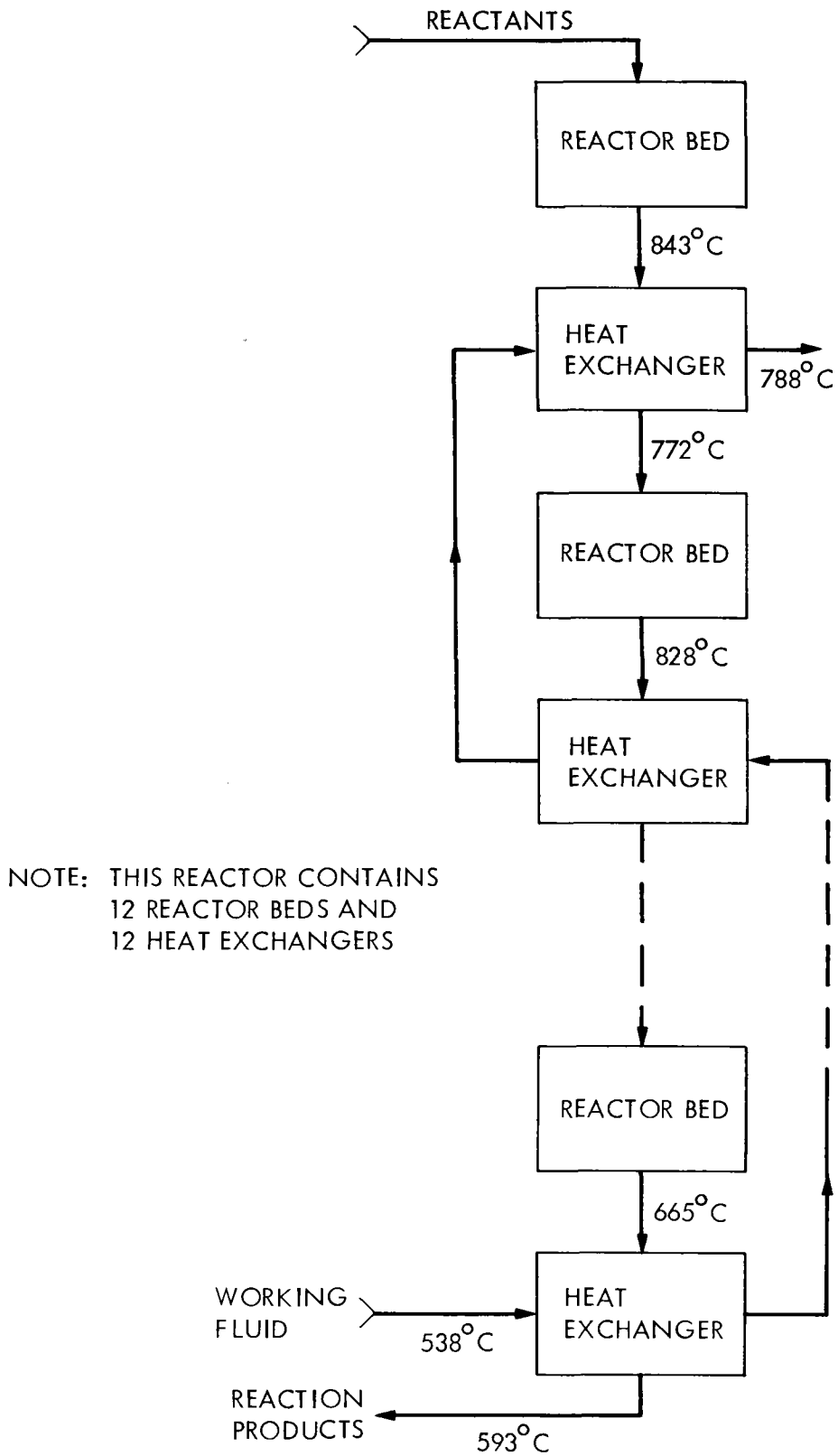


Figure 5-3. Exothermic Reactor Configuration, SO₃ System, Maximized Output Temperature

The above references, as well as a paper by Biddle, Revere, and Fujita (Reference 15) contain cost estimates for sensible and latent heat transport systems using steam and molten salts. Several of these estimates for systems delivering energy at 510°C are lower than 39 \$/kW_T, which is the lowest cost estimate reported in this study for a ceramic system without a piping network.

E. SOME SYSTEM TRADE-OFFS

1. Recuperator Effectiveness

The trade-off here is between heat exchanger cost, transport costs, and the need to take part of the collected energy as electricity rather than as the desired process heat. The temperature of the "cold" line is fixed at the lowest temperature at which condensable substances will not condense. Then the hot line temperature is determined by the size of the endothermic recuperator. A larger such recuperator results in lower transport costs, but is more expensive. A precise trade-off could not be performed because of time limitations. An effectiveness of 90% was selected for the endothermic recuperators because, at this level, further increases in effectiveness are bought at the expense of massive increases in area. This implies that transport lines will not be run at ambient temperature.

The other trade-off is between exothermic recuperator effectiveness and the size of the waste-heat recovery equipment. A larger recuperator cycles more heat back into the reactor and therefore less is processed by the heat-recovery equipment, which is thereby reduced in size. The exothermic recuperator effectiveness was chosen as 75% for the metal systems and 90% for the ceramic systems. The difference is due to the lower cost of ceramics, which favors large recuperators and smaller-capacity heat recovery equipment.

2. Endothermic Temperature

Table 5-1 compares two sulfur-trioxide systems, one with $T_{\text{endo}} = 1027^{\circ}\text{C}$ (the baseline) and the other with $T_{\text{endo}} = 827^{\circ}\text{C}$. The result obtained here should be applicable to all thermochemical transport systems.

It is seen that the lower conversion obtained at the lower endothermic temperature results in much larger mass flow rates in the system. This, in turn, results in higher costs, primarily due to larger heat exchangers. Although the piping network was not included in this study, its cost will also increase substantially.

3. Varying Pressure

The temperature drop between the endothermic and exothermic reactors can be reduced, and mass flow rates may also be reduced if the two reactors are run at different pressures. The endothermic reaction involves an increase in the number of moles of gas and is therefore favored by low pressure. The exothermic reaction is favored by higher pressure. A compressor can be added to the system to provide the desired pressure levels.

However, any gains made by doing the above are consumed by compressor work losses and compressor costs. Figure 5-4 is a schematic of a varying-pressure system, and Table 5-2 shows the cost and performance.

Table 5-1. SO₃ Dissociation System with T_{exo} = 627°C. (Comparison of system with T_{endo} = 827°C and system with T_{endo} = 1027°C -- all other parameters equal.)

T _{endo}	Moles/s from endothermic reactor				Moles/s from exothermic reactor			
	SO ₂	SO ₃	O ₂	Total	SO ₂	SO ₃	O ₂	Total
827°C	535.2	483.8	267.6	1286.6	153.4	865.6	76.7	1095.7
1027°C	413.1	86.9	206.6	706.6	75.3	424.8	37.5	537.6

Note: Lowering the endothermic temperature from 1027 to 827°C almost doubles the volumes of gas to be transported and processed, with expected effects on heat exchanger and piping network costs. To lower the endothermic temperature to 927°C may be more practical.

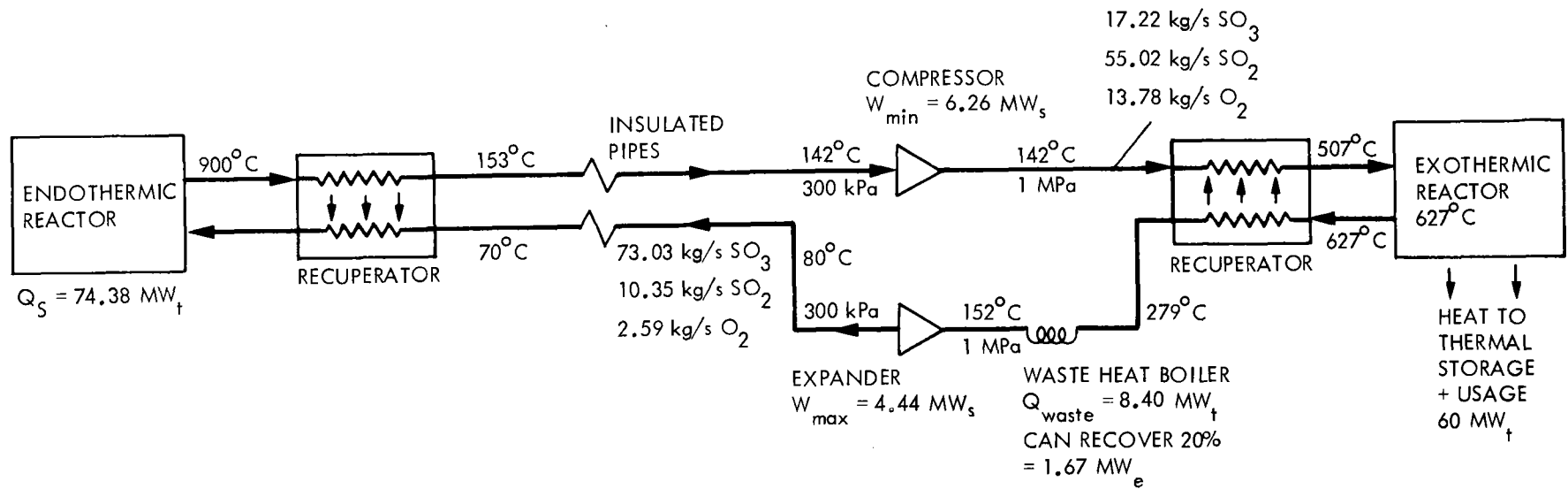
Figure 5-4. Varying-Pressure, SO_3 System

Table 5-2. SO₃ Dissociation System, T_{exo} = 627°C,
Uniform versus Varying Pressure

Type of Components	Type of Pressure Profile	Cost, \$/kW _t	Efficiency, %
Metal	Uniform	213 to 261	93
Metal	Varying	220 to 261	75
Ceramic	Uniform	50 to 94	93
Ceramic	Varying	142 to 181	75

SECTION VI

CONCLUSIONS

The results of the study can now be related to the objectives, as given in Section I and the Foreword.

Cost and performance estimates have been generated for the major components of reversible-reaction transport systems. The costs and energy losses of the piping network for a selected field of dishes will have to be included to arrive at an estimate for a complete system. Results published elsewhere (References 12 through 15) show cost estimates for steam or molten salt transport, in the 510°C range, that are lower than the lowest ceramic system estimate reported in this study. The thermochemical systems have a somewhat more favorable profile of delivery temperature versus units of heat, but unless a specific industrial process can take advantage of this, it seems unlikely that thermochemical transport will have a compelling advantage over sensible-heat transport in this temperature region. Thermochemical system output temperatures can be increased to 790°C and beyond, but the cost is more than doubled. Cost and performance of sensible-heat thermal transport at such temperatures had not been studied at the time this work was done.

It appears that low efficiency is inherent in reversible-reaction storage. For reasons of cost, no previous study has assumed the storage of all reactants as gases. To condense reactants, however, involves a major energy loss due to the heats of vaporization, which are exhausted at very low temperatures. If conversions in the reactors are significantly lower than shown in this report, distillation columns or other separation equipment may be necessary to separate reactants for storage. This will be another severe drain on system efficiency. (See Reference 2.) The low second-law efficiency of a thermochemical transport system, caused by the large end-to-end temperature drop, can be improved by circulating more material through the system. The effect on costs will probably be substantial. The second-law efficiency may also be improved for certain applications by using the cascaded exothermic reactor configuration.

An objective of this study was to identify factors unique to distributed dish systems. Earlier thermochemical transport studies were based on a centralized energy source and delivery to a user many miles away. A solar dish system is different in several ways. The relatively shorter distances make sensible- or latent-heat thermal transport a potentially viable option. In a centralized system, transfer of the sensible heat of the endothermic reactor output to another fluid stream is a possibility; in a distributed receiver system it is not. This imposes major design constraints on endothermic recuperators. Reactions involving solids may be viable candidates for a centralized system, but the equipment necessary to recover heat from solids and to separate solid from gaseous reactants is rather complex. It does not seem likely that such equipment can readily be installed and maintained at each dish.

Given the large volume of earlier reaction screening work, in particular that documented in the Rocket Research report, it is unlikely that any reactions have been overlooked that would yield systems with better performance or lower cost than have been estimated in this and previous studies.

SECTION VII

RECOMMENDATIONS FOR FURTHER WORK

A. STORAGE SYSTEMS

If it is assumed that the only useful product heat is that delivered at or above 427°C, then all of the studies referenced in this report that deal with storage systems with condensable reactants have concluded that roundtrip efficiencies would be below 60%. The present study shows that 60% is probably an upper limit, based on optimistic assumptions about factors that were not analyzed in detail. When actual thermal losses, pressure drops, reactor conversions, etc., are considered, efficiency projections will drop even more.

In view of these discouraging results, it is recommended that the use of reversible reactions for energy storage for dish collector systems not be considered further.

B. TRANSPORT-ONLY SYSTEMS

The present study has generated cost estimates for transport systems using three selected reactions. As indicated above, many factors that would degrade system performance and/or increase cost were not included, or optimistic assumptions were made as to their values.

The next necessary step in assessing the potential of reversible-reaction transport systems is to generate cost estimates for piping networks for both the reversible-reaction systems and "brute force" thermal transport. The piping network plus the installed components evaluated in this report should provide a reasonable estimate of the cost of an entire reversible-reaction transport system. This figure can then be compared with the cost for a thermal transport system.

It must be emphasized that, even if the projected cost of a reversible-reaction transport system appears competitive with thermal transport, a justification for further work has not yet been demonstrated. When actual pressure and temperature drops, reactor conversions, optimal receiver temperatures, and actual manufacturing costs (as opposed to the guesstimates that were the only information available for this study) are considered, system costs may increase significantly. Furthermore, the technical risks are formidable. A functioning reactor for a commercially-sized system has never been built; the components in their lowest-cost form, especially the exothermic reactors, pose some challenging manufacturing problems; and the ceramics technology is in its infancy. Also, the response of the system to transients in heat input is a potential source of trouble that has not been addressed in this study.

If the cost projections for chemical transport systems are not substantially lower than those for thermal systems, it is recommended that no further work be done.

If the chemical-transport costs look highly favorable, then the following studies are recommended:

- (1) One reaction should be chosen for detailed analysis. Because the use of reversible reactions for energy transport is speculative, a relatively small amount of time is all that can be allotted to a study of such a system. The author feels that such an amount of time is better spent if devoted to detailed analysis of one reaction.
- (2) A market study should be done to determine the temperature profiles of process-heat usage in potential user industries. An industry that needs to melt or boil a substance at 427°C, for instance, should be differentiated from one that requires superheated 427°C steam.
- (3) The feasibility of attaching ceramic plate-fin heat exchangers to tubular reactors needs to be established.
- (4) Heat-transfer coefficients and pressure drops for various heat-transfer surfaces need to be calculated, as do conversions and pressure drops for various endothermic and exothermic reactor sizes. These values, along with the associated costs, will provide inputs to a general optimization program, as will corresponding values for the piping network.
- (5) A reasonably detailed design for an exothermic reactor module (as described in the text) should be drawn up, and the feasibility and costs of manufacturing a reactor module should be ascertained.

SECTION VIII

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APPENDIX A

THERMODYNAMIC CALCULATIONS

For each reaction, equilibrium compositions were assumed. These were taken from computer runs performed by Drs. Kalfayan and Marsh or from a concept paper by Dr. Talbot A. Chubb of NRL. Thermodynamic properties were taken from Handbook of Thermodynamic Tables and Charts, by Kuzman Raznjevic, McGraw-Hill Publishing Co.¹ Heats of reaction were computed from data in Molecular Thermodynamics, by R. E. Dickerson.²

The work output of the organic-Rankine heat recovery equipment was estimated in the following manner: The heat input is the enthalpy change of the gases going from the heat-exchanger output temperature to the pipeline temperature. The maximum temperature of the organic working fluid is assumed to be 50°C less than the higher temperature of the inlet gases. The efficiency of the heat-recovery equipment was then assumed to be 55% of the Carnot efficiency of an engine operating between this maximum working fluid temperature and 25°C.

The turbine work associated with the varying-pressure system and the storage systems was computed using equations for isothermal compression and adiabatic expansion of ideal gases. Turbine efficiencies were assumed to be 85%.

Overall system efficiencies were calculated using the formula developed in the Rocket Research Co. report:

$$\eta_{\text{system}} = \frac{Q_0}{Q_S + \sum_i W_i}$$

where Q_S = solar input, Q_0 = thermal output, and W = work terms (positive if work input is required and negative if there is net work output). One unit of work was assumed equal to three units of heat. Pump work to overcome pressure drops in reactors and heat exchangers was not included in this study.

¹ Raznjevic, K.R., Handbook of Thermodynamic Tables and Charts, McGraw-Hill Publishing Co., Washington, D.C., 1976.

² Dickerson, R.E., Molecular Thermodynamics, W. A. Benjamin, Inc., Menlo Park, CA, 1969.

APPENDIX B

COST ANALYSIS

Process equipment peculiar to the systems with storage, such as compressors, drivers, and tanks, was costed using methods in K. M. Guthrie: Process Plant Estimating, Evaluation and Control, Craftsman Publishing Co.¹

For the low-pressure systems, the cost for a packed-bed endothermic reactor was taken from the Rocket Research Company report (Reference 2). The cost for a low-pressure wall-coated reactor was estimated by determining the amount of stainless-steel tubing required for the reactor design developed by Y. S. Won of JPL (see Section V, part C). This turns out to be four times the packed-bed estimate.

The cost for a high-pressure packed-bed reactor was taken from the Chemical Heat Pipe report by General Electric (Reference 4). The cost of a wall-coated reactor was then estimated as four times this value.

Exothermic reactor vessel costs were estimated as twice the bulk material cost of the metal required to fabricate the vessel.

Heat exchanger costs were estimated as $215 \$/m^2$ for metal exchangers for endothermic service and $182.80 \$/m^2$ for exothermic recuperators and intercoolers.

A survey of manufacturers yielded a range of 3.30 to 8.81 $\$/kg$ for fabricated ceramic components. This works out to a range of 21.50 to 53.75 $\$/m^2$ of plate-and-fin heat transfer area.

Cost of organic-Rankine heat recovery equipment was taken from a personal communication from Mike Santucci of Sundstrand Energy Systems to Mr. Toshio Fujita of JPL.

¹ Guthrie, K.M., Process Plant Estimating, Evaluation and Control, Craftsman Publishing Co., Solana Beach, CA, 1974.

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