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JPL PUBLICATION 79-81

# Potential Heat Exchange Fluids for use in Sulfuric Acid Vaporizers

D.D. Lawson  
G.R. Petersen

(NASA-CR-162548) POTENTIAL HEAT EXCHANGE  
FLUIDS FOR USE IN SULFURIC ACID VAPORIZERS  
(Jet Propulsion Lab.) 16 p HC A02/MF A01

CSCL 20D

N80-14358

Unclas  
G3/34 46430

October 1, 1979

Prepared for  
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Through an agreement with  
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## ABSTRACT

A series of liquids have been screened as candidate heat exchange fluids for service in thermochemical cycles for hydrogen production that involve direct contact of the fluid with sulfuric acid and vaporization of the acid. The required chemical and physical criteria of the liquids are described and the results of some preliminary high temperature test data are presented.

TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. JPL Pub. 79-81	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle POTENTIAL HEAT EXCHANGE FLUIDS FOR USE IN SULFURIC ACID VAPORIZERS		5. Report Date October 1, 1979	
		6. Performing Organization Code	
7. Author(s) D. D. Lawson, G. R. Peterson		8. Performing Organization Report No.	
9. Performing Organization Name and Address JET PROPULSION LABORATORY California Institute of Technology 4800 Oak Grove Drive Pasadena, California 91103		10. Work Unit No.	
		11. Contract or Grant No. NAS 7-100	
		13. Type of Report and Period Covered JPL Publication	
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Prepared by JPL for the U.S. Department of Energy through an agreement with NASA (ET-78-I-01-3112)			
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17. Key Words (Selected by Author(s)) Chemical Engineering Energy Production Physical Chemistry		18. Distribution Statement  Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 15	22. Price

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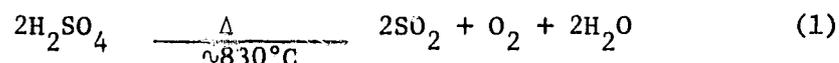
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SECTION I  
INTRODUCTION

In a number of thermochemical cycles under active investigation for hydrogen production, the oxygen release step is the thermal decomposition of sulfuric acid ( $H_2SO_4$ ):\*



It has been suggested that direct fluid contact heat exchange with  $H_2SO_4$  would have energy saving benefits over a conventional heat exchanger in the vaporization of  $H_2SO_4$  at  $\sim 330^\circ C$  before the high temperature cracking or decomposition step at  $\sim 830^\circ C$  (Reference 1).

Direct contact heat exchange occurs when two immiscible fluids at different temperatures are mixed. When one of the two fluids undergoes a change of phase, extremely high heat transfer rates result (References 2 and 3). In this preliminary work, the physical and chemical requirements of liquids in contact with  $H_2SO_4$  have been examined at temperatures up to the boiling point of the acid. Some candidate materials are proposed for high temperature heat transfer by direct fluid contact.

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\*The thermochemical cycles are General Atomic/Sulfur-iodine Cycle, Westinghouse/Hybrid Sulfur Cycle, and Euratom/Mark 13 Hybrid Sulfur Bromine Cycle.

SECTION II  
SELECTION OF MATERIALS

Liquids used for heat exchange in contact with  $H_2SO_4$  must meet the following criteria:

1. Liquids must be chemically stable to concentrated sulfuric acid in the temperature range of 300 to 400°C for the required service periods.
2. Liquids must have very low miscibility with sulfuric acid at use temperatures.
3. Liquids must have low vapor pressure at use temperature to prevent loss by vaporization.

It is also desirable that they should be liquid at room temperature and not be high in cost.

Since the contact is being made with hot concentrated sulfuric acid, most organics are not suitable because of reactivity with the acid. Thus, because of the inertness of fluorine substituted organic materials, they were selected for evaluation. Under very strong acidic conditions, aliphatic fluorocarbons should be stable because of the very high heats of formation of the carbon-fluorine bond. However, previous experience has indicated that other fluorinated compounds may be suitable, so perfluoro(propylene oxide) polymers, tertiary butyl amine and a chloro-trifluoro alkane were tested.

SECTION III  
EXPERIMENTAL

All compounds tested are perhalocarbons and a brief summary of their known physical and chemical properties is given in Table 1. All the thermal testing (except for several early runs) was done in fused quartz vessels because of the attack of concentrated sulfuric acid at high temperatures on Pyrex glass, and lack of thermal stress in quartz. Two types of thermal testing were conducted:

1. Refluxing sulfuric acid and the liquid was carried out in a quartz cylinder about 6 cm in diameter and about 20 cm in height, closed with a 100 ml Pyrex beaker. Any evolution of hydrogen fluoride was detected by etching of the beaker. The reflux apparatus with beaker in place is shown in the following figure:



2. One material, Fomblin U, was tested in a sealed tube. To a quartz tube of 1.25 cm I.D. (2mm thick walls) and 15 cm length was added 0.4 ml of Fomblin U and 0.4 ml of concentrated  $H_2SO_4$ . The tube was then sealed and heated in a muffle furnace for 6 hours at 370° to 400°C.

Only Fomblin U was tested in this manner because of concern the tube might break due to high vapor pressure of the compound or decomposition products. Table II gives a summary of the test results. The Fomblin liquids appear to be the most promising. Fomblin U was given the most rigorous treatment and infrared spectral analysis showed no detectable structural alterations, although evolution of hydrogen fluoride was detected.

In order to evaluate miscibility, Fomblin U tested in the refluxing quartz cylinder experiment was analyzed for sulfuric acid content by titration. It was found that the sample contained less than 0.1 mg acid per ml of Fomblin. The acid was most likely present as a suspension in the Fomblin, because when a drop of this material was placed on moistened pH paper, the acidity color change appeared as small isolated spots.

All infrared spectra were obtained with a Perkin-Elmer Infracord Model 137 using sodium chloride cells.

Table 3-1. Summary of Chemical and Physical Properties of Candidate Heat Transfer Liquids

Material Trade Name	Chemical Type	B.P. 760 mm	Vapor Pressure mm of Hg (at 25°C)	Solubility Parameter (at 25°C)	Source
Fluorolube 300/140	A low mol. wt. Polymer of ClFC=CF <sub>2</sub>	Above decomp temp.	Less than 1 mm	7.2	Hooker Chemical Corp. Niagara Falls, N.Y.
Medifluor FC-47	Perfluoro-tributylamine	183°C at 760 mm	2.5 mm	5.9	3M Co. Medical Product Div.
Freon E-4	Perfluoro (propylene oxide) polymer	193°C	~1 mm at	5.5	DuPont Freon Products Division
Flutec Liquid	Perfluoro-cyclic/hydrocarbon	200°C	Less than 1 mm	~5.8	ISC Chem. Ltd. Avonmouth, England
Fomblin L MW ~ 1800	Perfluoro (propylene oxide) polymer	170-410°C at 3mm	~3.5 mm	~5.8	Montecatini-Edison Italy
Fomblin U	Perfluoro (propylene oxide) polymer	Above decomp temp.	~0.06 mm	~5.8	Montecatini-Edison Italy

Table 3-2. Characteristic Results of High Temperature Contact Between Concentrated H<sub>2</sub>SO<sub>4</sub> and Selected Fluorocarbons\*

Fluorocarbon (Tradename)	Max Temp. attained (°C)	Hours of high temp H <sub>2</sub> SO <sub>4</sub> contact	Differences in IR Spectra before and after	Evidence of HF Evolution +	Comments, notes
1. Fluorolube	285 -300	93	Yes; CH and C=O stretches found	Yes	V. viscous at room temp. waxy after reflux
2. Mediflour	189	93	No change	Yes	All dis-tilled after 93 hrs. of reflux
3. Freon E-4	200	90	No change	No	All dis-tilled after 90 hrs.
4. Flutec PP7	190	240	No change	No	All dis-tilled after 240 hrs.
5. Fomblin L	310	96	No change	Yes	
6. Fomblin U	317	96	No change	Yes	
7. Fomblin U	400	6	No change	Yes	Carried out in sealed quartz tube (see experi-mental sec-tion)

+ Etching of pyrex covers or reflux column observed.

\* All mixtures (1-6) contained equal aliquots (10-15 ml) of concentrated H<sub>2</sub>SO<sub>4</sub> and the fluorocarbon. Mixtures 2-4 could not be pushed beyond these temperature plateaus. Temperature was measured by suspending a 360°C thermometer into the fluid just above the bottom of the vessel.

## SECTION IV

### DISCUSSION

This preliminary study indicates that it is possible to have stable liquids in the temperature range at which concentrated sulfuric acid is a vapor. The most promising candidate materials are the perfluoropropylene oxide polymers with a degree of polymerization (DP) of  $\sim 10$  to 50. It is desirable to have the DP in the high range because the vapor pressure of the material will decrease as the DP is increased, resulting in higher operating temperatures.

Immiscibility is important, since it minimizes the transport of  $H_2SO_4$  by the heat exchange fluid to the system heat source. Because the solubility parameters of these fluids are low, the solubility in acid should be very slight. (The solubility parameter of  $H_2SO_4$  at 298K is 18.0.)

The experiments showed very little acid was present in Fomblin U at room temperature, but there was concern that mutual solubility may increase at higher temperatures. Although the difference in solubility parameters is high and therefore immiscibility is expected, a more quantitative estimate of the degree of mutual solubility at the operating temperature can be obtained from the following approximate relationship (Reference 4).

$$\frac{1}{2} (V_1 + V_2) (\delta_1 - \delta_2)^2 > 2 RT \text{ when } V_1 \neq V_2$$

which indicates that mutual solubility will be low if the expression on the left is greater than 2 RT. At  $T = 603^\circ$ , the boiling point of  $H_2SO_4$ , 2 RT is 2395, and  $V_1$ ,  $V_2$ ,  $\delta_1$  and  $\delta_2$  are approximately 50,

2550, 15.5 and 5.0, respectively, (where the subscript one refers to  $H_2SO_4$  and two to Fomblin U). Using these values in the above relationships gives:

$$1.4 \times 10^5 > 2395$$

or a ratio of 58 to 1, which indicates that Fomblin U and sulfuric acid should be immiscible at the operating temperature.

The possible problem areas of the fluorocarbon fluids are:

1. The commercial polymer liquid materials are not pure compounds and tend to evolve hydrogen fluoride during the first hour or so on contact with sulfuric acid at these temperatures (Reference 5). A pretreatment with sulfuric acid may eliminate this problem.
2. Highly fluorinated fluids may react violently with metals such as aluminum and magnesium and their alloys under conditions where fresh active metal surfaces are created. Therefore, the system should be designed to avoid this condition and to avoid corrosive contamination of sulfuric acid.
3. The perfluoroethers are decomposed by halogenated Lewis acids such as  $AlCl_3$ ,  $SbF_5$ , and  $CoF_5$ , but are stable to oxygen or ozone. Therefore any use in other thermochemical cycles besides service with sulfuric acid should be evaluated with this in mind.

Since these tests were carried out with relatively pure materials, in contact with only quartz or pyrex, potential contamination with any other materials might have an adverse affect on stability or reactivity of sulfuric acid and heat transfer fluid.

The Fomblin compounds tested were only two of a series. It is likely that the other Fomblins will exhibit similar characteristics and are also worthy of some further consideration.

#### REFERENCES

1. Private communications from Dr. Armando Broggi, EURATOM, ISPRA (Varese) Italy, on August 1978 and March 1976.
2. Sideman, S., and Shabak, H., Can. J. of Chem. Eng., June 1954.
3. Sideman, S., "Direct Contact Heat Transfer Between Immiscible Liquids; Advances in Chemical Engineering;" Academic Press, New York, N.Y., Vol. 6, pp. 207-268, 1966.
4. Hildebrand, H. H. and Scott, R. L., The Solubility of Non-Electrolytes; 3rd Edition, Reinhold, New York, p. 253, 1952.
5. Literature on the Montecatini-Edison FOMBLIN fluorinated fluids may be obtained from PCR Inc., P.O. Box 1466, Gainesville, FL 32602.