Potential Heat Exchange Fluids for use in Sulfuric Acid Vaporizers

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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.
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.
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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 (H₂SO₄): *

\[
2\text{H}_2\text{SO}_4 \xrightarrow{\Delta \text{at } 830^\circ C} 2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O}
\]  

(1)

It has been suggested that direct fluid contact heat exchange with H₂SO₄ would have energy saving benefits over a conventional heat exchanger in the vaporization of H₂SO₄ at \(~330^\circ C\) before the high temperature cracking or decomposition step at \(~830^\circ C\) (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 H₂SO₄ 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.

*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 $\text{H}_2\text{SO}_4$ 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 H₂SO₄. 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 cyclinder 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>
<thead>
<tr>
<th>Material Trade Name</th>
<th>Chemical Type</th>
<th>Vapor Pressure mm of Hg (at 25°C)</th>
<th>Solubility Parameter (at 25°C)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorolube 300/140</td>
<td>A low mol. wt. Polymer of ClFC=CF₂</td>
<td>Above decomp temp.</td>
<td>Less than 1 mm</td>
<td>7.2</td>
</tr>
<tr>
<td>Medifluor FC-47</td>
<td>Perfluorotributylamine</td>
<td>183°C at 760 mm</td>
<td>2.5 mm</td>
<td>5.9</td>
</tr>
<tr>
<td>Freon E-4</td>
<td>Perfluoro (propylene oxide) polymer</td>
<td>193°C</td>
<td>&quot;&lt;1 mm at</td>
<td>5.5</td>
</tr>
<tr>
<td>Flutec Liquid</td>
<td>Perfluorocyclic/hydrocarbon</td>
<td>200°C</td>
<td>Less than 1 mm</td>
<td>&quot;&lt;5.8</td>
</tr>
<tr>
<td>Fomblin L MW ~ 1800</td>
<td>Perfluoro (propylene oxide) polymer</td>
<td>170-410°C at 3mm</td>
<td>&quot;&lt;3.5 mm</td>
<td>&quot;&lt;5.8</td>
</tr>
<tr>
<td>Fomblin U</td>
<td>Perfluoro (propylene oxide) polymer</td>
<td>Above decomp temp.</td>
<td>&quot;&lt;0.06 mm</td>
<td>&quot;&lt;5.8</td>
</tr>
</tbody>
</table>
Table 3-2. Characteristic Results of High Temperature Contact Between Concentrated H₂SO₄ and Selected Fluorocarbons*

<table>
<thead>
<tr>
<th>Fluorocarbon (Tradename)</th>
<th>Max Temp. attained (°C)</th>
<th>Hours of high temp H₂SO₄</th>
<th>Differences in IR Spectra before and after</th>
<th>Evidence of HF Evolution</th>
<th>Comments, notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fluorolube</td>
<td>285 -300</td>
<td>93</td>
<td>Yes; CH and (==O) stretches found</td>
<td>Yes</td>
<td>V. viscous at room temp, waxy after reflux</td>
</tr>
<tr>
<td>2. Mediflour</td>
<td>189</td>
<td>93</td>
<td>No change</td>
<td>Yes</td>
<td>All distilled after 93 hrs. of reflux</td>
</tr>
<tr>
<td>3. Freon F-4</td>
<td>200</td>
<td>90</td>
<td>No change</td>
<td>No</td>
<td>All distilled after 90 hrs.</td>
</tr>
<tr>
<td>4. Flutec PP7</td>
<td>190</td>
<td>240</td>
<td>No change</td>
<td>No</td>
<td>All distilled after 240 hrs.</td>
</tr>
<tr>
<td>5. Fomblin L</td>
<td>310</td>
<td>96</td>
<td>No change</td>
<td>Yes</td>
<td>Carried out in sealed quartz tube (see experimental section)</td>
</tr>
<tr>
<td>6. Fomblin U</td>
<td>317</td>
<td>96</td>
<td>No change</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>7. Fomblin U</td>
<td>400</td>
<td>6</td>
<td>No change</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

* All mixtures (1-6) contained equal aliquots (10-15 ml) of concentrated H₂SO₄, 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.

+ Etching of pyrex covers or reflux column observed.
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 ~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 H₂SO₄ 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 H₂SO₄ 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).

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

which indicates that mutual solubility will be low if the expression on the left is greater than 2 RT. At T = 603°, the boiling point of H₂SO₄, 2 RT is 2395, and V₁, V₂, \(\delta_1\) and \(\delta_2\) are approximately 50,
2550, 15.5 and 5.0, respectively, (where the subscript one refers to H₂SO₄ 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 AlCl₃, SbF₅, and CoF₅, 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.


5. Literature on the Montecatini-Edison FOMBLIN fluorinated fluids may be obtained from PCR Inc., P.O. Box 1466, Gainesville, FL 32602.