REPORT NO. 99-10600/12

RECOMMENDED MATERIALS OF CONSTRUCTION

PROJECT NO. 99-10600
PROCEESS DESIGN AND COST
ESTIMATION OF CRITICAL EQUIPMENT
IN THE BIOMASS TO ETHANOL PROCESS

NATIONAL RENEWABLE ENERGY LABORATORY
GOLDEN, COLORADO
SUBCONTRACT NO. ACO- 9-29067-01

DATE: FEBRUARY 3, 2000

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1. INTRODUCTION

National Renewable Energy Laboratory (NREL) requested information concerning the metallurgy required for various process conditions being considered in converting wood chips to ethanol via dilute sulfuric acid hydrolysis. NREL was also concerned with determining the price difference in reactor costs for the different metallurgies. Harris Group Inc. (HGI) researched available corrosion information provided by NREL, the Nickel Development Institute (NiDI) and other published information. With the help of Paul Dillon of C.P. Dillon and Associates, HGI chose specific metals for corrosion testing. HGI retained InterCorr International Inc., to do corrosion testing and Paul Dillon to help analyze the data. Corrosion studies were conducted at three different process temperatures and three different concentrations of acid with six different alloys.

2. SUMMARY

Corrosion testing done on various metals with varying temperatures and strengths of dilute sulfuric acid revealed the following:

- Reactors with operating temperatures of 210 °C at acid strengths near 1.5% and above require zirconium metallurgy.
- For operating conditions near 0.6% acid concentration and 190° C, Alloy 825 metallurgy would be required.
- For concentrations at 2.5% acid and operating conditions of approximately 80° C, Alloy 825 would be required.

The price of zirconium is roughly twice that of Alloy 825. The operating conditions listed in Table 3 highlight the substantial difference in the material and fabrication costs.

3. DISCUSSION

NREL is looking at a number of different processes to convert wood to ethanol. The combinations of high temperatures and dilute sulfuric acid raised questions about what sort of metallurgy would be required. HGI reviewed some early NREL corrosion testing, testing in literature and information provided by the Nickel Development Institute. With this information and the help of Paul Dillon of C. P. Dillon and Associates, six metals were chosen for testing at 3 different temperatures and acid concentrations. (See Table 2.) The solution temperatures and concentrations were based on the information provided in Table 1. This information was provided in a September 18, 1999 fax. The process equipment layout was based on the following PFD's:

- PFD-P100-A201 Revision D
- PFD-P202-A201 Revision A
- PFD-P301-A201 through A204 Revision C

Table 1: Process conditions

Condition	Temperature °C	% Sulfuric Acid	Residence Time (minutes)
Process 100 Stage 1			
Presteamer	100	0	Unknown
Reactor	175	0.8	10
Process 200 Stage 1			
Presteamer	100	0	Unknown
Reactor	183	0	9
Process 300 Stage 1			
Impregnator	20	0.8	Unknown
Reactor	185-190	0.5	4
Process 300 Stage 2			
Impregnator	80	2.5	Unknown
Reactor	210	1.7	2

InterCorr International Inc. performed the corrosion testing, and Paul Dillon assisted with the analysis. Tennessee Valley Authority provided solutions for the testing from actual cooks. The 2.5% concentration was prepared from the 0.6% solution by adding sulfuric acid to bring it to the desired percentage. No de-aeration was done to the solution during testing.

The test results are shown in Table 2. (The detailed test reports can be found in the appendix in both the January 18, 2000 letter from C.P. Dillon and Associates and the January 21, 2000 report from InterCorr.)

The alloys in Table 2 are in an order of increasing price. The metallurgy was first chosen based on low corrosion rates in terms of mils per year, mpy, (preferably below 5 mils per year) and no corrosion pitting. Then price and fabrication costs are considered. The corrosion results in Table 2 were quite definitive. For the 2.5 % @ 80 °C test Alloy 825 appears to be the best selection. No pitting was experienced under this condition. The corrosion rate is the lowest of the allowable metals and the price is the lowest as well. For higher temperatures as seen with the 1.5% Acid and 210° C test, zirconium is the best alloy. It also showed no pitting. For the 0.6% Acid @ 190 ° C test solution, Alloy 825, though a bit high on the corrosion rate in terms of mpy, showed no pitting. It is recommended over the zirconium due to its price difference and very close corrosion rates.

Table 2: Corrosion Test Results

Conditions	2.5 % acid @ 80 °C		1.5% Acid @ 210 ° C		0.6 % Acid @ 190 ° C	
Corrosion Rate	mpy	Pitting	mpy	Pitting	mpy	Pitting
Alloy 20 CB3	16	0	800+	3	14	0
Alloy 825	3	0	400+	3	8	0
Alloy G-30	3	0	400+	2	7	Less than 1
Alloy C276	6	0	50	0	15	0
Alloy 2000	4	0	140	0.5	11	0.5
Zirconium 702	Not run	N/A	5	0	6	0

The suggested metallurgy has been added to the Process Conditions in Table 3. The metallurgy factor for the material relative cost per square foot and a 150 PSIG design pressure has been included for each vessel. The relative strengths of the materials are taken into account for the metals considered and therefore the wall thickness may vary between metals. A fabrication factor is also included. Fabrication varies due to the difficulty in working with certain metals. These numbers are based on data from March of 1984 from Cosmos Minerals Corporation in Carmarillo, CA. (See appendix.) Due to variability in the price of metals and the age of the charts, the factors are relative numbers only and should not be used to calculate actual vessel costs. Budget numbers will be quoted by vendors for actual costs.

Table 3: Condensed Process Conditions

Condition	**Temperature °C**	**% Sulfuric Acid**	**Recommended Metallurgy**	**Relative Cost /Sq. Ft.**	**Fabrication Factor**
Process 100 Stage 1					
Presteamer	100	0	316 L SS	0.29	0.6
Reactor	175	0.8	Alloy 825	1.4	1.16
Process 200 Stage 1					
Presteamer	100	0	316 L SS	0.29	0.6
Reactor	183	0	316 L SS	0.29	0.6
Process 300 Stage 1					
Impregnator	20	0.8	316 L SS	0.29	0.6
Reactor	185-190	0.5	Alloy 825	1.4	1.16
Process 300 Stage 2					
Impregnator	80	2.5	Alloy 825	1.4	1.16
Reactor	210	1.7	Zirconium	2.87	2.46

The residence time in the vessels will also influence the relative price. Smaller vessels with less residence time will have a higher cost per volume than larger vessels.

4. CONCLUSIONS

The recommended metals for the process conditions are shown in Table 3. Lower acid concentrations or low temperatures with higher acid concentrations will make significant difference in metallurgy required for the different process conditions. If hydrolysis conversion results are similar, vessel pricing should be considered when determining which acid hydrolysis process to pursue.

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MEMORANDUM

TO: Ms. Andrea Slayton, Harris Group, Seattle, WA

COPY TO: Dr. Julio Moldanado, InterCorr International

SUBJECT: Corrosion Testing Results in NREL Solutions

DATE: January 18, 2000

INTRODUCTION: In accordance with your recent request, I have review the results of the laboratory corrosion tests conducted by Dr. Moldanado relative to the proposed process for conversion of biomasses to ethanol in the presence of dilute sulfuric acid at elevated temperatures. My observations and conclusion are as follows.

OBSERVATIONS: Tests of 24-hours duration were conducted at 190°C (375°F) and 210°C (410°F)in actual NREL solutions of 0.6% and 1.5% sulfuric acid concentration. A solution in which the acid concentration was artificially raised to 2.5% H_2SO_4 was also tested at 80°C (175°F). Following are general corrosion rates in mils per year (mpy) and pit depth in mils in 24 hours.

ALLOYS	2.5% H_2SO_4	1.5% H_2SO_4		0.6% H_2SO_4	
	80°C	210°C		190°C	
	mpy	mpy	Pitting	mpy	Pitting
Alloy 20Cb3	16	800+	3	14	0
Alloy 825	3	400+	3	8	0
Alloy G-30	3	400+	2	7	<1
Alloy C276	6	50	0	15	0
Alloy 2000	4	140	0.5	11	0.5
Zirconium 702	Not run	5	0	6	0

It should be noted that pit depth cannot be extrapolated to an annual rate (as one can with general corrosion) because pits may be arrested as new pits are incurred at other sites. Nevertheless, pitting and crevice corrosion indicate potential problems in the long run.

CONCLUSIONS: In the 80°C liquor at 2.5% H_2SO_4, Alloys 825 and G30 appear to be the obvious choices, with rates of <5 mpy. The latter may cost a little more and probably adds little in the way of improved resistance.

With 0.6% H_2SO_4 at 190°C, alloy 825 (UNS N08825) or Alloy G-30 look to be acceptable (with an adequate corrosion allowance) and would be far less expensive than zirconium (R70200). However, only the alloy 825 is devoid of pitting. The higher rates for Ni-Cr-Mo alloys suggest the presence of organic compounds capable of complexing nickel, such as amines. Also, it should be noted that even a rate of 5-6 mpy for zirconium *might* be unacceptable because of possible hydriding. Although the actual metal loss for zirconium is small, absorption of nascent atomic hydrogen at the local cathodes may cause hydriding, embrittlement and generally unacceptable mechanical properties.

Obviously, none of the superaustenitic alloys are resistant with 1.5% H_2SO_4 at 210°C. Alloy C276 is more resistant to pitting and crevice corrosion under these conditions than are the other nickel-rich alloys but is unacceptable in terms of general corrosion. Zirconium remains a possibility even under these rigorous conditions.

I believe the alloys of choice are Alloy 825 and Alloy G30, subject to actual experience and evaluation.

If we can be of further service, please call on us.

Respectfully submitted.

C.P. Dillon

C.P. Dillon