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Organic Rankine-Cycle Power Systems Working Fluids Study: Topical Report No. 1 – Fluorinol 85

M. L. Jain, J. C. Demircian, and R. L. Cole

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ORGANIC RANKINE-CYCLE POWER SYSTEMS
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TOPICAL REPORT NO. 1 -- FLUORINOL 85

by

M.L. Jain, J.C. Demirgian,* and R.L. Cole

Energy and Environmental Systems Division
Systems Engineering and Technology Group

September 1986

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11

CONTENTS

ACKNOWLEDGMENTS	vi
ABSTRACT	1
1 INTRODUCTION	1
2 EXPERIMENTAL APPARATUS	6
2.1 Working Fluid Loop	7
2.2 Fluid Heating Section	15
2.3 Heat Rejection System	16
2.4 Instrumentation, Controls, and Data Acquisition Systems	16
3 ANALYTICAL TECHNIQUES AND PROCEDURES	17
3.1 Gas Chromatography	17
3.2 Mass Spectrometric Gas Analysis	19
3.3 Ion Chromatographic Analysis	20
4 SUMMARY OF DYNAMIC LOOP OPERATIONS	21
4.1 Test Run No. 1	21
4.2 Test Run No. 2	23
4.3 Test Run No. 3	23
4.4 Test Run No. 4	25
4.5 Summary of Fluid Temperatures by Liquid Sampling Intervals	26
4.6 Summary of Operational Problems	27
5 DISCUSSION OF RESULTS	33
5.1 Results of Gas Chromatographic Analyses	33
5.2 Results of Mass Spectrometric Analyses	44
5.3 Results of Ion Chromatographic Analysis	48
5.4 Rate of Degradation	48
5.5 Correlation of Degradation Rates and Maximum Fluid Temperature	51
6 CONCLUSIONS AND RECOMMENDATIONS	54
REFERENCES	56
APPENDIX	57

FIGURES

2.1 Flow Schematic of Dynamic Test Loops	6
2.2 Test Cycle on a Temperature-Enthalpy Diagram	7
2.3 Overall View of Test Facility	8

FIGURES (Cont'd)

2.4	View of Evaporator/Superheater Section	9
2.5	View of Section Containing Pump, Condenser, Economizer, and Pressure Reduction Valves	10
2.6	View of Data Acquisition and Control Center	11
2.7	Ideal Test Cycle on a Pressure-Enthalpy Diagram	13
2.8	Schematic Diagram of Sampling Stations	15
3.1	Schematic Diagram of the Rapid Analysis System Used in the Study	18
4.1	Test Run No. 1: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time	28
4.2	Test Run No. 2: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time	29
4.3	Test Run No. 3: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time	30
4.4	Test Run No. 4: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time	31
5.1	Gas Chromatograms for Fluorinol 85 Test Run at 525°F	34
5.2	Gas Chromatograms for Fluorinol 85 Test Run at 550°F	36
5.3	Gas Chromatograms Expanded in the Solvent Tailing Region for Fluorinol 85 Test Run at 550°F	38
5.4	Gas Chromatograms for Fluorinol 85 Test Run at 575°F	40
5.5	Gas Chromatograms for Fluorinol 85 Test Run at 600°F	45
5.6	Increase of Hydrogen as a Function of Time and Temperature	48
5.7	Increase of Carbon Monoxide and Carbon Dioxide as Functions of Time and Temperature	49
5.8	Total Degradation as a Function of Time and Temperature	52
5.9	Correlation of Nonvolatile Degradation Rate with Evaporator Outlet Temperature	53

FIGURES (Cont'd)

A.1	Test Run No. 1: Average Evaporator Outlet Temperature vs. Elapsed Time	63
A.2	Test Run No. 2: Average Evaporator Outlet Temperature vs. Elapsed Time	63
A.3	Test Run No. 3: Average Evaporator Outlet Temperature vs. Elapsed Time	64
A.4	Test Run No. 4: Average Evaporator Outlet Temperature vs. Elapsed Time	64

TABLES

1.1	Rankine Cycle Systems Using Fluorinol 85	4
1.2	Thermal Stability and Materials Compatibility of Fluorinol 85	5
2.1	Design Conditions for Dynamic Loop	12
4.1	Summary of Dynamic Loop Operational Data Using Fluorinol 85 as the Working Fluid	21
4.2	Test Run No. 1: Summary of Dynamic Loop Operational Data	22
4.3	Test Run No. 2: Summary of Dynamic Loop Operational Data	24
4.4	Test Run No. 3: Summary of Dynamic Loop Operational Data	25
4.5	Test Run No. 4: Summary of Dynamic Loop Operational Data	26
4.6	Summary of Temperatures for Each Liquid Sampling Interval	27
5.1	Results of Mass-Spectrometric Analyses of Noncondensable Samples	46
5.2	Results of Gas-Chromatographic Analyses of Liquid Samples Using Alkane and Fluoroalkane Standards	50
A.1	Test Run. No. 1: Summary of Dynamic Loop Operational Data	59
A.2	Test Run No. 2: Summary of Dynamic Loop Operational Data	60
A.3	Test Run No. 3: Summary of Dynamic Loop Operational Data	61
A.4	Test Run No. 4: Summary of Dynamic Loop Operational Data	62

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ORGANIC RANKINE-CYCLE POWER SYSTEMS WORKING FLUIDS STUDY:

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ABSTRACT

An investigation to experimentally determine the thermal stability limits and degradation rates of Fluorinol 85 as a function of maximum cycle temperatures was initiated by the U.S. Department of Energy at Argonne National Laboratory in 1982. Following the design and construction of a dynamic test loop capable of closely simulating the thermodynamic conditions of possible prototypical organic Rankine-cycle (ORC) power systems, several test runs were completed. The Fluorinol 85 test loop was operated for about 3800 h, covering a temperature range of 525-600°F. Both liquid and noncondensable vapor (gas) samples were drawn periodically and analyzed using capillary column gas chromatography, gas chromatography/mass spectrometry, and mass spectrometry. Results to date indicate that Fluorinol 85 would not decompose significantly over an extended period of time, up to a maximum cycle temperature of 550°F. However, 506-h data at 575°F show initiation of significant degradation. The 770-h data at 600°F, using a fresh charge of Fluorinol 85, indicate an annual degradation rate of more than 17.2%. The most significant degradation product observed is hydrofluoric acid, which could cause severe corrosion in an ORC system. Devices to remove the hydrofluoric acid and prevent extreme temperature excursions are necessary for any ORC system using Fluorinol 85 as a working fluid.

1 INTRODUCTION

Recovery of waste heat in an economically acceptable manner from various industrial processes has been a vital facet of U.S. energy policy over the past several years. The Rankine-cycle power system (RCPS), using organic working fluids, has long been recognized as a viable recovery technology. (These systems operate on the Rankine cycle, in which a working fluid is alternately vaporized and condensed using the waste heat and a low-temperature heat sink. The high-temperature, high-pressure fluid is expanded through an expansion turbine to produce mechanical power or electricity.) Typically, an organic Rankine-cycle power system (ORCPS) can utilize single-stage turbines and still achieve higher efficiencies than systems using low-temperature steam, because of the relatively low enthalpy drop and full admission through the nozzle made possible by the high molecular weight of the organic fluid.

However, serious concerns over the long-term thermal stability of organic fluids and effects on system performance, reliability, and overall economic viability have impeded widespread development and deployment of this technology to date. Prototypical systems designed on the basis of thermal stability results of static capsule testing have failed to operate entirely to the satisfaction of their developers. The working fluid must also be compatible with the common materials of construction at system design temperatures. Reliable data are required to establish the maximum possible temperature and the fluid replacement rate. Dynamic loop testing of working fluids of interest could provide such data for system designers. The findings presented here are part of a concerted effort under way to alleviate performance, reliability, and economic concerns and accelerate development and deployment of this technology in the industrial sector of the U.S. economy.

The thermal stability of an organic fluid is a general term to describe the ability of the fluid to withstand a given temperature without significant decomposition. Above a certain temperature, an organic fluid will begin to decompose at a measurable rate, and this rate will increase with increasing temperature. In an "inert" environment, a fluid can decompose due to breakage of chemical bonds, without reacting with other materials. Stability against this type of decomposition is a measure of the inherent bond strength of the molecule and has been referred to as *thermal* stability.¹ The term *thermochemical* stability is used to describe the stability of a fluid in contact with the materials in the working environment. Thus, the thermochemical stability temperature of the fluid provides a limitation on the maximum allowable operating temperature of a prototypical ORCPS. The thermochemical stability temperature is typically less than the thermal stability temperature by approximately 100-400°F.¹ In this report, the single term *thermal stability* will be used to imply stability of a fluid in its working environment.

A previous study² analyzed the system performance and capital costs (including rate of return on investment) of Rankine-cycle systems using several working fluids, among them six organic fluids; these six fluids were identified as being able to harness the energy content of a range of industrial waste-heat streams. However, questions about long-term thermal stability temperatures of these fluids for this application could not be explicitly answered on the basis of the information available. In some cases, reliable data were either nonexistent or inconclusive. The need for more information became the motivation for undertaking the current dynamic loop testing program.

The six organic fluids to be investigated under this program are as follows:

- Fluorinol 85 (a mixture of 85 mole percent [mol %] trifluoroethanol, $\text{CF}_3\text{CH}_2\text{OH}$, and 15 mol % water),
- 2-methylpyridine/water (a mixture of 35 mol % 2-methylpyridine, $\text{C}_6\text{H}_7\text{N}$, and 65 mol % water),
- R-113 (1,1,2-trichloro-1,2,2-trifluoroethane, $\text{CCl}_2\text{F}-\text{CClF}_2$),
- Toluene (methylbenzene, $\text{C}_6\text{H}_5-\text{CH}_3$),

- Methanol (CH_3OH), and
- R-11 (trichlorofluoromethane, CCl_3F).

Details on thermodynamic properties and other characteristics of these fluids are available in Ref. 2. In this report, our discussion will be limited to Fluorinol 85.

Two approaches are used to obtain reliable data on the thermal stability of an organic fluid: static capsule tests and dynamic loop tests. Capsule tests of fluids serve as an important screening tool in qualitatively (and, to some extent, quantitatively) establishing the effects of pertinent variables on the fluid degradation rates. However, the results cannot be easily and reliably related to a prototypical system, because not all system operating conditions can be duplicated in the capsule tests. In comparison with a complete system test, small dynamic loop testing is a simpler and more cost-effective approach that still provides fairly good simulation of the system operating conditions. This approach also makes it possible to cover a wide range of operating temperatures and pressures, including those that could lead to detrimental effects on an ORCPS due to fluid degradation. It would be unwise to put an expensive, full-size system at risk by using it to conduct thermal stability experiments.

A review of previous studies was undertaken to develop a viable testing approach for Fluorinol 85. Table 1.1 lists the RCPS designs for which this fluid was chosen.³⁻⁶ From these data, it can be seen that the temperature range for Fluorinol 85 is 275–329°C (527–625°F). Previous work associated with thermal stability investigations is summarized in Table 1.2.^{1,4,7} It can be seen that, to a limited extent, both capsule and dynamic tests have been attempted. In some cases, capsule tests were conducted with metals at high temperatures (vaporizer materials compatibility) and with metals and elastomers at lower temperatures, below 177°C (350°F); these materials were in the economizer, condenser, pump, and adjacent components.⁷

Capsule tests on Fluorinol 85 were conducted at 316°C (600°F), 349°C (660°F), and 382°C (720°F), with and without lubricating oils and using carbon steel (SAE 1008) and stainless steel (SS) capsules. At 316°C (600°F) and 336 h of exposure in SAE 1008 carbon steel and SS capsules, it was observed that the color changed from clear white to straw yellow. A small amount of a strong acid was detected in the 740-h test at 316°C (600°F) in an SS capsule. A 336-h test at 349°C (660°F), in both carbon steel and SS capsules without oil, developed an unpleasant odor in 24 h and traces of some weak acid in 48 h, which did not increase with time; there was no evidence of any strong acid. A 500-h test at 660°F, in SAE 1008 capsules and with 15% refrigeration oil, had an odor and formation of a weak acid at 144 h. Some strong acid and noncondensable materials were detected at 500 h; no strong acid was detected in 336 h. Fluorinol 85, with 15% refrigeration oil at 720°F, showed extensive decomposition after 48 h. A heavy black, dusty deposit was formed, and large amounts of strong acids were also detectable.

Most recently, some dynamic loop tests have been conducted using a small carbon steel test loop. A 1000-h test at 550°F and 500 psia showed a neutralization number (a measure of acidity) between 0.013 and 0.023, well below the allowable value of 0.04. The acid observed was believed to be trifluoroacetic acid, but this was not

TABLE 1.1 Rankine-Cycle Systems Using Fluorinol 85

Organization	Application	Maximum Temperature of Fluorinol 85 (°F)	Reference
Thermo Electron Corp.	Automobile	550, 625 ^a	3
Thermo Electron Corp.	Long-haul truck	550	4
General Electric Co. and Thermo Electron Corp.	Push-tow boat	600	5
Mitsui Engineering and Shipbuilding (a licensee of Thermo Electron Corp.)	Heat recovery at Nippon Steel Corp. plant	527	6
Bertin and Creusot Loire, France; Lucciana Power Plant, Corsica	Diesel heat recovery	600	6

^aOriginally, 550°F was maximum temperature; later on, maximum temperature reached 625°F.

confirmed by analytical methods (such as ion chromatography). The gas chromatographic (GC) analysis did not reveal formation of any major degradation products. A 1506-h test at 575°F showed production of acid up to about three times the allowable level; therefore, it was necessary to use an ion exchange resin filter. The gas chromatograms of the final sample did not show any degradation products; however, the Fluorinol 85 changed from 85 mol % trifluoroethanol to 73 mol % trifluoroethanol, probably because of the residual water from the filter resin regeneration rinse procedure. A 1480-h run at 600°F produced an acid level more than five times the allowable limit. However, the ion exchange resin filters proved to be effective in maintaining the acid level below the allowable level. Again, the gas chromatogram of the final sample showed no degradation products (at 100-ppm sensitivity) during this test. The degradation products responsible for the change of acid level were not seen on the gas chromatogram, probably because of their reactivity and absorption in the chromatographic column.

On the basis of the data discussed above, it was decided to examine the thermal stability of Fluorinol 85 over the range of 525–650°F in a relatively nonreactive (stainless steel) dynamic test loop over a period of several thousand hours.

TABLE 1.2 Thermal Stability and Materials Compatibility of Fluorinol 85

Fluid	Type of Test	Test Duration (h)	Maximum Test Temperature, T _{max} (°F)	Materials in Contact with Fluid at T _{max}	Comments	Reference
F-61 ^a	Capsule	1974	600	Carbon steel	Only trace decomposition of of fluid.	7
F-85 ^b	Capsule	336	660	SAE 1009 low-carbon steel	Fluid showed traces of a weak acid.	1
F-85	Loop	1000	550	Carbon steel	No major degradation products were formed. Acid was formed, but the level was considered acceptable.	4
		1506	575		Acid level was more than three times the acceptable limit. Ion exchange resin filter was needed.	
		1480	600		Acid level reached more then five times the acceptable limit but was controllable with an ion exchange resin filter.	

^aF-61 = Fluorinol 61.

^bF-85 = Fluorinol 85.

2 EXPERIMENTAL APPARATUS

Dynamic test loops have previously been designed and constructed to study the thermal stability of organic working fluids for RCPS applications. Heat-addition methods have included direct electrical heating and indirect electrical heating by means of a salt bath or condensing heat-transfer fluid. Most of the loops built by others have used water-cooled condensers but have not included economizers. The types of pumps used have included diaphragm pumps, regenerative turbine pumps, and piston pumps. Fluid flow rates have varied from 10 to more than 250 lb_m/h. The fluid inventory circulation time has varied from 1.8 to 7.8 min for these systems. For comparison, the prototypical organic Rankine-cycle (ORC) engine systems that have been built and operated have a circulation time range of 2.1-12.6 min.

In our experiment, the basic loop consisted of a vaporizer/superheater, a pressure reduction station, an economizer/preheater (regenerative heat exchanger), a condenser, and a diaphragm-type metering pump. Indirect heating using condensing Dowtherm®* A was selected for our system because of its low vapor pressure at relatively high temperature (14.7 psia at 495°F). Figure 2.1 shows a flow schematic of the dynamic test loop used for this investigation. Figure 2.2 shows a test cycle on a temperature-enthalpy diagram. Figure 2.3 shows an overall view of the test facility. Figure 2.4 shows the uninsulated evaporator/superheater section, and Fig. 2.5 shows the section containing pressure-reduction valves, economizer, condenser, metering pump, pulsation damper, and sampling stations for liquids and noncondensable gases. Figure 2.6 shows the system controls and data acquisition center. Details of these components are given following a discussion of general design considerations.

FIGURE 2.1 Flow Schematic of Dynamic Test Loops

*"Dowtherm®" is a trademark of Dow Chemical USA, Midland, Mich.

FIGURE 2.2 Test Cycle on a Temperature-Entropy Diagram

The dynamic test loops are designed to conduct long-term thermal stability tests (up to two years) under simulated prototypical thermodynamic operational conditions. Stainless steel (types 304 and 316) is used to minimize potential degradation resulting from interaction with loop materials. The system is designed to be leak-tight to prevent potential contamination of the fluids by in-leakage of air. Appropriate sampling stations are provided to withdraw liquid and noncondensable vapor samples periodically for chemical analysis. Adequate instrumentation and controls are provided for monitoring the loops during steady-state operations, as well as to diagnose off-design operations. Safety controls and trip meters are provided for automatic shutdown of the system in case of major system malfunctions.

The design conditions for the dynamic loop are listed in Table 2.1. The ideal design point test cycle is represented in Fig. 2.7, a pressure-enthalpy (P-h) diagram. The system layout shown in Fig. 2.1 includes four major subsystems: the working fluid loop; the fluid heating section; the heat rejection section; and the instrumentation, control, and data acquisition system.

2.1 WORKING FLUID LOOP

The working fluid loop consists of an evaporator/superheater section, a set of pressure reduction valves, an economizer unit, a condenser, a metering pump, and a pulsation damper.

Evaporator/Superheater Section

The evaporator/superheater section is constructed of 0.375-in.-O.D., 0.035-in.-wall, type 304 SS tubing. A tube approximately 78 ft long is formed in a coil of 10 loops, each 4 ft long, to provide a total internal heat-transfer surface area of 6.23 ft². This

FIGURE 2.3 Overall View of Test Facility

FIGURE 2.4 View of Evaporator/Superheater Section

FIGURE 2.5 View of Section Containing Pump, Condenser, Economizer, and Pressure Reduction Valves

results in an average heat flux of $7960 \text{ Btu/h}\cdot\text{ft}^2$ for Fluorinol 85, operating at an evaporator outlet temperature of 550°F at 500 psia.

Pressure Reduction Station

This section serves the pressure reduction function of an expansion turbine, though without producing any power. Two Nupro Model 6BW-STE bellows-sealed stainless-steel valves rated at 1000 psi and 900°F serve to reduce the pressure of superheated vapor emerging from the evaporator/superheater to the condenser pressure. These valves are manually operated and require only minor adjustments during operation.

FIGURE 2.6 View of Data Acquisition and Control Center

TABLE 2.1 Design Conditions for Dynamic Loop

Component and Location	Temperature (°F)	Pressure (psia)	Fluid Flow Rate (lb _m /h ^a)
Evaporator			
Dowtherm® A vapor	575	<100	-
Working fluid, outlet	550	500	230
Pressure Reduction Station: Outlet	500	10	230
Economizer			
Vapor, outlet	170	10	230
Liquid, outlet	300	520	230
Condenser			
Vapor	150	10	230
Liquid	120	10	230
Water, inlet	90	50	[6.5]
Water, outlet	110	50	[6.5]
Pump			
Inlet	120	10	230
Outlet	120	525	230

^aWith the exception of water flow rates (in square brackets), which are given in gal/min.

Economizer

The purpose of the economizer (regenerative heat exchanger) is to recover a substantial amount of heat from high-temperature, low-pressure vapor after the pressure reduction station, rather than rejecting this heat through the condenser. In a prototypical system, this would result in increased system efficiency; in the dynamic loop, it reduces consumption of electricity.

The economizer shell is constructed of a 5-in.-O.D., 20-in.-long, schedule 40, type 304 SS pipe. The shell is fitted with a double coil made of a 42-ft-long, 0.5-in.-O.D., 0.035-in.-wall, type 304 SS tube. A tubular spacer baffle centers the coil in an annulus and provides cross-flow conditions across the tube bundle as the vapor moves

FIGURE 2.7 Ideal Test Cycle on a Pressure-Enthalpy Diagram

downward toward the outlet. The coil inlet and outlet pass through the bottom end of the shell via vertical welded nozzles. The high-pressure, low-temperature liquid from the pump is heated by the low-pressure superheated vapor before it flows to the evaporator/superheater section.

Condenser

The condenser is a shell-and-tube heat exchanger similar in construction to the economizer; the organic fluid condenses on the shell side and the laboratory cooling water flows through the tube section. The vapor from the economizer enters at the bottom of the condenser and flows upward in the shell, where it is condensed by contact with the cold tube. Noncondensable gaseous components tend to accumulate in the condenser, from which they are periodically removed for chemical analysis. The construction material is type 304 stainless steel. The shell is a 25-in.-long, 5-in.-O.D.,

schedule 40 pipe with spherical caps welded at both ends. The coil is fabricated from a 50-ft-long, 0.5-in.-O.D., 0.035-in.-wall tube. The coil is centered in the annulus by a baffle, which directs the vapor in a cross-flow pattern to the lower drain.

Diaphragm Metering Pump and Pulsation Damper

A Milton Roy Model FR 151-144 diaphragm metering pump with a rating of 27.9 gal/h and 600 psia at approximately 9-psia net positive suction head (NPSH) is used for pressurizing and circulating the fluids. This pump is constructed of stainless steel and uses a Teflon®* diaphragm. On the basis of capsule compatibility tests,⁷ Teflon® is expected to be relatively inert at the design fluid temperature levels. The pump flow rate is easily adjusted over a range of 0.1-0.4 gal/min by changing the stroke length (by means of a micrometer adjustment screw).

A pulsation damper is included in the loop following the metering pump to smooth out the pressure fluctuations from the main metering pump. A modified Pulsatrol Model 38 damper is used for the test loops. It is constructed of stainless steel and uses a Nordel®* (ethylene-propylene rubber) diaphragm. Nordel® has been found to be compatible with Fluorinol 85 in the temperature range of interest for this study.

Liquid and Vapor Sampling Stations

Figure 2.8 shows schematic diagrams of the sampling stations for liquids and for noncondensable vapors. Periodic withdrawal of both liquid and noncondensable vapor samples is required to monitor the fluid degradation during a test run. Adequate and appropriate precautions are taken to prevent contamination of the organic fluids during the sample withdrawal process. The liquid sampling station is located between the condenser and the pump. The liquid sampling procedure is simple and requires a 0.25-in.-O.D., 3-in.-long glass sample tube and a vacuum pump. After the tube is attached to the sample port and evacuated, the vacuum valve is closed and the sample valve opened to fill the sample tube. The sample valve is then closed, and the sample tube is removed from the sample port. Two such samples are taken from the loop at each sampling time; the first sample is discarded to remove any stagnant fluid that might be present in the lines leading to the sampling valve.

The noncondensable samples are drawn through the top of the condenser into a sample cooler. A 150-mL SS sampling cylinder is used to draw noncondensable samples from the sample cooler. To obtain a gas sample, a sampling cylinder is attached to the sample cooler and evacuated. After the sample cooler has been filled with vapor and noncondensable gas from the condenser, that cooler is valved off and cooled for one hour to condense whatever vapor is present. The valve between the sample cooler and the sample cylinder is then opened briefly to obtain the sample for analysis.

*"Teflon®" and "Nordel®" are trademarks of E.I. DuPont de Nemours and Co., Wilmington, Del.

a. Liquid Sampling Station

b. Noncondensable Vapor Sampling Station

FIGURE 2.8 Schematic Diagrams of Sampling Stations

2.2 FLUID HEATING SECTION

Heat is added to the fluids in a pressure vessel enclosing the evaporator/superheater tube bundle. In this vessel, Dowtherm® A is heated and vaporized using three Watlow electrical immersion heaters. Heat is transferred to the working fluid by condensing the Dowtherm® vapor on the outside surfaces of the evaporator/superheater coil. The test loop uses three 480-V (alternating current), 7.5-kW heaters of the 2-in. by

11-1/2 National Pipe Thread (NPT) screw-plug type; each heater has three elements. The heaters have a power density rating of 23 W/in.² with the steel sheath at 343°C (650°F). The heaters are wired to provide a variable output, up to a maximum of 17.5 kW. The pressure vessel is constructed of 16-in.-diameter, 50-in.-long, type 304 SS pipe. The vessel is designed to withstand 800°F at 150 psia. One end is closed by a welded cap, and the other end is closed by a flange through which the evaporator/superheater coils pass. The pressure vessel is fitted with a 150-psi rupture disk, a low-liquid-level alarm, a fluid drain, a fluid fill connection, and thermocouples.

2.3 HEAT REJECTION SYSTEM

The heat rejection system consists of a plate heat exchanger, a plastic storage tank, and a centrifugal pump. The cooling water is drawn from the storage tank by the pump and circulated through the condenser. Heated water passes through the plate heat exchanger, in which it is cooled by a chilled water supply before being returned to the storage tank. A valve in the line controls the flow rate of the cooling water. The flow rate is measured by a Cox Series 21 flowmeter. The system has adequate cooling capacity to cool the entire loop to room temperature about 20 min after the heat source has been turned off.

2.4 INSTRUMENTATION, CONTROL, AND DATA ACQUISITION SYSTEMS

Temperatures at various locations in the loop are measured by using type E Chromel/Constantan thermocouples, and pressures are measured using Sensotech T- and Z-Series strain-gauge pressure transducers. Mechanical gauges are installed to measure pressures at other locations and to verify the pressure transducer readings. A turbine flowmeter (Flow Technology Model FTM-N10LJS) is used to monitor the working-fluid flow rate. The signals from the flowmeters and other transducers are recorded by a Digistrip II data logger and are monitored by the safety circuit, which automatically turns the loop off if a malfunction is detected.

Rough control of the heat input to the loop is achieved by manually switching two of the three 480-V, three-phase, 7.5-kW heaters. Fine control is achieved by a Barber-Coleman Model 527Z proportional controller acting on the third heater. The controller and the third heater operate on 240-V, single-phase power to provide an additional 2.5 kW of heat. The condenser temperature and pressure are manually controlled by adjusting the coolant flow rate. The working-fluid pressure in the evaporator is controlled by manually adjusting the expansion valves. The working-fluid flow rate is controlled by manually adjusting the metering pump stroke.

A Digistrip II, 48-channel data logger is used to collect and record all temperature, pressure, and flow-rate data at intervals of 1 h. A two-channel strip chart recorder (Lenseis Model 6502) continuously monitors vaporizer outlet temperature and condenser pressure.

3 ANALYTICAL TECHNIQUES AND PROCEDURES

In the present investigation, both liquid and gaseous (noncondensable vapor) samples are periodically collected and analyzed. Noncondensable degradation components, such as hydrogen, tend to accumulate around the condenser and degrade its performance; high-molecular-weight components tend to accumulate in the evaporator and degrade its performance. The data presented in this report on accumulation rates for degradation products provide a qualitative guide to heat-exchanger fouling; additional research is necessary to quantify the effects. The rate at which degradation products accumulate is closely related to the rate at which the working fluid is consumed.

Components of the gaseous samples are identified and quantified by mass spectrometric (MS) analysis. Identification of liquid degradation products was attempted using gas chromatographic/mass spectrometric (GC/MS) analysis; however, most of the separated components had virtually identical mass spectra. This result is not unexpected, because the mass spectra of fluorocarbons do not commonly contain a molecular ion (a result of the rapid loss of fluorine atoms from the molecule). The degree of similarity among all the mass spectra was remarkable, with fragments (such as CF_3 and CF_2) observed in all cases. Degradation products appeared to be polymers of trifluoroethanol, with different degrees of carbon and oxygen alkylation. The lack of an existing fluorocarbon library and the similarity of the spectra prevented qualitative identification of the degradation products. Liquid degradation products are quantified using GC analysis. Ionic degradation products, such as acids, are identified by ion chromatographic analysis.

3.1 GAS CHROMATOGRAPHY

All liquid samples were analyzed on a Hewlett Packard (HP) 5880A gas chromatograph to provide a quantitative measure of the nonvolatile organic degradation products formed. Splitless injections were initially made using an HP fused silica (60 m x 0.32 mm), OV101 capillary column. However, later analyses used a J&W Model DB-1701 (60 m x 0.25 mm) capillary column, which provided significantly improved resolution. A flame ionization detector (FID) with a sensitivity limit of 0.1 ng was used to detect the degradation products. Detector and injection errors resulted in an average of 5% total error for peaks greater than 20 ng. For peaks in the 5-ng range, the error was 10%. Below 5 ng, other errors, such as adsorption of components on the glassware, became significant and increased the error to about 50% for peaks identified at the 0.2-ng level. Fluorinol 85 analyses required an initial temperature of 20°C for 2 min, after which the temperature was increased to 172°C at 4°C/min. The temperature was then increased to 320°C (at 10°C/min) to check out the column and to analyze degradation products with larger molecular weights.

A schematic diagram of a three-level Rapid Analysis System (RAS) used for data analysis is shown in Fig. 3.1. At level I, the computer included with the GC unit integrates the peaks and produces a report consisting of retention time, peak area, and area percent. The detector's analog output is connected via an analog-to-digital

FIGURE 3.1 Schematic Diagram of the Rapid Analysis System Used

converter to a Perkin Elmer (PE) Sigma 15 chromatography data station. This station collects the chromatogram (slice file), integrates the data (peak file), and transfers it (either real-time or post-run) to a Model PE 3600 Chromatography Intelligent Terminal (level II) for data calculation and generation of single chromatogram reports. If necessary, peak reintegration can be performed using the manufacturer's software. Integrations using the PE and HP integrators were compared as a further check on the accuracy of the data. To maintain uniformity, all final calculations were based on the HP integrator. Our software allows the PE 3600 to access the cartridge-tape unit of the HP 5880A and to transfer the data via a data communication interface (DCI) from the GC unit to disk storage on the PE 3600.

Software written for the PE 3600 is used to calculate the response factors of the standard and to store the results on disk. After each sample is run, another program accesses this calibrated standard file, uses the results to calculate the concentrations, and assigns a Kovats retention-index number to each peak. This single chromatogram report is both printed and stored on disk. The PE 3600 can transfer report files to the mainframe IBM 3033 computer (level III) for establishment of a data base and comparison of multiple runs.

Initially, a C9 to C30 external alkane standard was chosen arbitrarily because of lack of information on the nature of potential degradation products. An undecane (C11) internal standard was chosen, because its retention time is sufficiently long to avoid a solvent effect. However, to obtain a better quantitative picture of degradation, the fluoroalkane series was investigated for possible use as a standard. Compounds from this series exhibit behavioral characteristics very different from those of nonfluorinated compounds. The liquids C_6F_{14} and C_8F_{18} were found to elute almost immediately, even at very low temperatures. Higher-molecular-weight solids eluted later but were insoluble in common solvents. Two of these compounds, $C_{12}F_{26}$ and $C_{16}F_{34}$, were procured, and both were dissolved in C_6F_{14} . When injected, this solution showed $C_{12}F_{26}$ as a sharp peak tailing an impurity in C_6F_{14} , and $C_{16}F_{34}$ eluted much later as a very broad, nonintegrable peak. Based on this, $C_{12}F_{26}$ was ultimately chosen as the external standard. It has a response factor approximately four times that of the alkane standard. There is much less precision in the use of the fluoroalkane standard, probably due to solvent tailing. Day-to-day variation was observed to be approximately 15%; this should be kept in mind while interpreting the data. Thus, the alkane standard provides a measure of the minimum level of degradation (maximum response); the fluoroalkane standard provides a measure of the middle-to-upper level of degradation. Exact data can be obtained only after at least the functionality of the degradation products has been identified.

3.2 MASS SPECTROMETRIC GAS ANALYSIS

The gaseous samples (noncondensable vapor) were collected in 150-mL SS cylinders from the condenser and analyzed with a Consolidated Engineering Co. modified Model CEC21-620/gas mass spectrometer. The sample cylinder is connected to the spectrometer, and the air between the two is pumped out. After a satisfactory vacuum is attained, the sample container is opened. The sample is usually allowed to expand to 100 torr pressure in the inlet and a 3-mL calibrated volume; the 3 mL is further expanded in a 3000-mL reservoir and introduced into the spectrometer.

Gas molecules are ionized by bombardment with 70-eV electrons, and the ions are injected into a permanent magnetic field, where they are sorted according to mass number:

$$m/e = KH^2/V \quad (3.1)$$

where:

m = ion mass

e = number of electron charges on ion

K = constant of proportionality

H = magnetic field strength

V = applied voltage

The focused ions impinge on a collector, where they give up their charge, and the signal thus generated is amplified and delivered to a strip chart recorder. Every molecular species has a unique spectrum of fragments, isotopic ions, and multiply charged ions that identifies it. A tabulation of ion peak height at each mass number relative to the largest (base) peak is obtained from a spectrum of the pure gas. Since the height of the base peak is proportional to the pressure of the gas in the spectrometer, the spectrum is made at known pressure to determine the sensitivity coefficient (i.e., peak height/pressure).

In analyzing a gas mixture, therefore, the first step after reloading a spectrum and measuring the peak heights is to sort out the components by their patterns. The second step is to ascertain the true height of the base peak of each component and to calculate its partial pressure, pp_x :

$$pp_x = \text{peak height}_x / \text{sensitivity}_x \quad (3.2)$$

The percentage of each component is obtained by summing the partial pressures of all the components and normalizing:

$$\text{Component percentage}_x = \frac{pp_x}{\sum_i pp_i} \times 100 \quad (3.3)$$

The accuracy of analysis depends on various factors, including the accuracy of pressure measurements for the standard, the stability of the electronic components, and the nature of the sample. If two or more components -- such as N_2 , CO , and C_2H_4 -- have the same base peaks, the sorting out by pattern becomes more difficult and less reliable. For relatively simple mixtures, an overall accuracy of about $\pm 2\%$ can be achieved. For complex mixtures, $\pm 5\%$ accuracy is more realistic. For some highly reactive components, such as HCl or HBr , much lower accuracy is anticipated.

3.3 ION CHROMATOGRAPHIC ANALYSIS

A Dionex Model 16 ion chromatograph -- with a fast-run anion separator column and a fiber suppressor, 0.003M bicarbonate-0.0024M carbonate eluent, and a 1.2-mL/min flow rate -- was used to identify and measure the concentrations of acidic products.

4 SUMMARY OF DYNAMIC LOOP OPERATIONS

As was mentioned earlier, the Fluorinol 85 test has been operated for about 3800 h, covering a nominal evaporator outlet temperature range of 525-600°F. During the test runs, vapor temperatures and pressure at the evaporator/superheater exit, condenser pressure and the temperatures of condensate (along with flow rates), and temperatures of vapor and liquids at the economizer inlet and exit ends were recorded every hour. The maximum and minimum cycle operating temperatures and pressures were analyzed for each of the runs to verify relatively steady-state operation of the loops. A summary of these data for each of the runs is presented in Table 4.1.

4.1 TEST RUN NO. 1

The nominal operating conditions for this 1175-h run were 525°F and 500 psia at the evaporator/superheater exit, 10-psia condenser pressure, and 120°F subcooled condensate temperature. Against these nominal conditions, the minimum and maximum temperatures at the evaporator/superheater exit were 494.1 and 560.5°F, respectively,

TABLE 4.1 Summary of Dynamic Loop Operational Data Using Fluorinol 85 as the Working Fluid

Test Run No.	Elapsed Time (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
		Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
1	1175	494	560	524	407	555	505	11	30 ^a	20
2	1173	543	557	550	468	530	502	12	29 ^a	14
3	565 ^b	567	581	576	483	530	505	15	21 ^c	18
4	504 ^d	593	607	599	467	544	504	17	25 ^e	22

^aPressure surge due to diffusion of damper gas into the condenser.

^bA portion of test run hours was excluded due to temperature excursion.

^cApproximately 1.5-2.0 psia per day pressure increase due to buildup of degradation products. Frequent purging was required.

^dInitial 176 h and last 90 h of data were excluded due to data logger malfunctions during those periods. Last 30 h of data were excluded because of large pressure and temperature excursions.

^eApproximately 3 psia per day pressure increase due to buildup of degradation products.

whereas the overall average temperature for the entire run was 524.0°F. Similarly, the minimum and maximum values of the pressure at the evaporator/superheater exit were 406.9 and 555.1 psia, respectively, with an overall average value of 505.1 psia. The condenser pressure was between 10.96 and 29.90 psia, with an overall average value of 19.47 psia. During this run, the condenser required frequent purging due to diffusion of nitrogen from the damper.

A further insight into loop operation for this run can be developed by examining the data in more detail. Table 4.2 gives 48-h minimum, maximum, and average values for the three parameters. The minimum temperature varies between 494.1 and 526.1°F, the maximum temperature varies between 523.2 and 560.5°F, and the average temperature varies between 517.3 and 528.8°F. Generally, the average temperature is within 5°F of the nominal value. Because the temperature excursion to 560.5°F lasted less than one hour, it was not likely to have a significant effect on overall degradation. The minimum, maximum, and average values of pressure, P_{eo} , vary between 406.9 and 503.3 psia, 491.9 and 555.1 psia, and 482.0 and 27.1 psia, respectively. Generally, the average value of P_{eo} is within 10 psia of the nominal value of 500 psia. Finally, the minimum,

TABLE 4.2 Test Run No. 1: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
1- 48	506.5	524.9	519.2	482.9	536.5	506.0	10.96	17.44	14.52
49- 96	494.1	530.4	523.2	406.9	526.5	486.0	11.48	17.62	14.93
97- 144	523.3	526.0	524.8	468.6	491.9	482.0	12.90	16.31	14.42
145- 192	518.8	526.7	524.4	476.1	499.9	493.0	13.10	16.85	15.29
193- 240	519.2	523.2	520.6	494.2	514.4	504.3	15.86	21.35	18.18
241- 288	520.8	523.6	522.0	500.6	513.8	508.6	17.84	20.49	19.21
289- 336	516.1	524.0	520.6	494.6	515.4	502.3	17.99	21.19	19.12
337- 384	501.7	530.9	517.3	495.6	504.5	501.2	18.82	20.83	20.03
385- 432	521.1	526.1	524.1	492.0	505.3	498.9	18.45	21.48	19.80
433- 480	502.2	526.3	524.4	479.0	512.6	504.9	20.37	22.15	21.43
481- 528	-	525.5	523.9	-	513.3	505.9	-	24.33	23.05
529- 576	521.1	560.5	525.4	491.3	517.5	508.7	11.92	25.91	21.98
577- 624	518.7	524.6	522.3	502.2	529.7	519.0	15.49	18.45	16.91
625- 672	-	526.0	524.3	-	530.4	509.3	-	20.05	18.86
673- 720	522.8	526.7	524.9	503.3	517.9	511.3	19.68	21.99	20.91
721- 768	520.1	527.5	524.9	481.5	540.1	511.2	14.81	22.04	17.18
769- 816	-	529.9	521.8	-	555.1	527.1	-	18.55	17.29
817- 864	524.9	542.4	528.8	481.9	514.7	501.0	15.10	18.67	16.62
865- 912	524.9	526.9	526.1	497.2	506.8	502.3	17.83	21.91	19.93
913- 960	-	526.9	526.1	-	515.7	509.9	-	27.35	24.17
961-1008	526.1	527.5	526.7	497.9	517.3	507.2	19.82	28.64	23.11
1009-1056	525.9	528.1	526.8	487.8	514.2	503.9	17.32	27.65	23.57
1057-1104	524.8	533.3	528.2	490.9	517.1	504.7	18.55	23.25	20.41
1105-1152	-	531.1	525.8	-	523.0	514.0	-	29.90	26.38

maximum, and average values for the condenser pressure vary between 10.96 and 20.37 psia, 16.31 and 29.90 psia, and 14.42 and 26.38 psia, respectively.

4.2 TEST RUN NO. 2

Except for the 25°F increase in nominal fluid temperature at the evaporator/superheater exit, the nominal conditions for the second test run (1173 h at 550°F) are the same as those of the 525°F run. The minimum and maximum values of temperature at the evaporator exit were 500.9 and 556.7°F, and the overall average for the entire run was 549.9°F. The vapor pressure at the superheater exit ranged between 467.6 and 529.7 psia, with an overall average value of 502.1 psia. Finally, the condenser operated at pressures between 12.03 and 29.03 psia; the overall average for the entire run was 14.28 psia. The cause of the gradual pressure increase was identified as diffusion of nitrogen or argon from the pulse damper. This finding led to replacement of these damper pressurization gases by the Fluorinol 85 vapor, acting over the diaphragm through a liquid layer of Fluorinol 85.

A further insight into the dynamic loop operation for this run may be gained by examining the 48-h summary in Table 4.3. The average temperature ranged between 545.5 and 552.8°F. The minimum and maximum values ranged between 500.9 and 550.3°F and 548.9 and 556.7°F, respectively. The pressure, P_{eo} , averaged between 494.4 and 509.7 psia, while the ranges of minimum and maximum values were 467.6-502.6 psia and 503.2-529.7 psia, respectively. The condenser pressure averaged between 12.55 and 21.54 psia, while the ranges of minimum and maximum values were 12.03-14.66 psia and 12.92-29.03 psia, respectively.

In addition to the 48-h summary of Table 4.3, a daily summary of data is included in the Appendix (Table A.2), and a graphical presentation of average temperature vs. elapsed run duration is given in Fig. A.2.

4.3 TEST RUN NO. 3

The nominal fluid temperature at the evaporator/superheater exit was set to 575°F for this 691-h run. Evaporator and condenser pressures continued at the nominal values of the two previous runs. The Fluorinol 85 remaining after the 550°F run was reused for this test run.

During the first 565 h, the evaporator/superheater temperature ranged between 546.5 and 580.8°F, with an overall average of 575.9°F. At about 584 h, the temperature began rising over 584°F, and it reached about 593°F in the next 4 h. Thus, the data obtained after hour 565 are considered invalid and are excluded from further consideration. During the valid portion of the run, the pressure at the evaporator/superheater exit varied between 483.3 and 530.0 psia, with an overall average value of 505.3 psia. The condenser pressure varied between 14.49 and 20.92 psia, and the overall average was 17.85 psia. During this run, condenser pressure increased approximately 1.5-2.0 psia per day, and frequent purging was required.

TABLE 4.3 Test Run No. 2: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
1- 48	-	552.2	546.7	-	515.1	501.0	-	20.39	15.39
49- 96	542.6	548.9	545.7	494.6	510.0	502.7	14.66	19.04	16.54
97- 144	-	554.8	545.5	-	529.7	498.2	-	26.00	21.58
145- 192	-	554.0	551.3	-	514.5	503.5	-	29.03	21.14
193- 240	547.9	554.6	551.5	496.9	510.9	504.8	13.29	14.64	13.69
241- 288	550.3	554.2	552.4	502.6	515.2	507.8	13.66	14.18	13.97
289- 336	548.0	553.5	551.6	478.8	516.2	496.8	12.30	14.16	12.95
337- 384	544.0	553.7	549.0	491.3	515.9	503.8	12.59	13.41	13.16
385- 432	546.9	551.9	548.9	499.7	513.7	505.6	13.13	13.53	13.29
433- 480	547.6	556.1	550.5	476.2	512.8	502.0	12.06	13.58	13.15
481- 528	500.9	552.4	548.4	484.4	521.1	500.6	12.45	13.22	12.77
529- 576	545.9	552.1	549.0	467.6	506.9	496.6	12.03	13.37	13.09
577- 624	547.4	552.2	550.0	491.8	503.2	497.5	13.24	13.76	13.45
625- 672	547.9	554.4	550.6	473.2	507.6	494.4	12.18	13.61	12.73
673- 720	547.2	551.1	549.2	495.8	510.3	502.4	12.43	13.12	12.84
721- 768	548.2	553.7	550.9	495.4	511.8	502.9	12.88	13.47	13.14
769- 816	549.3	556.7	551.8	486.6	516.2	505.4	12.28	13.68	13.20
817- 864	549.9	555.7	552.8	493.3	513.2	501.4	12.12	12.92	12.55
865- 912	547.5	553.8	551.3	494.7	509.3	502.6	12.75	13.39	12.98
913- 960	547.6	551.6	549.7	496.6	513.0	504.5	13.10	13.81	13.40
961-1008	547.8	552.9	550.1	487.9	515.4	505.3	13.27	13.86	13.58
1009-1056	548.1	552.5	550.1	488.0	506.4	498.0	13.29	14.57	14.05
1057-1104	548.6	552.9	550.4	493.3	514.6	502.8	14.05	15.36	14.92
1105-1152	548.5	553.0	550.8	490.3	512.1	501.7	13.04	15.83	15.06
1153-1200	547.1	551.8	549.5	496.9	519.6	509.7	13.95	14.71	14.28

The data presented in Table 4.4 provide some additional insight into the dynamic loop operation for this run. The 48-h average temperature ranged between 569.6 and 592.0°F, while the ranges of minimum and maximum values were 546.5-576.4°F and 577.0-643.6°F, respectively. The last 126 h of data, however, were not considered useful due to the large temperature excursion. The 48-h average fluid pressure at the evaporator exit ranged between 474.1 and 513.7 psia, while the ranges of minimum and maximum values were 421.6-498.7 psia and 509.0-530.0 psia, respectively. Finally, the 48-h condenser pressure averaged between 15.20 and 22.14 psia, while the ranges of minimum and maximum values were 14.49-19.72 psia and 15.96-23.69 psia, respectively.

In addition to this discussion, Table A.3 and Fig. A.3 provide information about the data at daily intervals.

TABLE 4.4 Test Run No. 3: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
1- 48	546.5	579.4	569.6	490.0	519.4	503.2	14.49	15.96	15.20
49- 96	576.1	580.4	578.8	483.3	511.9	499.6	15.76	17.98	16.89
97- 144	573.8	581.2	578.4	485.5	526.8	502.8	17.45	19.94	18.54
145- 192	566.8	578.6	575.4	484.1	519.5	503.9	17.60	18.74	18.16
193- 240	574.2	578.2	576.3	487.1	520.7	503.3	18.55	20.14	19.39
241- 288	575.3	578.9	577.4	485.0	525.8	504.7	19.72	20.78	20.27
289- 336	574.7	577.3	576.4	487.4	525.8	505.3	16.59	20.92	18.59
337- 384	572.6	577.0	575.1	487.8	527.6	505.2	15.18	18.28	16.41
385- 432	576.2	577.3	576.8	498.7	530.0	513.7	16.54	20.13	18.36
433- 480	574.0	577.2	575.2	494.0	522.2	507.8	15.87	20.68	17.63
481- 528	573.4	577.0	575.5	497.6	523.6	509.5	16.13	18.09	17.19
529- 576	576.4	578.3	576.9	486.0	518.3	503.7	16.33	18.39	17.44
577- 624	574.3	593.2	581.1	485.0	513.5	502.8	17.11	21.29	19.05
625- 672	574.2	577.5	575.1	480.2	509.0	499.4	17.51	20.74	19.05
673- 696	563.3	643.6	592.0	421.6	516.6	474.1	17.94	23.69	22.14

4.4 TEST RUN NO. 4

The nominal evaporator/superheater temperature value for this 800-h run was 600°F; other parameters remained at the previously stated values. A fresh charge of Fluorinol 85 was used for this run. The operation remained relatively trouble-free until hour 684, when the vapor pressure at the evaporator exit suddenly jumped to over 550 psia. The expansion valve was manually adjusted more than once, but this action proved only temporarily helpful. Towards the end of the run, the pressure rise was followed by a flow reduction, causing significant over-temperature and system shutdown due to a rupture-disk failure and a low Dowtherm level. During the first 798 h of operation, no large temperature surges were noted, and data obtained up to this point are considered valid. However, almost 226 h of data were lost due to data logger malfunction; therefore, Table 4.1 presents values for only 504 h. For this period, data are considered valid on the basis of the temperature record obtained by the strip chart recorder.

During this run the evaporator outlet temperature varied from 593.4 to 606.7°F, and the overall average was 599.4°F. The evaporator pressure varied from 470.2 to 543.8 psia, and the overall average for the run was 505.4 psia. The condenser pressure varied from 17.09 to 25.36 psia, and the overall average was 21.28 psia. The condenser pressure increased almost 3 psia every 24 h, so that frequent purging of the condenser was necessary.

Table 4.5 presents a summary of data at 48-h intervals. As seen in this table, the ranges of minimum, maximum, and average values of evaporator outlet temperature, T_{eo} , were 593.4-602.1°F, 600.4-606.7°F, and 595.7-604.5°F, respectively. The ranges of

TABLE 4.5 Test Run No. 4: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
177- 224	593.9	601.3	598.9	482.4	504.5	492.5	20.28	23.98	22.28
225- 272	595.7	601.1	598.9	470.2	501.0	488.9	20.15	23.53	21.88
273- 325	594.7	600.8	598.7	479.3	499.9	490.6	17.09	22.26	19.58
321- 368	594.4	600.8	597.5	480.6	509.2	499.9	20.71	24.66	22.43
369- 416	595.4	600.9	598.5	492.0	532.6	510.9	19.41	23.96	21.53
417- 464	593.4	600.4	595.7	466.6	532.6	498.4	17.92	21.70	19.83
465- 512	595.3	603.6	599.9	485.5	540.1	523.0	18.79	24.10	21.07
513- 560	595.8	602.9	599.2	491.1	535.0	510.3	20.69	25.36	22.43
561- 608	596.8	602.5	599.5	494.5	527.5	510.8	18.48	22.80	20.91
609- 656	600.1	606.0	602.4	480.6	537.9	507.2	18.65	24.20	21.91
657- 680	602.1	606.7	604.5	510.8	543.8	527.3	19.23	21.67	20.28

minimum, maximum, and average values for evaporator outlet pressure, P_{eo} , were 470.2-510.8 psia, 499.9-543.8 psia, and 488.9-527.3 psia, respectively. Finally, the ranges of minimum, maximum, and average values for condenser pressure were 17.09-21.71 psia, 21.67-25.36 psia, and 19.58-22.43 psia, respectively.

In addition, a summary of these data at one-day intervals is presented in Table A.4. Figure A.4 provides a graphical presentation of data on average temperature T_{eo} vs. elapsed test run duration.

4.5 SUMMARY OF FLUID TEMPERATURES BY LIQUID SAMPLING INTERVALS

To correct the degradation data for temperature variations between each of the liquid sampling intervals, the operating data were analyzed to determine minimum, maximum, and average values of the temperatures. Table 4.6 presents a summary of temperatures observed for each of the liquid sampling intervals. For test run No. 1, the ranges of minimum, maximum, and average values were 494.1-524.8°F, 523.6-560.5°F, and 515.2-526.8°F, respectively. For test run No. 2, the ranges were 441.8-547.5°F (minimum), 551.9-556.7°F (maximum), and 546.5-551.4°F (average). For test run No. 3, the valid duration was only 528 h; the temperature ranges were 546.5-573.8°F (minimum), 577.3-581.2°F (maximum), and 575.3-576.5°F (average). For test run No. 4, due to a data logger malfunction, data are available for only two of the four sample intervals; the temperature ranges were 593.4-595.3°F (minimum), 600.9-603.6°F (maximum), and 597.4-599.5°F (average). In Figs. 4.1-4.4, variation of average temperatures (relative to nominal values) vs. elapsed run time is presented in a graphical format for each of the four runs.

TABLE 4.6 Summary of Temperatures for Each Liquid Sampling Interval

Test Run No.	Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)		
		Min.	Max.	Avg.
1	1- 192	506.5	530.4	522.9
	193- 336	516.1	524.0	521.0
	337- 595	501.7	560.5	522.9
	596- 931	520.1	542.4	525.0
	932-1076	524.8	533.3	526.8
2	1- 102	542.6	552.2	546.2
	102- 435	544.0	554.8	550.0
	436- 698	544.9	556.1	549.6
	699- 860	548.2	556.7	551.5
	861-1173	547.5	553.8	551.4
3	1- 22	546.5	577.0	563.7
	23- 190	566.8	581.2	577.2
	191- 362	574.2	578.9	576.5
	363- 528	572.6	577.3	575.7
4	177- 286 ^a	593.9	601.3	598.8
	287- 596	593.4	603.6	598.4

^aData from 25 to 176 hours are not available.

4.6 SUMMARY OF OPERATIONAL PROBLEMS

During the testing of Fluorinol 85, several operational problems were encountered that caused or required unplanned system shutdowns. Early in the program, we experienced difficulty with the pulse damper. The nitrogen gas used to pressurize the damper continuously diffused through the Nordel® diaphragm and collected in the condenser. This malfunction was mostly responsible for the continuous increase of condenser pressure during the 525°F test run (no. 1). The first attempt to modify the damper was unsuccessful, but a second modification was successful. The successful modification amounted to pressurizing the damper by means of the working fluid vapor through a layer of liquid working fluid. The required pressure was developed and maintained by electrically heating the fluid in a small cylinder to the corresponding saturation temperature.

FIGURE 4.1 Test Run No. 1: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time

FIGURE 4.2 Test Run No. 2: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time

FIGURE 4.3 Test Run No. 3: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time

FIGURE 4.4 Test Run No. 4: Variation of Average Evaporator Outlet Temperature between Liquid Samples with Respect to Nominal Temperature vs. Elapsed Time

A second factor responsible for some operational instabilities appears to be cooling-water temperature and flow fluctuations. Some startup problems were also experienced due to this factor. Failure of pump seals, causing fluid leakage, also required some system shutdowns. The 600°F test run (no. 4) was terminated due to apparent blockage (by black powdery deposits) of one of the expansion valves, which caused reduced flow of the working fluid. These deposits were chemically examined and found to be metals (in proportions similar to those of stainless steel) and iron fluoride. A significant quantity of hydrofluoric acid was found in the fluid after the run, which led us to conclude that the black powdery deposits were caused by the action of hydrofluoric acid upon the stainless steel of the loop. It was anticipated that the low-flow alarm would shut down the system. When this did not occur, temperature and pressure continued to increase in the Dowtherm® A vessel, ultimately leading to failure of the rupture disk in that vessel and subsequent shutdown of the system.

5 DISCUSSION OF RESULTS

The results of the investigation completed to date are presented and discussed here. As stated earlier, for this investigation both liquid and gaseous (noncondensable vapor) samples were periodically drawn for each of the four test runs and were analyzed using GC and MS techniques. The GC data are presented in graphical format, and the MS data are presented in tabular format. The GC data are approximately corrected for the variation in the amount of fluid in the system. Each inch of liquid level in the condenser is equivalent to approximately 5.6% of the total fluid inventory (about 1.25 gal) in the system.

5.1 RESULTS OF GAS CHROMATOGRAPHIC ANALYSES

Chromatograms for the four runs appear on the following pages for each temperature studied. At 525 and 550°F (Figs. 5.1-5.3), a type OV101 column was used. To improve resolution, a J&W DB-1701 column was used for studies at 575 and 600°F. Following the initial tryouts, appropriate precautions were taken to ensure complete cleanliness of the flame ionization detector, injector, and column ends. Figure 5.1 shows the chromatograms taken for the 525°F run. At this temperature, there is little degradation.

Figure 5.2 (a-f) shows the replotted chromatograms taken for the 288°C (550°F) run initially (at 0 h) and at 102, 435, 698, 860, and 1173 h. As can be seen from this figure, the impurities have shifted to a solvent tailing region. The replotted chromatograms were electronically expanded over this region to better illustrate the solvent-tailing region; these expanded versions are shown in Fig. 5.3 (a-f). The degradation at this temperature has taken place in two stages. During the first 400 h, the higher-boiling-point impurities decomposed into lower-boiling-point compounds, while the total concentration of impurities remained constant. The products in the 5-7 min region increased from 0 ppm to about 44 ppm. A steady increase of products in the 0-6 min region, as well as the increasing concentration of products in the 6-9 min region, was observed. For this run, the analysis was done using a longer column (i.e., a 50-m OV101 column), which provided slightly longer retention time, although resolution was not completely satisfactory.

Figure 5.4 shows numerous small peaks at 575°F, each corresponding to a new degradation product that was not present at lower temperatures. It is apparent that at 575°F Fluorinol 85 has just crossed the threshold level at which significant degradation begins. There is a systematic increase in degradation throughout the run. Initially, the 0-6 min region showed a slight decrease (i.e., 69.5% of the total degradation at 190 h vs. 64.5% of the total degradation at 362 h). However, an increase of degradation products in the 6-9 min region was seen (i.e., from about 23% of the total at 190 h to about 28% of the total at 362 h). At 528 h [as shown in Fig. 5.4 (d)], the relative concentration of degradation products in the 0-6 min region became about 59%, and the 6-9 min region concentration of degradation products increased to about 35%. Subsequent GC/MS analysis revealed that all fragments are fluorinol-based degradation products. However,

a. 4 h **b. 192 h** **c. 595 h****FIGURE 5.1 Gas Chromatograms for Fluorinol 85 Test Run at 525°F**

d. 931 h **e. 1175 h****FIGURE 5.1 (Cont'd)**

a. Initial **b. 102 h** **c. 435 h****FIGURE 5.2 Gas Chromatograms for Fluorinol 85 Test Run at 550°F**

d. 698 h **e. 860 h** **f. 1173 h****FIGURE 5.2 (Cont'd)**

a. Initial **b. 102 h** **c. 435 h**

FIGURE 5.3 Gas Chromatograms Expanded in the Solvent Tailing Region for Fluorinol 85 Test Run at 550°F

d. 698 h **e. 860 h** **f. 1173 h****FIGURE 5.3 (Cont'd)**

a. 22 h

FIGURE 5.4 Gas Chromatograms for Fluorinol 85 Test Run at 575°F

b. 190 h

FIGURE 5.4 (Cont'd)

c. 362 h

FIGURE 5.4 (Cont'd)

d. 528 h

FIGURE 5.4 (Cont'd)

the fragmentation pattern in the MS data indicates that multiple degradation mechanisms are in operation. The major degradation products observed initially remain, but they become minor constituents in comparison with new products. Thus, it appears that at this temperature there is sufficient activation energy to initiate new mechanisms of degradation. In addition to the lower-molecular-weight degradation products, a much higher-molecular-weight degradation component was also observed for the first time. The high-molecular-weight components, which are less volatile than the parent material, tend to accumulate in the evaporator. This accumulation causes the heat-transfer coefficient in the evaporator to decrease (i.e., the high-molecular-weight components foul the heat exchanger).

As Fig. 5.5 indicates, the degradation at 316°C (600°F) is quite significant. There are three distinct regions of degradation at this temperature. The first of these regions is unique: it elutes before the spike solvent, methylene chloride. This region was not observed at lower temperatures, and therefore, not quantified. The degradation products in this region are volatile and, as such, are difficult to quantify accurately without using "purge and trap" techniques. The second region contains a large number of isomers, which are again difficult to resolve chromatographically. However, computerized reintegration of this region was possible. The products were identified as low-molecular-weight fluorocarbons. This is the primary degradation region and has been increasing steadily. The third region (14-25 min) consists of heavier-molecular-weight fluorocarbons, which are readily amenable to quantification. These components are also seen to be increasing steadily, both in numbers and in total concentration. These products, being unstable themselves, degrade and isomerize. To the extent that degradation results in noncondensable gases, the concentration of chromatographable degradation products is limited. (The total concentration of degradation products is the sum of noncondensable gases and chromatographable degradation products.) A large number of lower-concentration isomers is probably below threshold detection limits; because these isomers would not appear as integrated peaks, they would give the appearance of a slower rate of degradation. The fluid, which had been colorless, became pale blue at this temperature. Upon overheating (i.e., at about 2 h at a temperature above 700°F), the fluid color changed to yellow; after about two weeks in storage, the fluid then turned blue again.

5.2 RESULTS OF MASS SPECTROMETRIC ANALYSES

Noncondensable gases were quantified to provide information on their rate of accumulation in an ORC system. As they accumulate, the noncondensable gases tend to blanket the condenser and reduce its heat-transfer coefficient, thereby fouling the condenser. The construction of devices to remove the noncondensable gases periodically (or, if the rate of accumulation were rapid, continuously) would be relatively simple.

A summary of MS analyses of noncondensable samples drawn for Fluorinol 85 test runs is given in Table 5.1. For the 274°C (525°F) test run (no. 1), H₂ concentration varies from 0.5 to 4.2%; for most of the samples, however, it is between 2.3 and 2.6%. Another component, CH₄ (methane), is relatively small and remains fairly constant. The large percentages of N₂ (nitrogen) and argon are due to diffusion of these gases from the

a. Initial

b. 286 h

c. 596 h

FIGURE 5.5 Gas Chromatograms for Fluorinol 85 Test Run at 600°F

d. 770 h

FIGURE 5.5 (Cont'd)

TABLE 5.1 Results of Mass-Spectrometric Analyses of Noncondensable Samples

Test Run No.	Elapsed Time (h)	Concentration (mol %)										
		H ₂	He	CH ₄	H ₂ O	N ₂	O ₂	Ar	CO	CO ₂	CF ₃ CH ₂ OH	Other
1	25	0.5	-	<0.02	0.2	84.1	<0.03	0.2	4.2	0.2	10.6	-
	91	1.1	-	<0.03	0.4	84.6	<0.03	0.1	4.1	0.3	9.4	-
	192	2.6	0.9	<0.03	0.2	88.4	<0.03	0.1	1.6	0.4	5.8	-
	264	2.5	0.9	<0.03	0.5	79.3	<0.03	0.1	4.7	0.2	11.8	-
	432 ^a	2.5	0.7	<0.03	0.1	88.3	2.1	0.1	2.0	0.3	3.9	-
	595	2.3	0.3	<0.04	0.4	78.9	<0.03	0.03	4.5	0.4	13.0	-
	931	4.2	0.5	<0.03	0.1	42.7	0.04	47.3	-	0.5	4.7	-
	1076	2.4	0.2	<0.03	0.08	22.3	0.02	70.8	-	0.4	3.8	-
2	125	4.4	0.2	<0.02	0.1	14.0	0.03	74.8	0.8	0.5	5.2	-
	270	6.6	0.01	0.05	0.1	13.7	<0.02	71.5	0.4	1.2	6.4	-
	365 ^a	3.7	<0.03	0.05	1.3	44.6	11.8	36.9	1.4	0.09	0.2	-
	435	9.0	0.07	0.08	0.08	14.2	0.06	68.4	0.9	1.5	5.7	-
	603	9.6	<0.03	0.1	0.1	14.2	0.03	66.4	1.6	2.0	6.0	-
	766	11.9	-	0.2	0.06	15.1	0.03	63.4	1.0	2.5	5.8	Trace
	1100	20.1	2.7	0.3	0.08	12.2	0.07	53.3	3.0	3.1	5.1	2.8
3	113	41.4	-	0.6	0.1	8.9	0.06	37.1	2.9	3.6	12.6	1.3 ^b
	290	52.6	-	2.5	0.08	5.6	0.07	24.8	5.4	3.7	3.8	1.4
	434	59.3	-	4.2	0.1	2.4	0.07	14.2	8.4	5.0	4.1	2.2
	603	64.3	-	5.3	0.2	0.9	0.04	5.8	8.9	5.7	6.4	2.5
4	116	52.6	2.4	1.7	0.1	11.3	2.3	4.4	15.1	4.6	4.3	1.2 ^c
	284	63.3	-	2.9	0.1	0.9	0.1	0.8	17.0	9.2	3.8	1.5
	458	61.6	-	3.5	0.06	1.1	0.1	0.5	15.8	11.5	3.4	2.4
	596	61.1	-	3.7	0.06	0.7	0.1	0.3	16.0	12.4	3.1	2.5
	770	62.6	-	3.7	0.03	0.3	0.1	0.1	14.7	13.1	3.1	2.3

^aApparent air leak into the sample bottle after the sample was drawn. Condenser pressure dropped from 14.1 to 12.5 psia.

^bIncludes hydrocarbons and CF₄. (C₂H₄ = 0.2, C₂H₆ = 0.3, CF₄ = 0.8).

^cIncludes CF₃H, CF₄, c₂F₂H₂, CF₂H₂, etc.

pulsation damper. Carbon monoxide concentration varies between 1.6 and 4.7%, but it is generally between 4.1 and 4.7%. Carbon dioxide concentration is less than 0.5% and increases very slowly. A sharp increase in oxygen and nitrogen in the 432-h sample is probably due to air leakage into the sample cylinder.

For the 288°C (550°F) test run (no. 2), H₂ varies between 4.4 and 20.1% and, with the exception of the sample taken at 365 h, increases by approximately 1.6%/100 h. Methane (CH₄) increases steadily, though the amount is still small. The nitrogen and argon components are once again the residual amounts from earlier diffusion of these gases from the damper. The amount of carbon monoxide varies between 0.4 and 3.0% and appears to increase slowly, although there is considerable scatter in the data. The carbon dioxide concentration increases steadily from 0.5% at 125 h to 3.1% at 1100 h. Finally, the 1100-h sample also shows a small amount of other hydrocarbons and CF₄.

For the 575°F test run (no. 3), we again see a gradual increase in the amount of hydrogen, beginning with high concentration in the 113-h sample. This large initial hydrogen concentration occurs because the run was continued with the fluid used in the previous two runs, and the system was not completely purged at the beginning of this run. Methane concentration systematically increases at a much higher rate (i.e., 1.1%/100 h) than occurs at the lower temperatures. Carbon monoxide and carbon dioxide concentrations also increase. The amount of other hydrocarbons and CF₄ increases steadily at almost twice the rate for the 550°F run, indicating a higher rate of degradation. Condenser pressure buildup of almost 1.5 psia to 2.0 psia per day was observed; this buildup required almost daily purging after about 300 h of operation. (The last data point is not considered here, because just preceding it for about 12 h, the temperature was between 584°F and 593°F.)

For the 600°F test run (no. 4), we observe a high concentration of hydrogen. The rate of increase cannot be estimated from the data, because almost daily purging of the system was necessary due to a condenser pressure increase of about 3 psia per day. We also see a fairly constant amount of CH₄, which on the average is present in higher concentration than that observed for the 575°F run. Both CO and CO₂ are present in larger quantities than they were at lower temperatures, and, although the amount of CO is not amenable to any correlation, the CO₂ concentration increases systematically. The amounts of other hydrocarbons and CF₄ show an initial increase but remain fairly constant thereafter.

The mass spectrometer data for H₂ and CO and CO₂ vs. test run duration are presented in Figs. 5.6 and 5.7 as test-run duration vs. concentration in mole percent. Wherever possible, the data are correlated by appropriate linear least-squares fits. As seen in Fig. 5.6, H₂ concentration increases by only about 0.2 mol %/100 h at 525°F (274°C) test run temperature, but it increases by 1.5 mol %/100 h at 550°F (288°C) and by 4.7 mol %/per 100 h at 575°F (302°C). The data at 600°F (316°C) are not amenable to rate calculation due to frequent purging of the condensers. The slope of the least-squares fits in Fig. 5.7 shows that CO₂ concentration rate increases from 0.26 mol %/100 h at 550°F (288°C) to 1.25 mol %/100 h at 600°F. The rate of increase for CO goes from 0.22 mol %/100 h at 550°F (288°C) to 1.3 mol %/100 h at 575°F (302°C). As was the case for the hydrogen data, the CO data at 600°F (316°C) are not amenable to least-squares fit due to necessary purging of gases during this test run.

FIGURE 5.6 Increase of Hydrogen as a Function of Time and Temperature

5.3 RESULTS OF ION CHROMATOGRAPHIC ANALYSIS

The liquid sample taken after the completion of the 600°F test run was analyzed with the ion chromatograph. After 770 h operation at that temperature, 1707 ppm of F⁻ was measured, indicating the presence of hydrofluoric acid (HF). Less than the threshold detection level (0.4 ppm) of trifluoroacetic acid was indicated. The pH of the fluid decreased from 5.5 for the unused fluid to less than 1.0 after 770 h at 600°F. Finally, FeF₂ was detected by x-ray diffraction in the black powdery substance that was removed from the loop. These are all indications that HF is a significant degradation product of Fluorinol 85.

5.4 RATE OF DEGRADATION

A summary of the total nonvolatile degradation products (ppm) for the four runs is presented in Table 5.2. In Fig. 5.8, total degradation (ppm) is based on the fluoroalkane-standard column of Table 5.2; data in the figure showing degradation vs. duration of each test run are correlated by the respective least-squares fits, obtained by linear regression. The slope of these linear least-squares fits gives the degradation rate in ppm/h for the fluid in the dynamic loop. The annual degradation rate for fluid in a

FIGURE 5.7 Increase of Carbon Monoxide and Carbon Dioxide as Functions of Time and Temperature

TABLE 5.2 Results of Gas-Chromatographic Analyses of Liquid Samples Using Alkane and Fluoroalkane Standards

Test Run No.	Time (h)	Total Degradation (ppm)	
		Alkane Standard	Fluoroalkane Standard
1	192	11.9	37
	336	12.8	40
	595	13.8	43
	931	16.5	52
	1175	21.0	66
2	102	39.4	123
	435	59.4	189
	698	82.6	258
	860	83.5	264
	1173	95.3	300
3	22	0	0
	190	92.2	266
	362	157.8	484
	528	304.7	946
4	25	1.8	6
	286	261.2	807
	596	366.5	1129
	770 ^a	386.2	1192

^aThis sample was taken after a pressure excursion at 684 h. A temperature excursion occurred at 798 h.

prototypical RCPS is estimated by linear extrapolation. This is done by multiplying the dynamic loop hourly rate by 8000 h/yr and then multiplying the result by the ratio of the percentage of fluid inventory in the superheater of a prototypical system to the percentage of fluid inventory in the superheater of the dynamic loop.

A prototypical stationary ORCPS is estimated to have 6.9% of its fluid inventory in the superheating region.⁸ The dynamic loop is estimated to have approximately 1% of its fluid inventory in the superheating region, giving a ratio of the two inventories of 6.9:1. (The superheating region is considered the primary reaction zone for the purpose of this estimation, because in that region the temperature level is highest.)

As can be seen from the 525°F data, a prototypical system would have an annual degradation rate of less than 0.25%. At 550°F, the rate increases to about 1.0%. At 575°F, the annual rate is about 4.4%. At 600°F evaporator outlet temperature, a 17.2% annual degradation rate is predicted.

5.5 CORRELATION OF DEGRADATION RATES AND MAXIMUM FLUID TEMPERATURES

The degradation rates determined from the slopes of lines in Fig. 5.8 are correlated in Fig. 5.9. As Fig. 5.9 shows, the degradation rate increases with working fluid temperature; when degradation is plotted vs. $1/T$ (T in degrees Kelvin), the result is an approximately linear relationship.

FIGURE 5.8 Total Degradation as a Function of Time and Temperature

FIGURE 5.9 Correlation of Nonvolatile Degradation Rate with Evaporator Outlet Temperature

6 CONCLUSIONS AND RECOMMENDATIONS

Based on results of the investigation to date, some general conclusions can be derived about the thermal stability limits of Fluorinol 85 as a working fluid for Rankine-cycle power systems. Fluorinol 85 appears to be relatively stable up to a maximum cycle temperature of 288°C (550°F). At a maximum cycle temperature of about 302°C (575°F), this fluid begins to form significant amounts of degradation products. The buildup of noncondensable materials (H_2 , CH_4 , CO, CO_2 , and other hydrocarbons and fluorocarbons) in the condenser is observed to take place at a significant rate -- i.e., at a pressure rise of 10-14 kPa (1.5-2 psia) per day. The results, when extrapolated to a stationary RCPS, could amount to approximately 4.4% decomposition annually.

The 316°C (600°F) test run shows evidence of volatile organic products for the first time; as in the lower-temperature test runs, the 600°F fluid also contains nonvolatile products. On the basis of a rough estimate of volatile products, it appears that the total degradation rate at this temperature could amount to approximately 17.2% annually in a stationary RCPS. The condenser pressure increase observed during this run was approximately 20 kPa (3 psia) per day. The gaseous decomposition products included hydrogen, carbon monoxide, methane, carbon dioxide, and other hydrocarbons and fluorocarbons. These products were present in much higher quantities than were observed in the 302°C (575°F) test run, indicating a higher rate of degradation.

An examination of some of the components exposed to high-temperature/high-pressure vapor showed some hard deposits and some black powdery deposits. An analysis of these deposits showed that they contained metals in the same proportions as are found in the stainless steel of the loop and iron fluoride (FeF_2). A significant degradation product is hydrogen fluoride (HF), found in the final sample of the 600°F run and identified by ion chromatography. The hydrogen fluoride becomes hydrofluoric acid in the presence of water, which constitutes 15 mol % of Fluorinol 85.

Fluorinol 85 is extremely stable at temperatures below 550°F. If there is a temperature excursion, however, the fluid will degrade, and hydrofluoric acid will form. At a temperature of 600°F, it has been shown, the hydrofluoric acid attacks the stainless steel loop. We therefore recommend that, if Fluorinol 85 is considered for use as an organic Rankine-cycle fluid, an additional technology (such as an improved ion-exchange system) be developed to neutralize or remove the hydrofluoric acid in the event of a moderate temperature excursion.

For some applications, such as diesel-engine bottoming using 1100°F exhaust heat, there is a risk of extreme temperature excursions that could cause major degradation in a short time (i.e., in less than 10 h). In such an event, the ORC system could be damaged by way of acid attack in two ways:

- The buildup of acid could be sufficiently rapid to overwhelm the ion exchange system.

- Even if the ion exchange system remained functional, the acid concentration could become dangerously high in that portion of the ORC system between the evaporator and the ion exchanger.

Therefore, a reliable means of preventing extreme temperature excursions is necessary.

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APPENDIX

TABLE A.1 Test Run No. 1: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} ($^{\circ}$ F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
1- 24	506.5	524.5	515.2	487.4	536.5	509.9	10.96	17.44	13.53
25- 48	521.1	524.9	523.1	482.9	508.4	502.0	13.71	17.20	15.50
49- 72	494.1	530.4	522.4	406.9	526.5	485.2	11.48	17.62	14.91
73- 96	523.2	524.7	524.0	461.2	500.5	486.8	14.17	15.76	14.94
97- 120	523.3	525.6	524.6	472.9	491.9	481.7	13.25	15.65	14.61
121- 144	523.8	526.0	525.0	468.6	491.9	482.2	12.90	16.31	14.22
145- 168	523.8	526.7	525.4	482.9	498.5	490.6	13.10	16.39	14.82
169- 192	518.8	526.3	523.4	476.1	499.9	495.4	14.70	16.85	15.76
193- 216	519.3	521.7	520.0	494.2	507.1	500.8	15.86	20.22	17.37
217- 240	519.2	523.2	521.1	502.8	514.4	507.7	17.36	21.35	18.98
241- 264	520.8	523.6	522.0	500.6	508.6	505.9	17.84	19.29	18.54
265- 288	521.2	523.1	522.0	507.9	513.8	511.2	19.32	20.49	19.88
289- 312	518.3	523.9	521.6	494.6	515.4	504.2	18.01	21.19	19.55
313- 336	516.1	524.0	519.5	495.1	503.2	500.4	17.99	19.93	18.68
337- 360	510.7	521.3	518.0	499.7	504.1	501.7	18.82	20.31	19.56
361- 384	501.7	530.9	516.5	495.6	504.5	500.6	20.05	20.83	20.50
385- 408	521.1	525.9	523.6	492.0	499.5	497.1	18.45	21.48	19.87
409- 432	522.9	526.1	524.5	498.2	505.3	500.7	19.13	20.38	19.73
433- 456	522.7	526.0	524.8	502.8	508.0	505.1	20.37	21.73	21.04
457- 480	502.2	526.3	523.9	479.0	512.6	504.6	21.13	22.15	21.82
481- 504	522.3	525.4	524.1	500.5	513.3	505.3	21.89	22.94	22.46
505- 528	-	525.5	523.7	-	508.7	506.4	-	24.33	23.63
529- 552	522.8	526.1	524.4	505.7	515.8	510.4	24.36	25.57	24.96
553- 576	521.1	560.5	526.4	491.3	517.5	506.9	11.92	25.91	19.00
577- 600	518.7	524.4	521.9	502.2	529.7	517.3	15.49	16.77	16.21
601- 624	520.9	524.6	522.7	515.4	525.0	520.7	16.77	18.45	17.60
625- 648	522.1	525.9	523.7	492.9	530.4	511.6	17.92	20.05	18.68
649- 672	-	526.0	524.8	-	511.8	506.9	-	19.74	19.04
673- 696	522.8	526.0	524.4	503.3	516.2	510.5	19.68	21.06	20.39
697- 720	523.6	526.7	525.3	507.4	517.9	512.0	21.12	21.99	21.43
721- 744	523.5	527.5	525.9	481.5	517.0	503.0	14.81	22.04	18.25
745- 768	520.1	526.9	523.9	496.9	540.1	519.4	15.26	16.89	16.10
769- 792	517.0	521.9	519.6	525.0	555.1	536.9	16.80	18.12	17.43
793- 816	-	529.9	524.0	-	543.1	517.2	-	18.55	17.14
817- 840	526.3	542.4	531.6	481.9	514.7	499.2	15.10	16.83	15.79
841- 864	524.9	527.1	526.0	494.2	512.6	502.8	16.89	18.67	17.45
865- 888	524.9	526.9	525.9	497.2	502.6	500.1	17.83	20.77	19.19
889- 912	524.9	526.9	526.2	502.0	506.8	504.4	19.26	21.91	20.67
913- 936	-	526.9	526.0	-	510.3	507.7	-	24.07	22.58
937- 960	525.0	526.9	526.2	508.7	515.7	512.0	24.22	27.35	25.75
961- 984	526.1	527.0	526.7	498.1	517.3	507.4	19.82	28.64	24.01
985-1008	526.3	527.5	526.7	497.9	515.7	506.9	21.20	23.42	22.20
1009-1032	525.9	527.4	526.7	498.2	507.9	503.1	23.64	26.51	25.09
1033-1056	526.4	528.1	526.8	487.8	514.2	504.7	17.32	27.65	22.05
1057-1080	525.0	532.1	527.1	490.9	515.0	503.2	18.55	19.89	19.19
1081-1104	524.8	533.3	529.2	498.2	517.1	506.1	20.07	23.25	21.62
1105-1128	-	531.1	526.6	-	521.2	513.8	-	26.92	25.08
1129-1152	86.2	526.0	525.0	6.6	523.0	514.2	7.00	29.90	27.67

TABLE A.2 Test Run No. 2: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
1- 24	-	552.2	545.6	-	515.1	504.7	-	20.39	15.64
25- 48	-	550.4	547.7	-	505.2	497.3	-	16.14	15.14
49- 72	543.9	548.9	546.2	494.6	506.9	501.5	14.66	16.33	15.34
73- 96	542.6	547.2	545.1	496.1	510.0	503.8	16.47	19.04	17.73
97- 120	544.9	551.7	547.8	492.9	516.9	506.4	19.11	21.58	20.38
121- 144	-	554.8	543.1	-	529.7	490.0	-	26.00	22.77
145- 168	546.7	554.0	551.2	496.8	514.5	505.0	20.74	23.31	22.15
169- 192	-	553.8	551.3	-	513.5	501.9	-	29.03	20.12
193- 216	547.9	554.0	551.0	496.9	508.2	504.3	13.43	14.64	13.85
217- 240	549.8	554.6	551.9	501.6	510.9	505.3	13.29	13.87	13.53
241- 264	550.8	553.7	552.4	502.6	511.8	507.6	13.66	14.16	13.87
265- 288	550.3	554.2	552.3	502.9	515.2	508.0	13.95	14.18	14.07
289- 312	550.2	553.4	552.1	478.8	512.7	497.4	12.30	14.16	13.19
313- 336	548.0	553.5	551.0	480.5	516.2	496.1	12.30	13.32	12.71
337- 360	545.5	553.7	550.0	491.3	513.5	501.9	12.59	13.30	13.02
361- 384	544.0	551.3	548.0	495.4	515.9	505.7	13.10	13.41	13.30
385- 408	547.2	551.2	549.0	499.7	510.0	504.2	13.13	13.53	13.29
409- 432	546.9	551.9	548.8	501.2	513.7	507.0	13.15	13.47	13.29
433- 456	547.9	552.5	550.0	501.0	512.8	506.6	13.14	13.58	13.37
457- 480	547.6	556.1	550.9	476.2	510.0	497.4	12.06	13.45	12.93
481- 504	500.9	552.4	547.9	484.4	518.8	500.7	12.45	13.16	12.75
505- 528	544.9	551.8	548.8	485.8	521.1	500.4	12.52	13.22	12.78
529- 552	546.2	552.1	549.1	467.6	506.9	493.9	12.03	13.27	12.98
553- 576	545.9	551.9	548.9	493.2	504.9	499.2	13.03	13.37	13.20
577- 600	547.4	552.2	549.9	491.8	500.5	496.3	13.24	13.51	13.36
601- 624	548.1	551.8	550.1	493.8	503.2	498.6	13.33	13.76	13.53
625- 648	547.9	552.9	550.4	473.6	507.6	496.5	12.34	13.61	12.96
649- 672	547.9	554.4	550.7	473.2	504.3	492.3	12.18	12.72	12.50
673- 696	547.2	550.4	548.7	497.5	510.2	502.5	12.43	13.12	12.77
697- 720	548.7	551.1	549.7	495.8	510.3	502.2	12.80	13.00	12.90
721- 744	548.2	553.3	550.7	495.4	509.9	501.8	12.88	13.24	13.05
745- 768	548.6	553.7	551.0	495.7	511.8	504.0	13.04	13.47	13.23
769- 792	549.3	552.5	551.2	500.8	514.2	507.2	13.28	13.68	13.47
793- 816	550.4	556.7	552.3	486.6	516.2	503.6	12.28	13.65	12.92
817- 840	550.1	555.7	553.2	493.8	513.2	501.4	12.12	12.73	12.43
841- 864	549.9	554.8	552.3	493.3	511.6	501.4	12.50	12.92	12.67
865- 888	549.2	553.8	552.1	496.1	509.1	501.1	12.75	12.99	12.85
889- 912	547.5	552.2	550.5	494.7	509.3	504.1	12.78	13.39	13.10
913- 936	548.4	551.6	550.0	497.5	508.5	503.6	13.10	13.50	13.29
937- 960	547.6	551.5	549.4	496.6	513.0	505.4	13.20	13.81	13.51
961- 984	547.8	552.9	550.3	497.1	515.0	508.5	13.33	13.80	13.58
985-1008	548.4	551.6	549.9	487.9	515.4	502.1	13.27	13.86	13.57
1009-1032	548.4	552.5	550.1	488.0	506.4	498.2	13.77	14.24	13.98
1033-1056	548.1	552.0	550.1	488.4	505.1	497.7	13.29	14.57	14.12
1057-1080	549.3	552.9	550.8	493.3	512.7	500.5	14.05	15.01	14.70
1081-1104	548.6	551.4	550.0	499.1	514.6	505.1	14.90	15.36	15.14
1105-1128	548.6	553.0	550.7	495.1	512.1	503.2	15.27	15.83	15.52
1129-1152	548.5	553.0	550.8	490.3	506.8	500.2	13.04	15.77	14.59
1153-1176	548.2	551.8	549.8	496.9	515.6	508.1	13.95	14.30	14.14
1177-1200	547.1	551.2	549.2	504.5	519.6	511.2	14.21	14.71	14.41

TABLE A.3 Test Run No. 3: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
1- 24	546.5	577.0	563.7	490.0	519.4	504.6	14.49	15.20	14.84
25- 48	569.8	579.4	575.5	492.5	509.1	501.7	15.06	15.96	15.55
49- 72	576.1	580.4	578.4	483.3	511.9	499.3	15.76	16.95	16.36
73- 96	576.9	580.4	579.1	487.9	511.9	499.8	16.76	17.98	17.41
97- 120	578.2	581.2	579.7	491.0	526.8	503.5	17.77	19.05	18.48
121- 144	573.8	580.8	577.1	485.5	512.9	502.0	17.45	19.94	18.59
145- 168	566.8	577.8	574.7	491.4	513.4	502.8	17.60	18.29	17.98
169- 192	574.6	578.6	576.1	484.1	519.5	505.0	17.84	18.74	18.34
193- 216	574.2	577.6	576.2	487.1	520.7	505.4	18.55	19.50	19.07
217- 240	574.6	578.2	576.4	488.4	515.1	501.1	19.34	20.14	19.71
241- 264	576.4	578.9	577.5	485.0	515.0	500.8	19.98	20.62	20.27
265- 288	575.3	578.9	577.2	492.9	525.8	508.6	19.72	20.78	20.27
289- 312	575.8	577.3	576.7	487.4	525.8	509.1	17.67	20.92	19.38
313- 336	574.7	577.3	576.1	488.1	511.3	501.5	16.59	18.51	17.79
337- 360	573.7	576.9	575.1	494.6	527.6	506.1	15.18	18.28	16.53
361- 384	572.6	577.0	575.0	487.8	511.7	504.2	15.35	17.02	16.29
385- 408	576.3	577.3	576.8	498.7	520.5	509.0	16.54	18.36	17.42
409- 432	576.2	577.2	576.7	504.9	530.0	518.4	18.42	20.13	19.29
433- 456	574.3	577.2	575.6	494.0	522.2	511.3	16.37	20.68	18.42
457- 480	574.0	575.4	574.7	495.2	518.4	504.2	15.87	17.88	16.83
481- 504	574.2	577.0	575.1	497.6	523.6	510.6	16.13	18.06	17.14
505- 528	573.4	577.0	575.8	498.3	517.4	508.3	16.48	18.09	17.24
529- 552	576.4	577.4	576.8	495.7	512.9	505.7	16.33	18.39	17.46
553- 576	576.4	578.3	576.9	486.0	518.3	501.7	16.69	18.07	17.42
577- 600	577.0	592.7	581.6	493.7	513.5	504.7	18.09	20.40	19.16
601- 624	574.3	593.2	580.5	485.0	513.1	500.8	17.11	21.29	18.93
625- 648	574.6	577.5	575.2	484.0	509.0	499.5	17.96	19.91	18.99
649- 672	574.2	576.0	575.0	480.2	507.8	499.2	17.51	20.74	19.11
673- 696	563.3	643.6	592.0	421.6	516.6	474.1	17.94	23.69	22.14

TABLE A.4 Test Run No. 4: Summary of Dynamic Loop Operational Data

Interval (h)	Evaporator Outlet Temperature, T_{eo} (°F)			Evaporator Outlet Pressure, P_{eo} (psia)			Condenser Pressure, $P_{condenser}$ (psia)		
	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
177- 200	593.9	600.5	597.9	484.0	504.5	494.7	20.86	23.98	22.57
201- 224	598.1	601.3	599.8	482.4	500.7	490.2	20.28	23.52	21.99
225- 248	596.0	601.1	599.3	479.0	498.4	487.5	20.54	23.53	22.05
249- 272	595.7	600.2	598.4	470.2	501.0	490.3	20.15	23.07	21.70
273- 296	594.7	600.8	598.6	479.3	499.1	490.3	17.09	22.26	19.45
297- 320	596.7	600.2	598.7	480.5	499.9	490.8	18.57	20.84	19.70
321- 344	594.4	600.8	597.3	480.6	506.5	497.0	20.71	23.08	21.89
345- 368	594.9	600.2	597.6	495.8	509.2	502.7	21.25	24.66	22.96
369- 392	596.5	600.9	598.6	492.0	526.6	506.3	20.13	23.96	22.07
393- 416	595.4	600.4	598.4	498.5	532.6	515.5	19.41	22.63	20.98
417- 440	593.4	600.4	595.8	471.6	532.6	502.7	18.91	21.70	20.15
441- 464	593.4	598.6	595.6	466.6	505.8	494.1	17.92	20.94	19.51
465- 488	595.3	601.7	598.6	485.5	534.0	517.6	18.79	21.06	19.94
489- 512	599.5	603.6	601.2	513.1	540.1	528.3	21.17	24.10	22.20
513- 536	595.8	602.9	599.5	499.1	535.0	514.8	20.69	25.36	22.77
537- 560	596.6	600.5	598.8	491.1	517.5	505.7	20.73	23.50	22.08
561- 584	596.8	600.9	599.3	494.5	522.7	510.6	20.13	22.80	21.50
585- 608	598.0	602.5	599.7	497.9	527.5	511.0	18.48	21.71	20.31
609- 632	600.4	603.3	601.8	490.8	512.7	503.7	20.59	22.93	21.83
633- 656	600.1	606.0	602.9	480.6	537.9	510.7	18.65	24.20	21.99
657- 680	602.1	606.7	604.5	510.8	543.8	527.3	19.23	21.67	20.28

FIGURE A.1 Test Run No. 1: Average Evaporator Outlet Temperature vs. Elapsed Time

FIGURE A.2 Test Run No. 2: Average Evaporator Outlet Temperature vs. Elapsed Time

FIGURE A.3 Test Run No. 3: Average Evaporator Outlet Temperature vs. Elapsed Time

FIGURE A.4 Test Run No. 4: Average Evaporator Outlet Temperature vs. Elapsed Time