(2)

WL-TR-92-2040

A CONDENSED PHASE TEST CELL ASSEMBLY FOR THE SYSTEM FOR THERMAL DIAGNOSTIC STUDIES (STDS)

R.C. Striebich and W.A. Rubey

University of Dayton Research Institute
300 College Park Avenue, KL 102
Dayton, OH 45469-0132

August 1992

Final Report for the Period June 1990 to December 1991

Approved for public release; distribution is unlimited.

AERO PROPULSION AND POWER DIRECTORATE
WRIGHT LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6563

NOTICE

This technical report has been reviewed and is approved for publication.

Ellen Steward
ELLEN STEWARD, Project Engineer
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion and Power Directorate

Charles Delaney
CHARLES L. DELANEY, Chief
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion and Power Directorate

LEO S. HAROOTYAN, JR., Chief
Fuels and Lubrication Division
Aero Propulsion and Power Directorate

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
Aug 1992

3. REPORT TYPE AND DATES COVERED
Final June 1990 to December 1991

4. TITLE AND SUBTITLE
A CONDENSED PHASE TEST CELL ASSEMBLY FOR THE SYSTEM FOR THERMAL DIAGNOSTIC STUDIES (STDS)

5. FUNDING NUMBERS
PE: 62203F
PR: 3048
TA: 05
WU: AF
C: F33615-90-C-2047

6. AUTHOR(S)
R.C. Striebich and W.A. Rubey

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Dayton Research Institute
300 College Park Avenue, KL 102
Dayton, OH 45469-0132

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Aero Propulsion and Power Directorate (WL/POSF)
Wright Laboratory
Wright-Patterson Air Force Base, OH 45433-6563

Ellen Steward (513/255-4025)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
WL-TR-92-2040

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; Distribution is Unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A reactor and its associated peripherals were designed to be an integral part of the System for Thermal Diagnostic Studies (STDS), a versatile mainframe thermal system. The Condensed Phase Test Cell (CPTC) can be used to conduct experiments for flowing liquids at temperatures up to approximately 800°C and pressures up to 1500 psig. In the area of thermal stability, the CPTC can be used to conduct flowing experiments on jet fuels, jet fuel candidates and model mixtures at both subcritical and supercritical conditions. By subjecting condensed phase liquids to controlled conditions of temperature, pressures, reactive atmosphere (dissolved oxygen concentration) residence time and distribution, etc., thermal degradation experiments could be conducted. Product distributions from the exposure of liquid phase and condensed phase material were performed via high pressure liquid sampling valves in line with gas chromatography-mass spectrometry (GC-MS); thus, technique is capable of measuring dissolved fixed gases (nitrogen, oxygen, argon, carbondioxide, etc.), cracking gases (methane, ethane, ethylene, propylene, etc.) and thermal reaction products of the parent material. The system was also designed to perform in-line extraction of

(CONTINUED ON ATTACHED SHEET)

14. SUBJECT TERMS
Condensed Phase
Thermal Stability
Dodecane
Supercritical Fluids
Supercritical fluid extraction

15. NUMBER OF PAGES
54

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18
298-102

REPORT DOCUMENTATION PAGE (Concluded)

13. ABSTRACT (Concluded)

deposits from the reactor using supercritical CO_2. Results indicated pyrolysis and autoxidation mechanisms were taking place at various temperatures and conditions affecting product formation. Reaction products were identified which may be precursors to deposit formation.

FOREWORD

This report documents the work performed under Air Force Contract F33615-90-C-2047, entitled "Molecular Structure and Fuel Performance: Liquid Phase/Dense Gas Thermal Decomposition Experiments with the System for Thermal Diagnostic Studies (STDS)". The authors wish to acknowledge the effort of Ms. Ellen Steward who was the Technical Monitor for this effort.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF TABLES

LIST OF ABBREVIATIONS

STDS	System for Thermal Diagnostic Studies
P_c	critical pressure
T_c	critical temperature
CPTC	Condensed Phase Test Cell
n-	normal (as in "normal-dodecane")
IHPTET	Integrated High Performance Turbine Engine Technology
ID	internal diameter
OD	outer diameter
GC	gas chromatography
MS	mass spectrometry
MSD	mass selective detector
FID	flame ionization detector
mm	millimeter
cm	centimeter
TRC	Thermal Reaction Compartment

SECTION 1
INTRODUCTION

The development of advanced fuels for both commercial and military aircraft has come to a critical juncture. Aircraft of today typically employ the fuel to cool those portions of the system which generate heat; the engine lubricating oils and hydraulic fluids both exchange heat with the fuel, as do the avionics and electrical systems. In addition, higher mach travel (greater than mach 4.5) will cause airframe surfaces to experience increased temperatures. Current development programs, such as the Integrated High Performance Turbine Engine Technology (IHPTET) initiative, seek to increase the performance of current jet engines by a factor of 2 (1). These performance increases will necessitate that the higher temperatures generated will be dissipated, and at this time, the only efficient on-board coolant is the fuel.

Thus, if the fuel is used as a coolant, it must be able to withstand higher and higher temperatures without degrading. Although current systems operate with an air-cooled heat exchanger, higher mach travel will cause the stagnation temperature of air to be too high to use in a heat exchanger. The operating temperature of the fuel must, therefore, be expanded to allow it to be used as a coolant. The accompanying problem, of course, is that current hydrocarbon type fuels exposed to higher temperatures can form gums and deposits which cause nozzle fouling, fuel flow control sticking, and heat exchanger deterioration. A great deal of research in this area had been performed during the past three decades (2-5) but significant advances in analytical chemistry and related fields have allowed problems associated with higher temperature fuels to be addressed.

Two of the major goals of thermally stable fuels are to:

(1) Develop an improved JP-8 type fuel which will increase fuel thermal stability from 325°F to 425°F (JP-8+100).

(2) Develop a JP-900 jet fuel which will have an operating temperature of 900°F without significant deterioration of fuel quality.

In addition to these goals associated with thermal management of current and future aircraft fuels, there is great interest in exploiting, if possible, the supercritical nature of fuels. When the fuel is above a critical pressure (P_c) and a critical temperature (T_c), it is considered a supercritical fluid, having properties in some ways similar to liquids (density, solubility) and in some ways similar to gases (viscosity, surface tension).

Since current systems operate above critical pressures and are expected to operate above critical temperatures, the behavior of fuel above the critical point is important to understand. However, it is also important from a mission perspective to realize what changes the fuel encounters as it is heated and cooled through its critical temperature. Every aircraft mission conducted at higher mach numbers, will by necessity, experience subcritical and supercritical fuel conditions. The understanding of the behavior in this regime is paramount in designing and producing future aircraft fuels.

The research system produced under this effort was designed to demonstrate the feasibility of conducting flowing experiments for subcritical and supercritical fluids, collecting basic information about changes occurring with the bulk fluid as it is exposed to various temperatures, pressures, residence times, reactive atmospheres, etc. Important advances in instrumental analysis have allowed experimenters to determine what products are formed and what reactants are consumed from controlled exposures of candidate fuels and model mixtures. The identity of products which may be precursors to the formation of gums and solids in the fuel will help to determine reaction kinetics, reaction mechanisms, and the effect of trace components in the degradation and decomposition processes for both the subcritical and supercritical regime.

SECTION 2
BACKGROUND

The Condensed Phase Test Cell (CPTC) is just one of several test cell assemblies which have been conceptualized for the System for Thermal Diagnostic Studies (STDS) over the past several years. This particular test cell assembly is different from all other test cells developed thus far for the STDS in that it is a high pressure assembly made entirely of metal. Until this design, all previous test cells were constructed of high temperature quartz, specifically for low pressure (less than 2 absolute atmospheres) applications. Although low pressure gas phase experiments are different than condensed phase or supercritical phase experiments, the design of experiments and the concepts of testing are very similar. One aspect of condensed phase and gas phase experiments involves the determination of a degradation "profile" where all variables are held constant except temperature. The profile is developed by conducting experiments at various temperatures and observing the degradation of the "parent" or reactant material. The major goal is to accurately control all experimental variables to determine the effect of temperature, or any other important parameter, on the stability of the sample of interest and to determine what products are formed in the degradation process.

The same general concepts can be applied to condensed phase testing. The variables that are critical in gas phase experiments are the important ones in liquid phase and supercritical phase experiments, i.e., temperature, residence time (and residence time distribution), reaction atmosphere, reactant concentration and degree of mixing. In addition to these variables, pressure has become a critical variable in the condensed phase; concentration of the reactant material has also increased in condensed phase analyses. Clearly, the design and development of the CPTC have grown out of what we consider to be important in gas phase thermal degradation experiments.

2.1 GAS PHASE REACTIONS ON THE STDS

The STDS (6-8) is a versatile mainframe system for conducting many types of thermal analyses on any organic material. It incorporates sophisticated in-line analytical instrumentation to determine both the stability of the parent material and the identity of products formed from the thermal degradation of the parent material at various conditions.

Many authors have used the STDS and similar systems to conduct gas phase thermal decomposition experiments for a variety of organic materials including hazardous wastes (9), pesticides (10), model mixtures (11), replacement utility materials (12), and other compounds; these have typically been related to high temperature incineration research. One published study was performed on the gas phase thermal degradation of candidate turbine engine high density fuels (13) and unpublished studies are available on the thermal decomposition characteristics of n-dodecane (14,15). Results from decalin decomposition (13) describe the gas phase stability of various endothermic fuel candidates, and show the formation of aromatic products at elevated temperatures (greater than 700°C) in flowing nitrogen (see Figure 1). This finding was entirely consistent with typical product formation observed for many other organic materials under similar conditions.

Products formed from trans-decalin at lower temperature pyrolysis conditions (substituted cyclohexadiene compounds, cyclohexenes, etc.), were consistent with a mechanism primarily involving C-C bond rupture followed by C-H bond homolysis or H-abstraction type reactions. The fact that these reactions were followed by the formation of aromatics led the authors to cite other experiments in which aromatic species were formed from various lower molecular weight olefinic and acetylenic species by addition/displacement and other types of "molecular growth" reactions (16).

Similar studies conducted for n-dodecane have indicated that the same types of reactions are important in the gas phase pyrolysis of straight-chain compounds. In Figure 2, the first formed products from the pyrolysis of dodecane at 700°C were a homologous series of olefins (15). When the temperature was increased to 800°C as in Figure 3, aromatic formation was apparent. These studies, although qualitative in nature, show some significant trends in predicting product formation over a wide range in temperature. In addition, these few experiments produced information useful in developing the global reaction kinetics for this compound.

A testing apparatus and experiments for condensed phase flow reactors have developed out of this experience with gas phase reactors. Although the gas phase experiments provide important information about product formation and possible reaction pathways, the more realistic conditions of pressure (and the change in fluid properties at these pressures) were necessary to conduct experiments of wider applicability. However, the design of the condensed phase reactor has incorporated the ability to control parameters that we know to be important from gas phase testing. Because temperature in such an important parameter and is readily varied with the STDS, experiments for condensed phase reactions can (and should) be conducted in much the

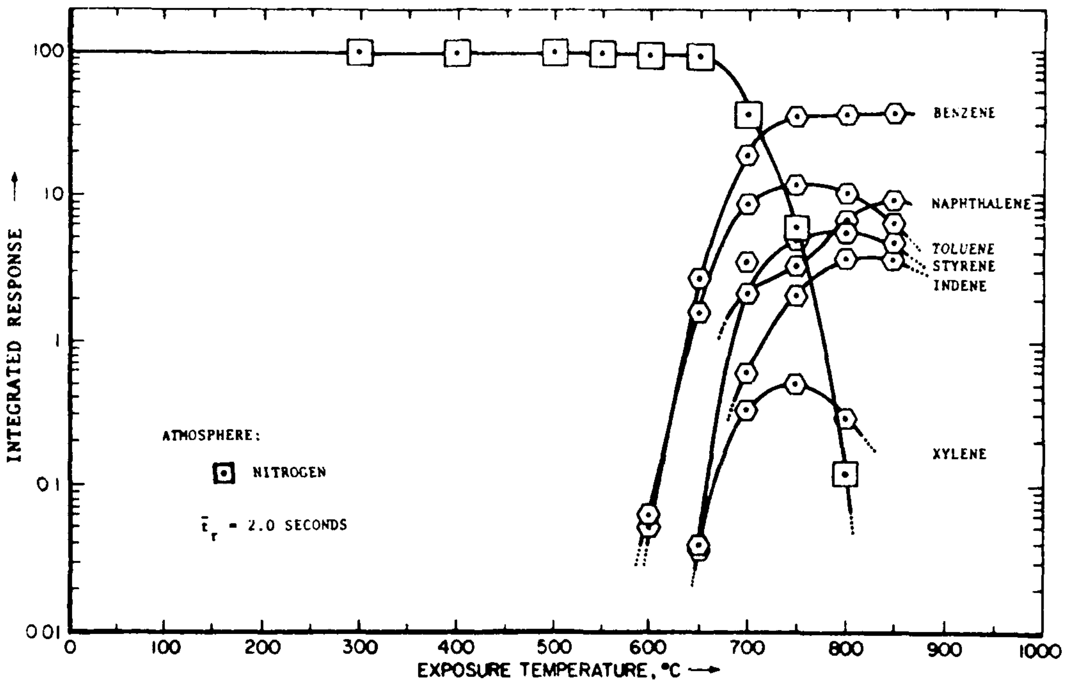


Figure 1. Trans-Decalin Thermal Decomposition at 700°C Under Gas Phase Pyrolysis Conditions.

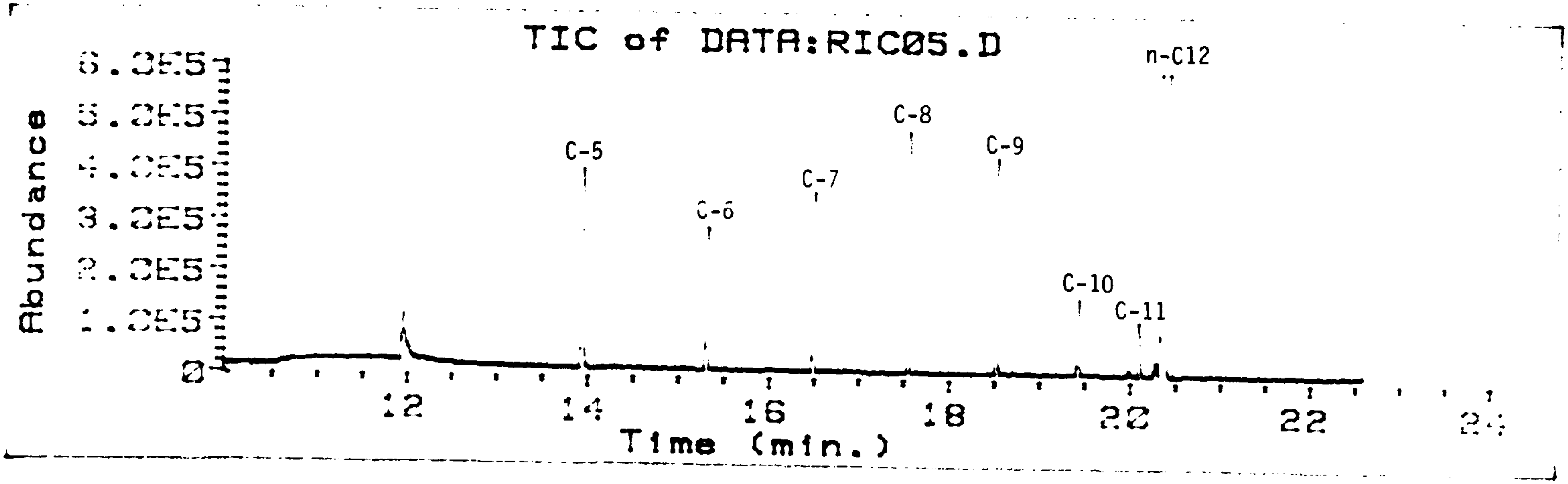


Figure 2. Initial Products from the Gas Phase Pyrolysis of n-Dodecane at 700°C; a Homologous Series of 1-Olefins.

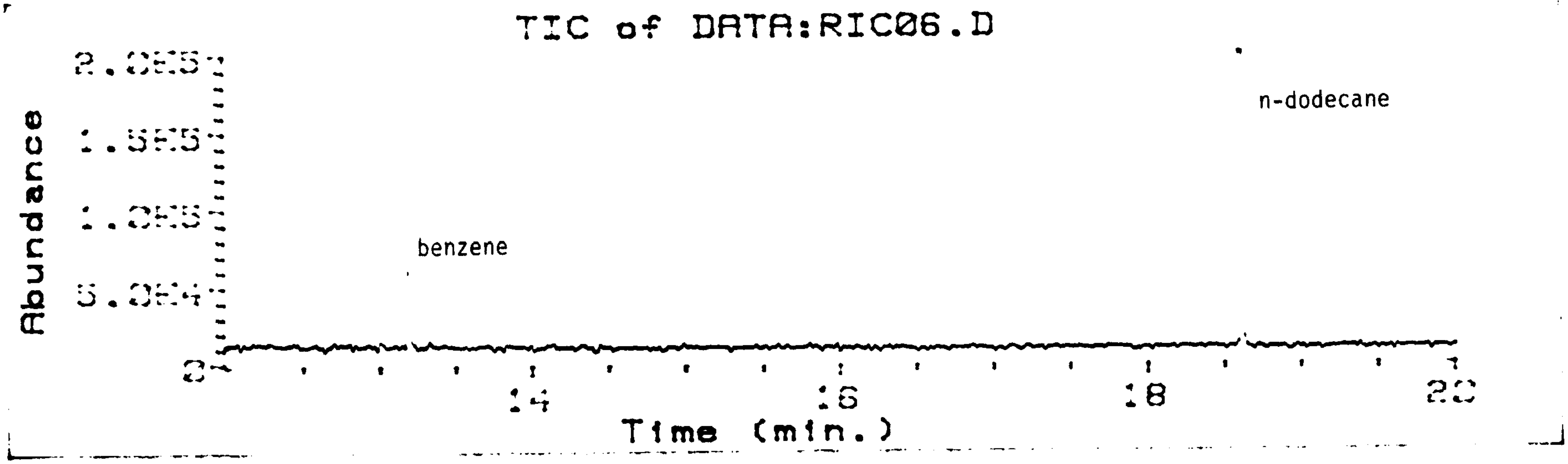


Figure 3. Pyrolysis Products from n-Dodecane at 800°C; Benzene Formation.

same way as for gas phase reactions: constructing thermal decomposition and product yield profiles for various residence times, temperatures, reactive atmospheres, and pressures.

2.2 CONDENSED PHASE REACTORS

A number of different experiments have been conducted over the years to precisely control residence time, temperature and reactive atmosphere, while measuring product and apparent deposit precursor formation. Many flow reactor studies have been conducted on the Jet Fuel Thermal Oxidation Tester (JFTOT) or modified JFTOT using both real fuels and model mixtures. The following paragraphs will briefly outline some of the pertinent studies that have been conducted for both real fuels and model mixtures similar to those that have been investigated in these experiments.

Hazlett, et al. (17) conducted investigations on the initial reaction products of dodecane exposed to temperatures between 200 and 540°C in the JFTOT (18). In these experiments, hydroperoxides were the major initial products but these compounds were thermally labile at temperatures above about 300°C, forming a variety of alcohols and ketones. Olefin and lower normal alkane formation were also observed at higher temperatures (340°C to 480°C) indicating pyrolysis type reactions. The explanation of product formation was the combination of competing reactions--autoxidation (less than 260°C) and pyrolysis (greater than 480°C) with other thermal decomposition reactions occurring between the two temperatures.

Similar studies by Reddy, et al. (19), have been successful in verifying Hazlett's results. Reddy, however, used residence times much shorter than Hazlett (9 seconds vs. 28 seconds, respectively) and still observed similar products. Reddy reiterated that alkyl hydroperoxides were thermally fragmenting in the intermediate temperature regions (300-400°C) to form the alcohols, ketones and aldehydes for C12 compounds and lower. The reactor, as in Hazlett's work, was a JFTOT apparatus, with annular flow around an aluminum or stainless steel tube.

The excellent work provided by Taylor (ref. 20-23) incorporated a heated tube to transport the fuel into a four-zone high temperature furnace at pressures up to 1,000 psi (69 atm) and temperatures to 649°C. The reactor was a 304 stainless steel tube which was 1/4 inch OD and 0.084 inch ID (2.13 mm ID) with 12 inches of reactor in each zone. The fuels and model mixtures used in this study were delivered by means of a nitrogen driven piston, with an average residence time calculated to be 25 seconds. The average temperatures in the four-zone furnace were as follows for the 1,000 psi (69 atmosphere) tests: 149°C, 204°C, 260°C, and 316°C (20). Taylor's work demonstrated the importance of dissolved oxygen in the deposition process, the rate of deposit formation at various conditions of pressure and temperature, and the effect of trace sulfur, nitrogen and oxygen for jet fuels and model mixtures.

Marteney and Spadaccini (24) and TeVelde et al. (25) reported on the use of an electrically heated metal reactor with dimensions of 0.317 cm OD by 0.277 cm ID by 240 cm in length. The residence times used in these tests were varied between 0.16 second and 8.0 seconds. Comparisons of deposit formation at various conditions were performed in the experiments conducted. Velocity and test duration were found to be important variables while fuel bulk temperature and pressure above the critical point had a secondary influence on deposition. These authors also concurred that different regimes characterized deposit formation with the autoxidation regime occurring below 262°C and the pyrolysis regime at approximately 342°C with a transition region between these temperatures.

Fabuss, et al. (26), reported on the rapid thermal cracking of n-hexadecane. The reactor used in this study was a 3/8 inch OD, 1/8-inch ID, 51-inch long, 347 stainless steel tube. The tube was heated by placing it in a three-zone furnace with a preheating section, and residence times calculated for this reactor were between 0.25 and 10 seconds. Higher temperature reactions (1100 to 1300°F) were investigated in these experiments, with chemical identification being performed on the reaction products.

A second reactor used in this study was referred to as a "micro-reactor" and a small number of experiments were performed in conjunction with those experiments performed on the larger reactor tube. This 114 cm tube was 0.02 inch ID. Residence times of approximately 83 seconds were calculated for flow rates of 10 ml per hour through the tube. The experiments were conducted at a pressure of 500 psi and the same high temperatures as the larger reactor. Results showed little deposit formation, probably due to the small flow rates; product data on the smaller reactor was not reported.

A summary of the important conditions and reactor dimensions for studies reported in the literature are summarized in Table 1.

TABLE 1

Summary of Reactor Conditions and Dimensions from Selected Literature Studies Conducted in the Condensed Phase

Authors	Reactor	Residence Time	Pressure	Temperature
Hazlett, et al. (17)	annular (JFTOT)	28 secs	500 psi (34.0 atm)	200-540°C (392-1004°F)
Reddy, et al. (19)	annular (JFTOT)	9 secs	500 psi (34.0 atm)	100-300°C (212-572°F)
Taylor, et al. (20-23)	tubular (0.084" ID, 1/4" OD, 48" long)	25 secs	15-1,000 psi (1-68.0 atm)	<649°C (<1200°F)
Marteney, et al. (24) TeVelde, et al. (25)	tubular (0.277 cm ID, 0.317 cm OD, 240 cm long)	0.16-8.0 secs	400-800 psi (27.2-54.4 atm)	207-527°C (405-981°F)
Fabuss, et al. (26)	tubular (1/8" ID, 3/8" OD, 51" long)	0.25-10 secs	200-1,000 psi (13.6-68.0 atm)	1,100-1,300°F (593-704°C)
	micro (0.02" ID, 1/4 cm long	≈83 secs*	500 psi (34.0 atm)	1,100-1,300°F (593-704°C)

*83 seconds-calculated

2.3 SUPERCRITICAL FLUIDS

The operating conditions for fuels to be used in advanced aircraft may include conditions above the fuel critical temperature and pressure. The critical temperature for a liquid can be defined as the temperature above which a gas cannot be liquefied, no matter how great the pressure (27). The pressure corresponding to this temperature on the gas/liquid coexistence line is called the critical pressure (see Figure 4). When a liquid or dense gas is above its critical temperature and pressure, i.e., above its critical point, it is considered a supercritical fluid.

Supercritical fluids possess several important properties which are characteristic of both gases and liquids. For example, supercritical fluids have high solvating power, viscosities approaching those of gases, and have no surface tension. The densities above the critical point approach those of liquids and diffusivities are like gases rather than liquids. It is these properties which will allow supercritical fluids to have interesting mass transport and thermal properties.

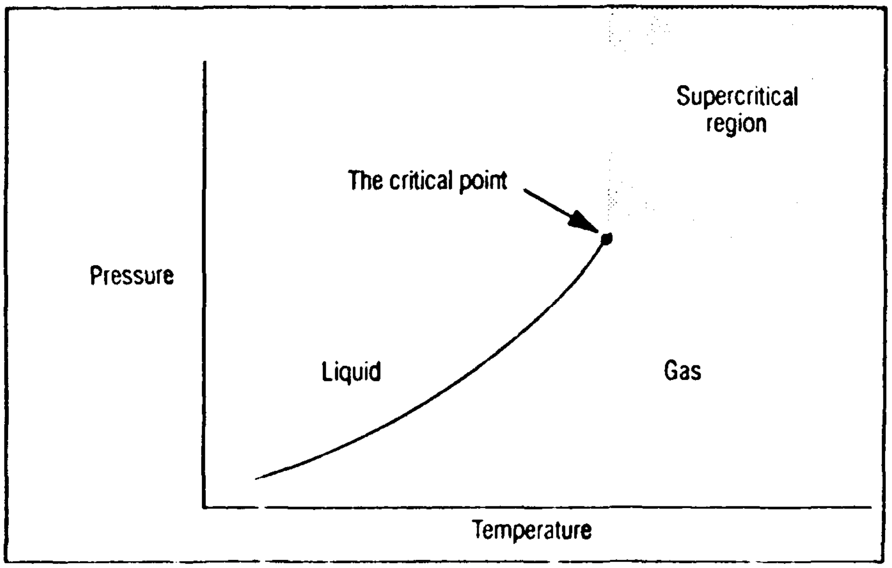


Figure 4. The Supercritical Regime Above the Critical Temperature and Pressure.

Supercritical fluid behavior in jet fuels may provide significant advantages with regard to thermal stability. Because supercritical fluids have high solvating power due to their gas-like diffusitivity, solutes which may ordinarily form solids (insoluble in the fuel matrix) may be solubilized and remain in the liquid phase. Because solvating power is proportional to supercritical fluid density (27), temperature and pressure, the physical properties of fluids are of great importance. In a practical sense, the formation of deposits at high temperature and pressure (above the critical point) may not be as important as the formation of deposits after the fuel is cooled and depressurized to subcritical conditions.

Table 2 shows some of the major differences between liquids, gases and supercritical fluids.

TABLE 2

Differences Between Liquids, Gases, and Supercritical Fluids

	Liquid	Supercritical Fluid	Gas
solvation (mass solute/ mass solvent, g/g)	1.0	0.1	≈0
density (e.g., dodecane, g/ml)	0.75 (25°C)	≈0.2	P,T dependent
diffusivity (cm^2/sec)	10^{-5}	10^{-3}	10^{-1}
viscosity (antipoise)	10^{-2}	10^{-3}	10^{-4}

SECTION 3
EXPERIMENTAL

3.1 EXPERIMENTAL OVERVIEW

The CPTC Assembly was constructed as an integral part of the STDS. The thermal reaction compartment (TRC) and the analytical GC were modified to accommodate the condensed phase reactor assembly for conducting product analysis. A sketch of the TRC, GC and sample introduction system are provided in Figures 5-8.

In this system, the fuel or model mixture to be investigated was filtered through a 0.22 μm Millipore filter into a clean Alltech HPLC reservoir. Sparge gases (air for oxygen saturated liquids, or helium/nitrogen for oxygen-free liquids) were introduced through a stainless steel porous sparger to bring the fuel to a desired oxygen level. Off-line analyses of sparging efficiencies were performed to evaluate the ability of the sparger to remove the oxygen from the liquid system (see Figure 9). This initial study, performed using selected ion monitoring, indicated that sparging could be conducted to achieve various levels of dissolved oxygen in the feed reservoir for the system. Sparging gas flow was maintained throughout an analysis, which was especially important when conducting oxygen free experiments.

A SSI Model 300 constant delivery pump (0-5 ml/min) was used to provide constant flow rates to the reactor tube. The reactant liquid was pumped into a Rheodyne/Rainin pressure relief valve, through a tee connected to an Alltech pressure gauge and then through two pulse dampeners (SSI and Alltech). The liquid, being pumped through 0.02-inch ID 316 stainless steel tubing, was filtered through a 0.5-μm high pressure filter (SSI) and sent on to a flow switching valve (Upchurch Scientific). The same 1/16-inch tubing was then used to direct the liquid into the reactor assembly (Figure 10) inside of the high temperature furnace (Lindberg). The reactor was connected to two high pressure, high temperature sampling valves (Valvco) and to a back pressure regulator (Upchurch Scientific) which was the main pressure control point for the system.

The reactor was a 1/16-inch OD, 0.02-inch ID, 316 stainless steel tube with radial fins and cooling devices to maintain control of temperature (Figure 10). Reactor temperature was assumed to be constant due to uniformity provided by the radial fin design; only one thermocouple was used in the 4.0-centimeter heated zone. The difference between the wall temperature and the bulk temperature was assumed to be

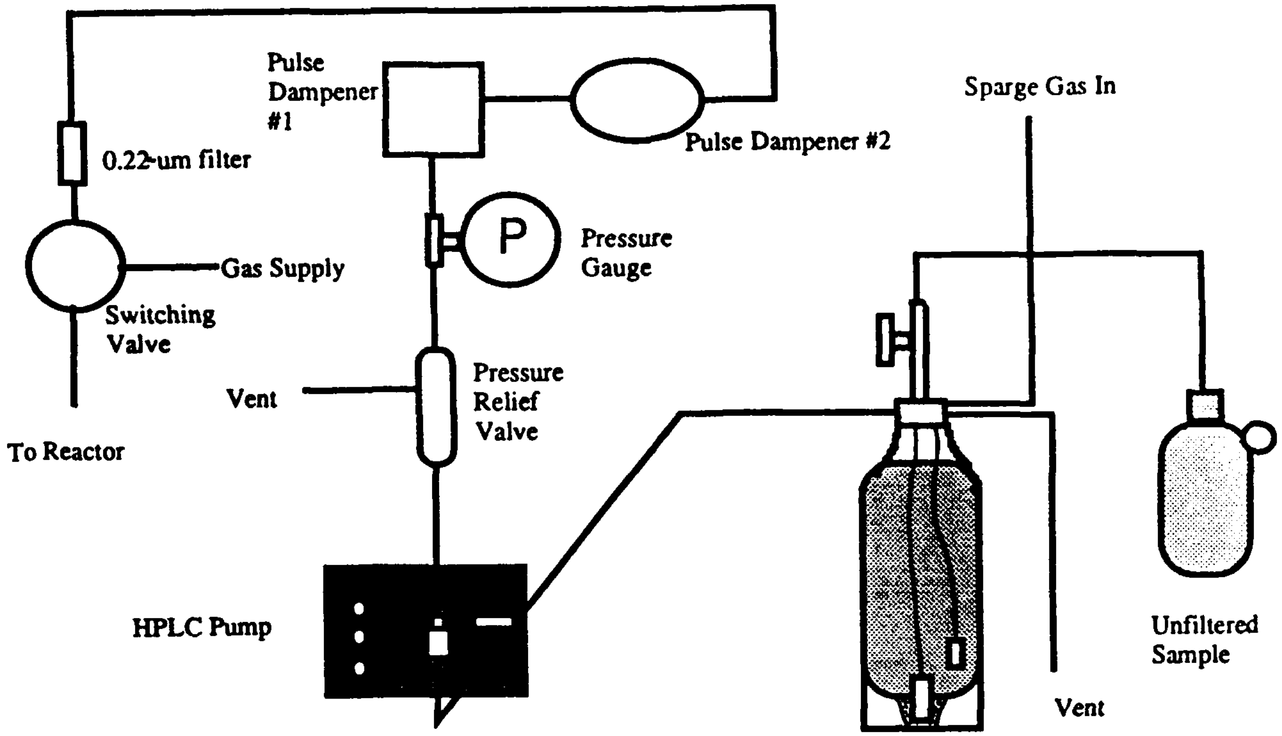


Figure 5. Sample Introduction System for the CPTC.

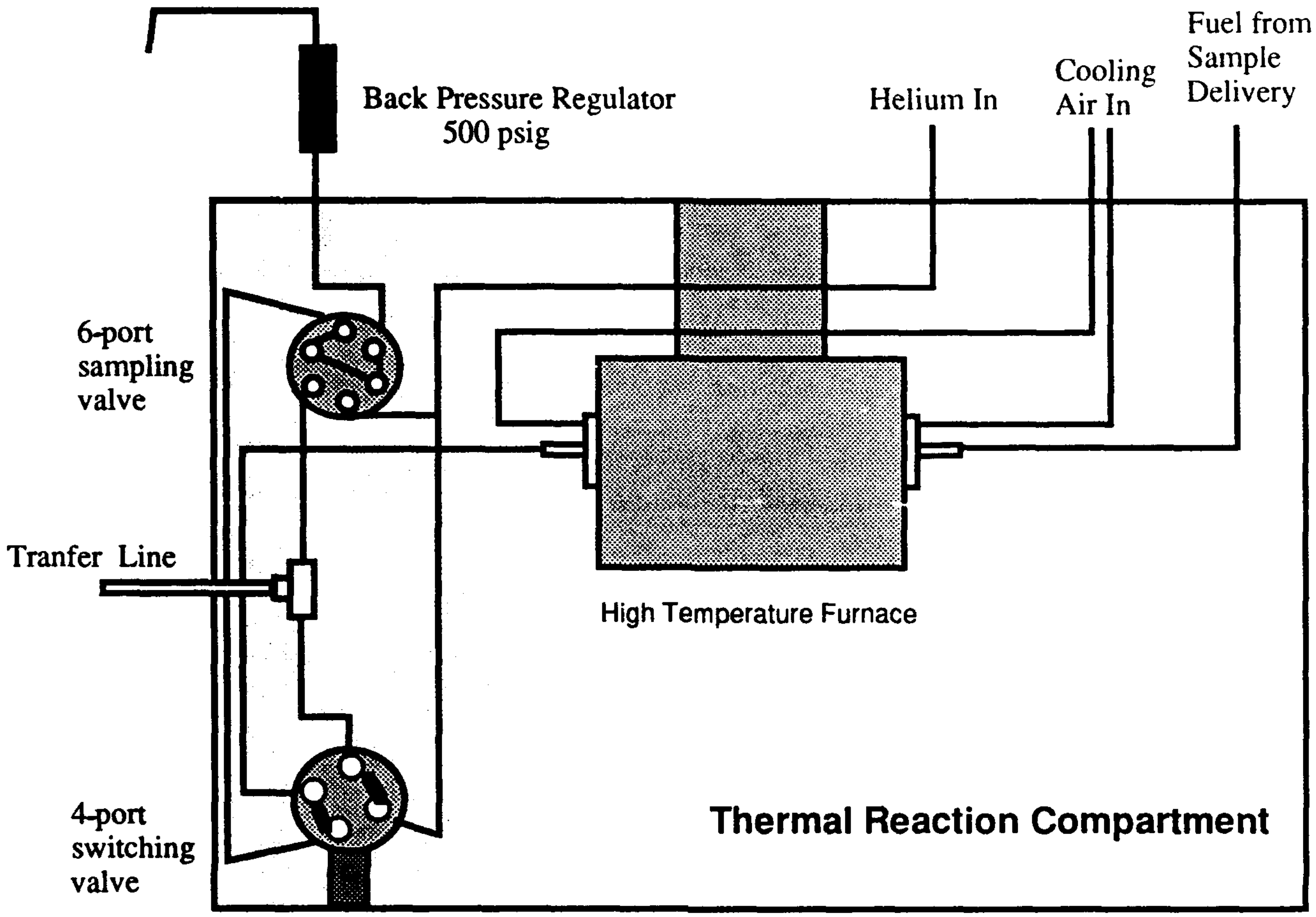


Figure 6. Thermal Reaction Compartment (TRC) for the CTPC Assembly.

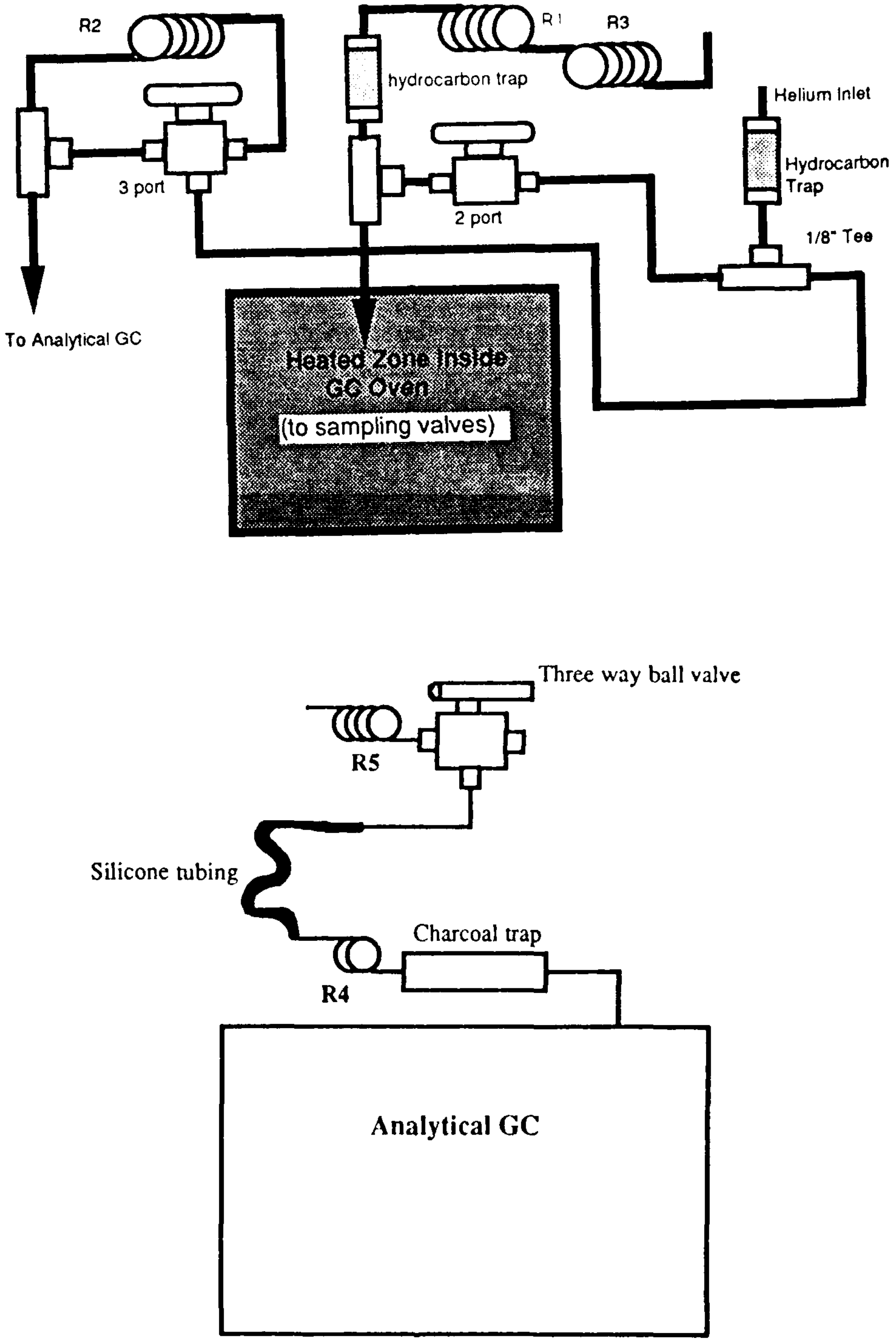


Figure 7. (top) Schematic of Flow Patch for Helium Carrier and Backflush with Pneumatics (R1 = 50 cm (0.01" ID); R2 = 50 cm (0.01" ID); R3 = 100 cm (0.005" ID) (bottom) GC Top Deck Schematic, R4 = 5 cm (0.01" ID), R5 = 25 cm (0.01" ID)).

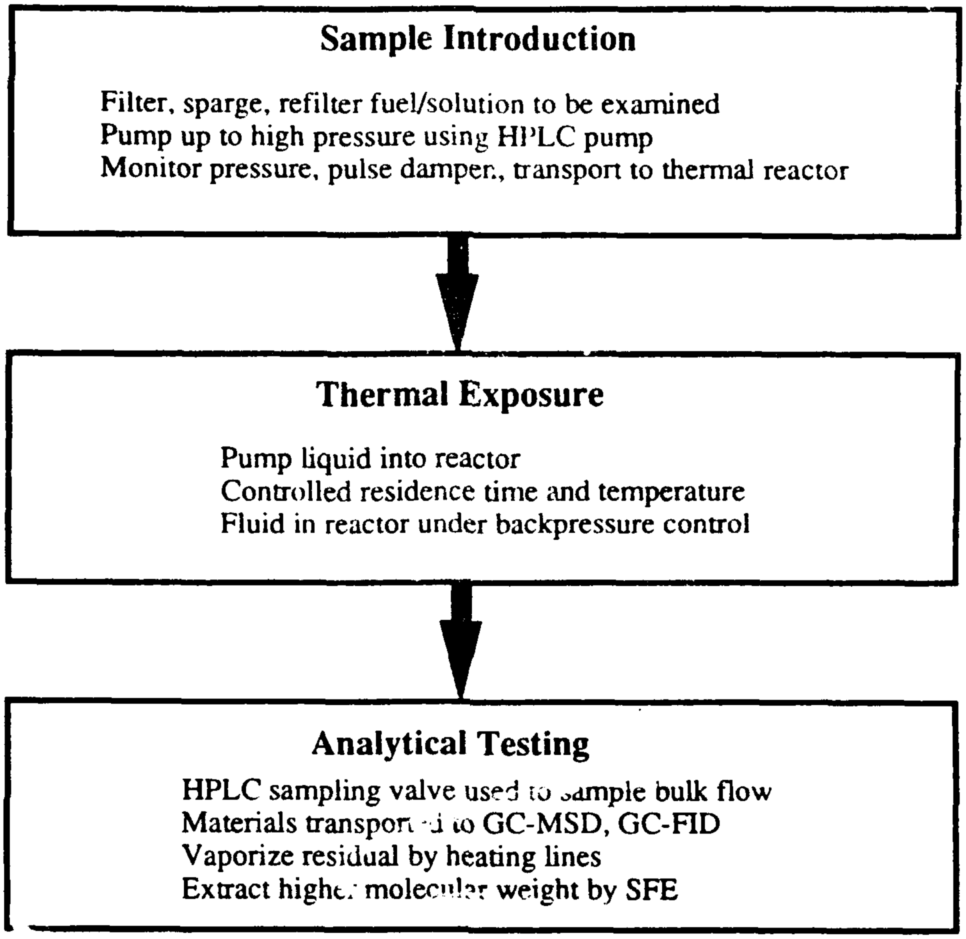


Figure 8. Simplified Flow Chart for CPTC Experiments.

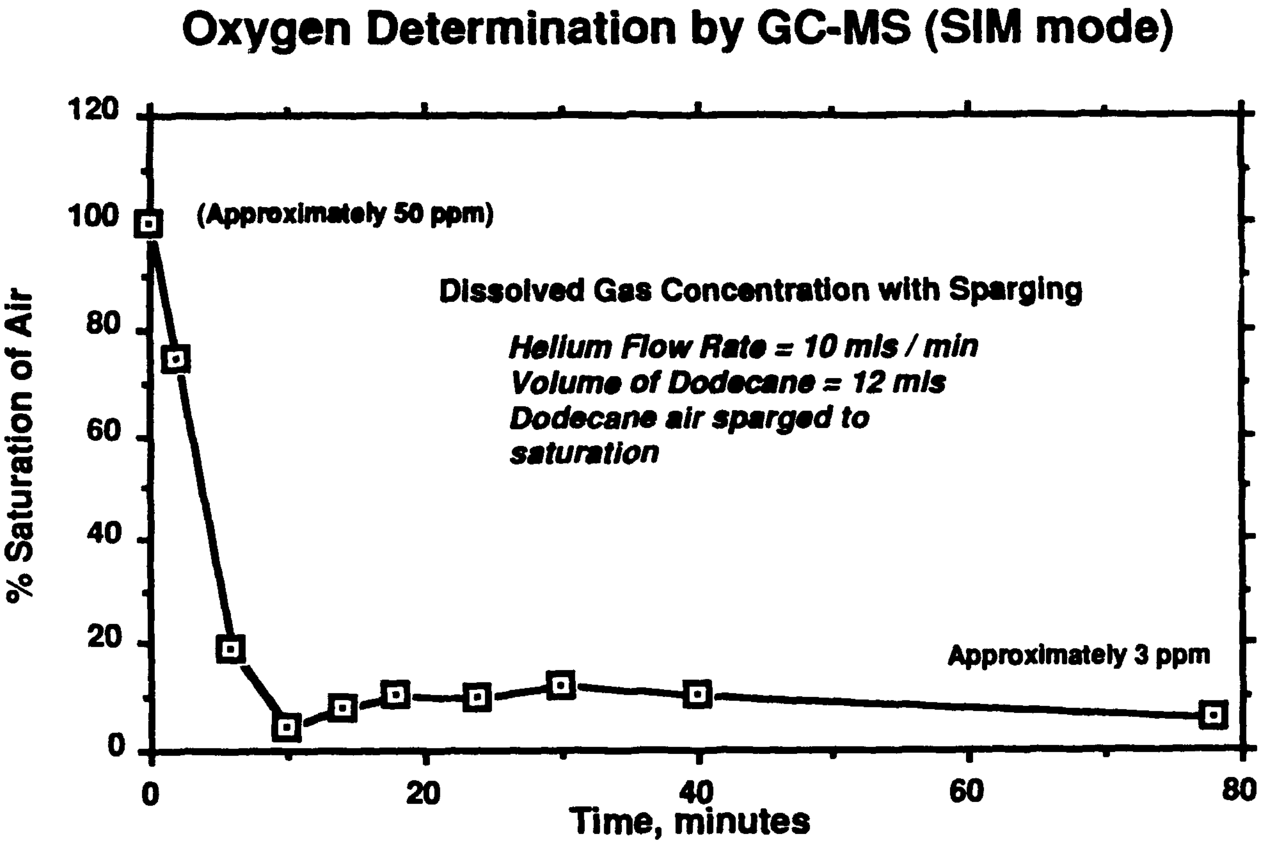


Figure 9. Experimental Results for Sparging of Dodecane (Air Saturated) With Helium.

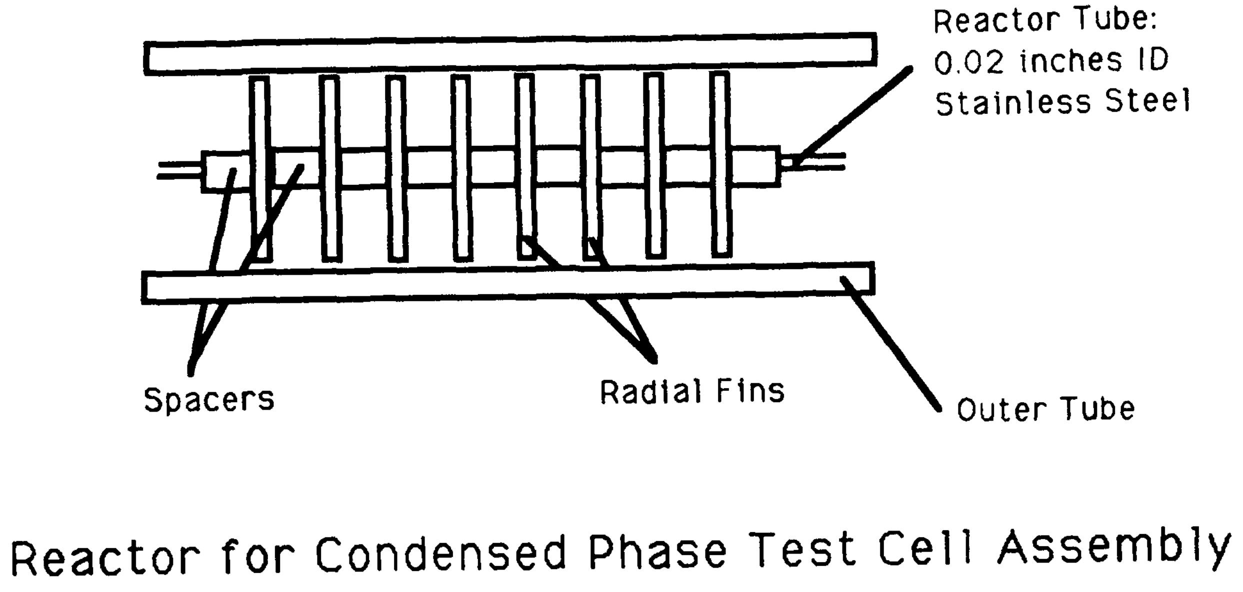


Figure 10. Reactor Assembly for the Condensed Phase Test Cell Assembly.

negligible due to the extremely small diameter tubing and small flow rates. It is recommended that this assumption be studied in more detail.

The valves were capable of switching the liquid/dense gas material by means of a sample loop (Figure 11) to the transfer line and gas chromatograph (Hewlett Packard 5890A). The inlet of the GC system provided for splitting of the sample to vent and to each of two chromatographic capillary columns. These 0.25-mm ID, 0.25 μm film thickness columns (J&W) were connected to two detectors: a 5970B Mass Selective Detector and Chemstation (Hewlett Packard) and a flame ionization detector connected to a recording integrator (Hewlett Packard, 3390A).

A back flushing flow path was incorporated into the system to reduce the amount of carryover and sample memory from one run to another (Figure 7).

An experiment was conducted by establishing liquid flow through the sampling valves to the back pressure regulator. When the reactor temperature reached the desired value and equilibrated, the main sampling valve was actuated, thereby sampling a portion of the dense gas stream as it left the thermal reactor. The sampling loop with the liquid sample was then exposed to a low pressure, high velocity helium stream, and the entire sample compartment was heated in order to vaporize the material in the sample loop. The heated vapor phase material was then swept into the cryogenically controlled GC-MS-FID system for analytical detection of everything from dissolved gases to parent material. Off-line samples were typically collected downstream of the back pressure regulator for other GC-MS type analyses.

3.2 FLUID USED IN CPTC EXPERIMENTS

The mixture used in these experiments was n-dodecane with 0.3 weight percent n-hexadecane and 35 parts per million by weight of butyl hydroxytoluene (BHT), a phenolic antioxidant. The n-dodecane was used as received (Aldrich, 99% purity) and it did have at least two impurities which were isomers of C12. The n-hexadecane (Supelco) also contained impurities but was used as received. This mixture was chosen to study n-dodecane with a small component of another hydrocarbon which would act as an internal standard and provide information about any adsorptive effects or carryover in the system.

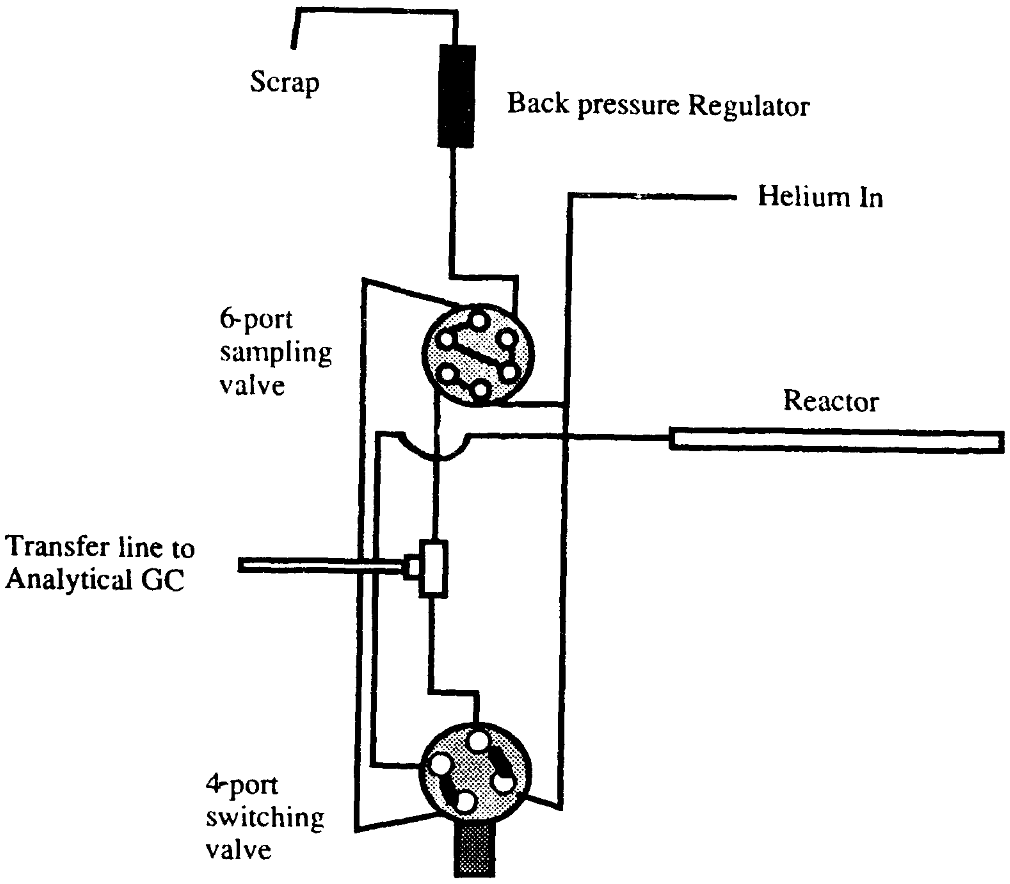


Figure 11. Valve Assemblies for Sampling Flow Stream Out of the Thermal Reactor.

3.3 ANALYTICAL CONSIDERATIONS

After the sample had been removed from the high pressure portion of the CPTC, it was exposed to a flowing helium stream in the analysis train at relatively low pressure. The material condensed on the wall of the transfer tubes was then stripped of its fixed gases and dissolved light gases. The temperature of the entire thermal reaction compartment was then raised to vaporize all of the condensed material (again in a helium stream) in the transfer lines. As the gas phase solutes were swept into the cryogenically controlled GC-FID-MSD, the light gases (<C4)were transported through the capillary column unaffected by the subambient temperatures. By monitoring for various fixed gases and light gases in the Selected Ion Monitoring (SIM) mode and with the FID, an entire set of non-retained compounds could be detected before the bulk of the fuel was analyzed.

After the light gas analysis, the computer acquisition program was restarted and the GC programmed up in temperature as in the typical operation of a GC-MSD system. This action allowed the higher molecular weight (>C4) material to be transported through the chromatographic column for separation and into the mass selective detector for identification.

SECTION 4
RESULTS

A number of different experiments were conducted to verify the operation of various aspects of the CPTC. Examples demonstrating the feasibility of each technique are provided in the following sections.

4.1 ANALYSIS OF DISSOLVED OXYGEN BY GC-MSD

Experiments were performed to demonstrate the ability of the Mass Selective Detector (MSD) to perform an analysis of the level of dissolved oxygen in the n-dodecane sample as it was pumped through the system at high pressure. Figure 12 illustrates analyses at 30°C reactor temperature (500 psi) for both the air sparged and helium sparged n-dodecane mixture. The mass spectrometer was operated in the selected ion monitoring mode for higher sensitivity, monitoring the 32 ion. Results indicate that the mass spectrometer can be used to monitor the dissolved oxygen level of mixtures exposed to high temperatures and pressures. In fact, the mass spectrometer was capable of separating all of the components of the dissolved gases (nitrogen, oxygen, argon, trace carbon dioxide) due to the different atomic mass units of each compound in air.
Figure 13 shows the chromatographic response of argon and oxygen for one of the analyses of dissolved gases.

4.2 ON-LINE DETERMINATION OF LIGHT GASES BY GC-MSD

The in-line analysis of products from thermal experiments performed in a closed system is desirable. In the case of high temperature experiments, thermal cracking products and dissolved oxygen are difficult measurements to perform off-line. Therefore, fixed gases and C1 through C4 compounds were monitored using the mass spectrometer and the flame ionization detector. Figure 14 shows an example of the analysis of C1 through C3 compounds in a low conversion exposure of n-dodecane.

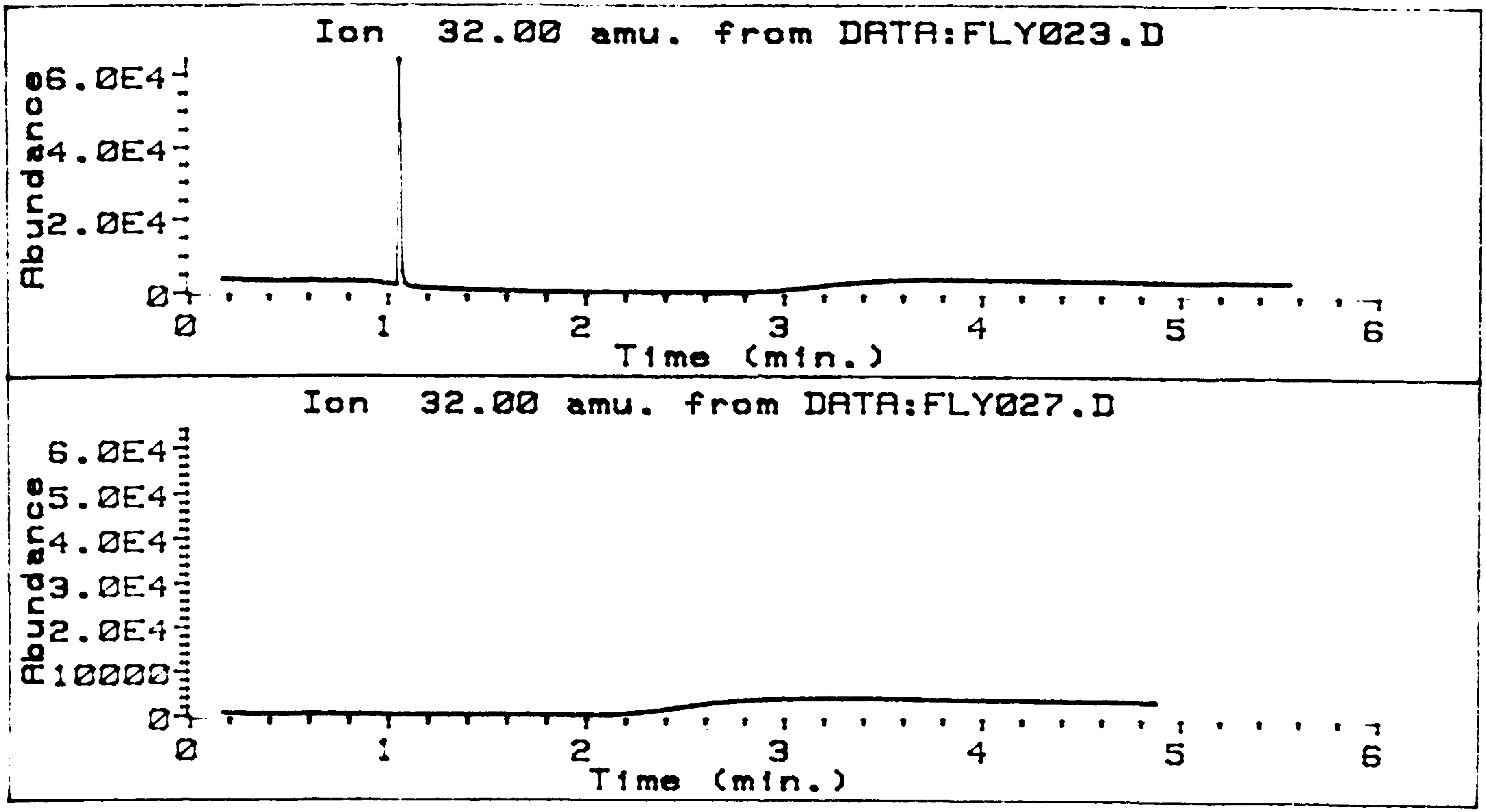


Figure 12. Dissolved Oxygen Analysis for Air-Sparged Dodecane Sample (top) and Helium Sparged Dodecane Sample (bottom).

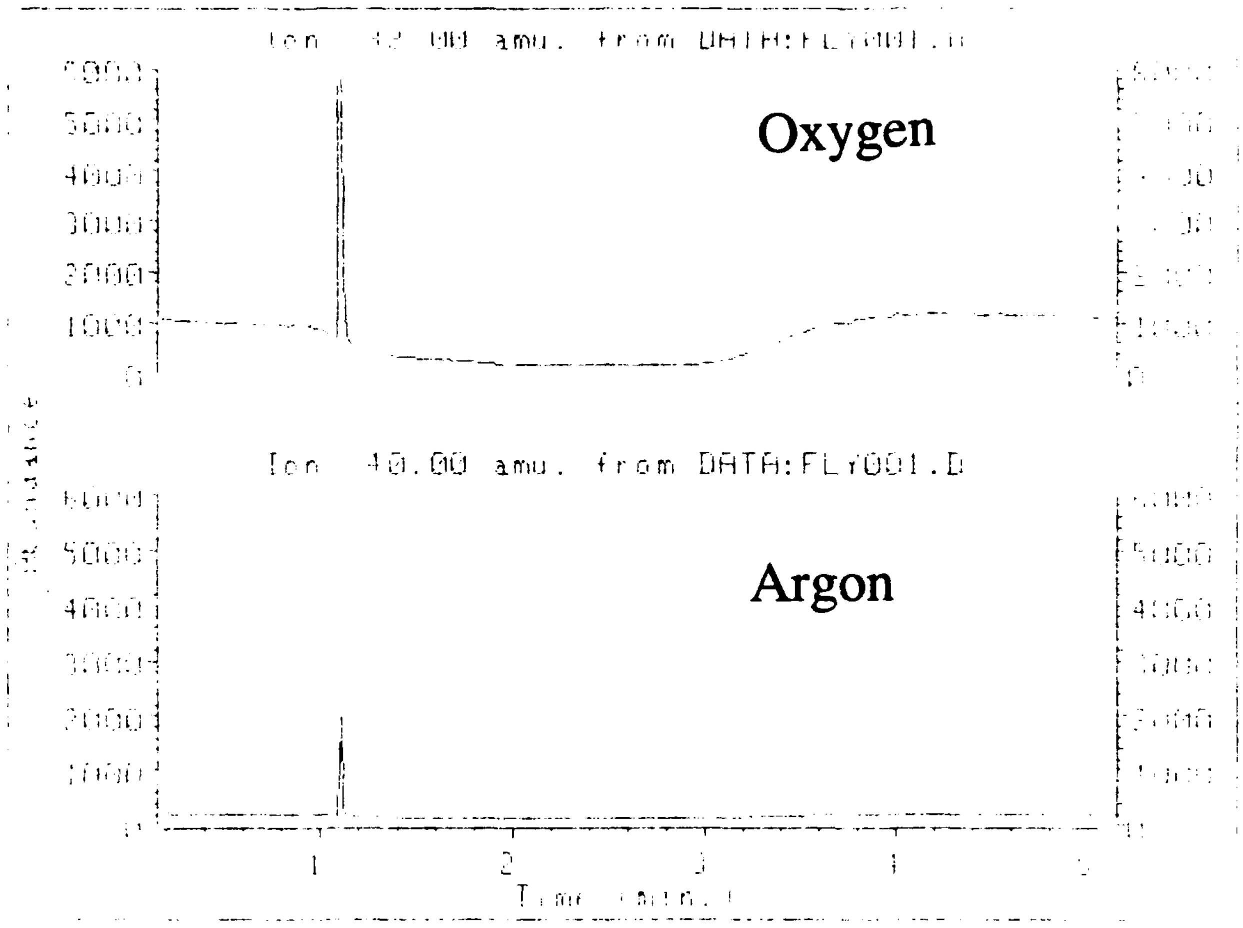


Figure 13. Mass Spectral Identification of Oxygen and Argon from Dissolved Gases in Dodecane at 30°C.

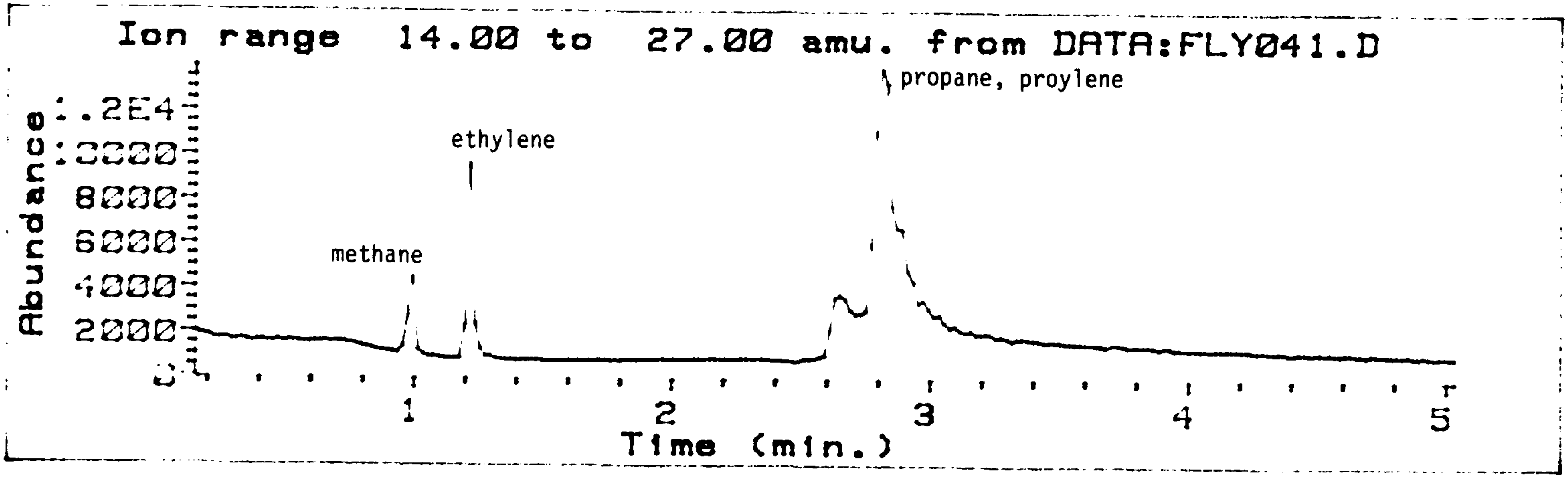


Figure 14. Light Gas Analysis from a Low Level Conversion of Dodecane at Supercritical Temperature and Presssure.

4.3 CONSISTENCY OF GC-MSD AND GC-FID ANALYSES

Two GC columns were employed to detect the products from the thermal reactions. Their results were compared to verify that no selective splitting was occurring in either column, so that the FID could be used for quantitation of reaction products while the MSD could be used for qualitative identification of reaction products. Figure 15 shows the excellent agreement between these two sensitive detectors in these types of analyses.

4.4 THERMAL REACTION PRODUCTS FORMED FROM DODECANE MIXTURE AT 30, 200 AND 400°C

A baseline analysis at 30°C showed no degradation of any of the compounds to be examined in this series of experiments. The chromatograms shown in Figure 16 represent the changes that occur in the fuel as the reactor temperature is increased from 30 to 400°C. The dissolved oxygen was consumed in the highest temperature run, and there were a variety of products forming that were identified as a homologous series of alkenes. It is interesting to note that the peak at 15.8 minutes was the antioxidant BHT which was blended into the dodecane at 35 ppm and was present at a somewhat lower level at 400°C. Even though the dissolved oxygen was eliminated there was still some antioxidant left. The 400°C and 500 psi experiment represented a set of conditions above the critical temperature which, for dodecane is 386°C (28).

4.5 THERMAL REACTION PRODUCTS FORMED FROM DODECANE MIXTURE AT 480°C

The results, shown in Figure 17 a and b, are the chromatograms for the highest temperature experiment conducted under this effort. This analysis showed a significant amount of cracking reaction products. These products were tentatively identified by GC-MS as a homologous series of olefins and n-alkanes (see Figure 18). The larger of the two peaks was the n-alkane for C-6,7 and 8 but other chain lengths have different distributions between the isomers produced.

Peaks eluting between the dodecane peak and the BHT were not positively identified as either olefins or n-alkanes. Future experiments will be performed to isolate and detect these compounds.

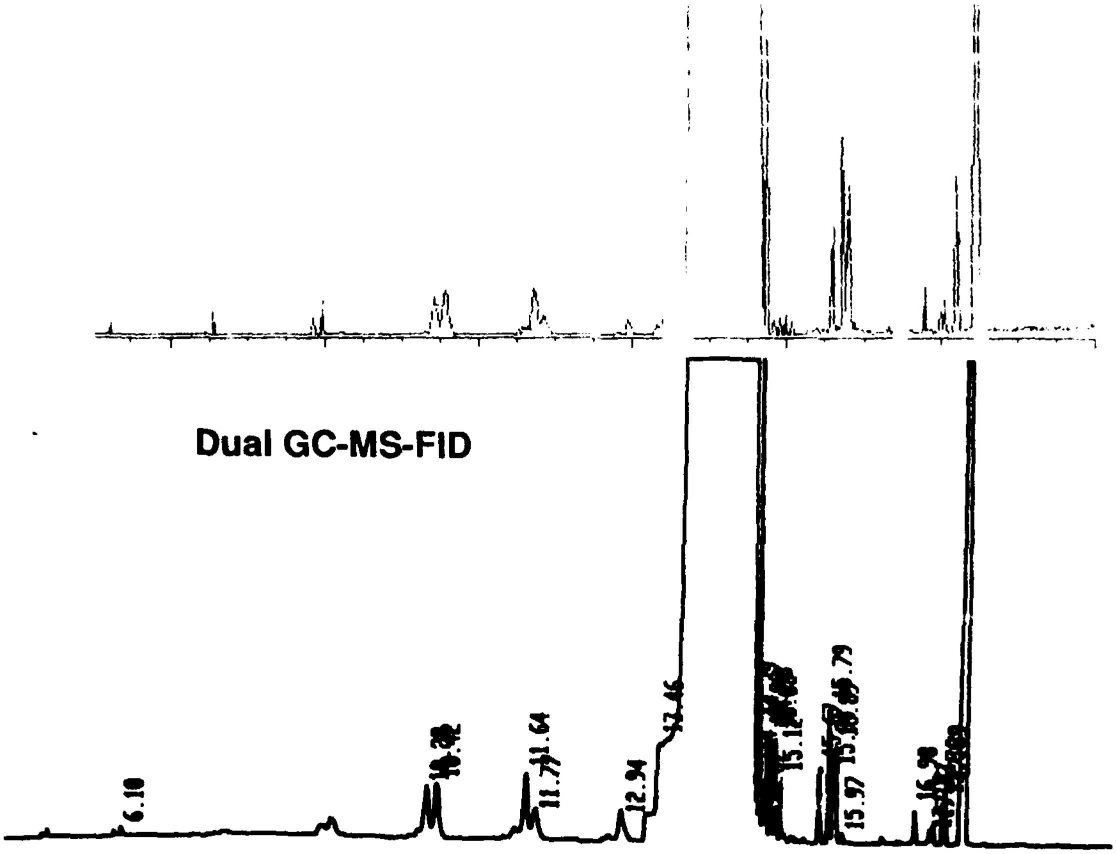


Figure 15. GC-FID and GC-MSD Tracings for Dodecane Degradation Sample.

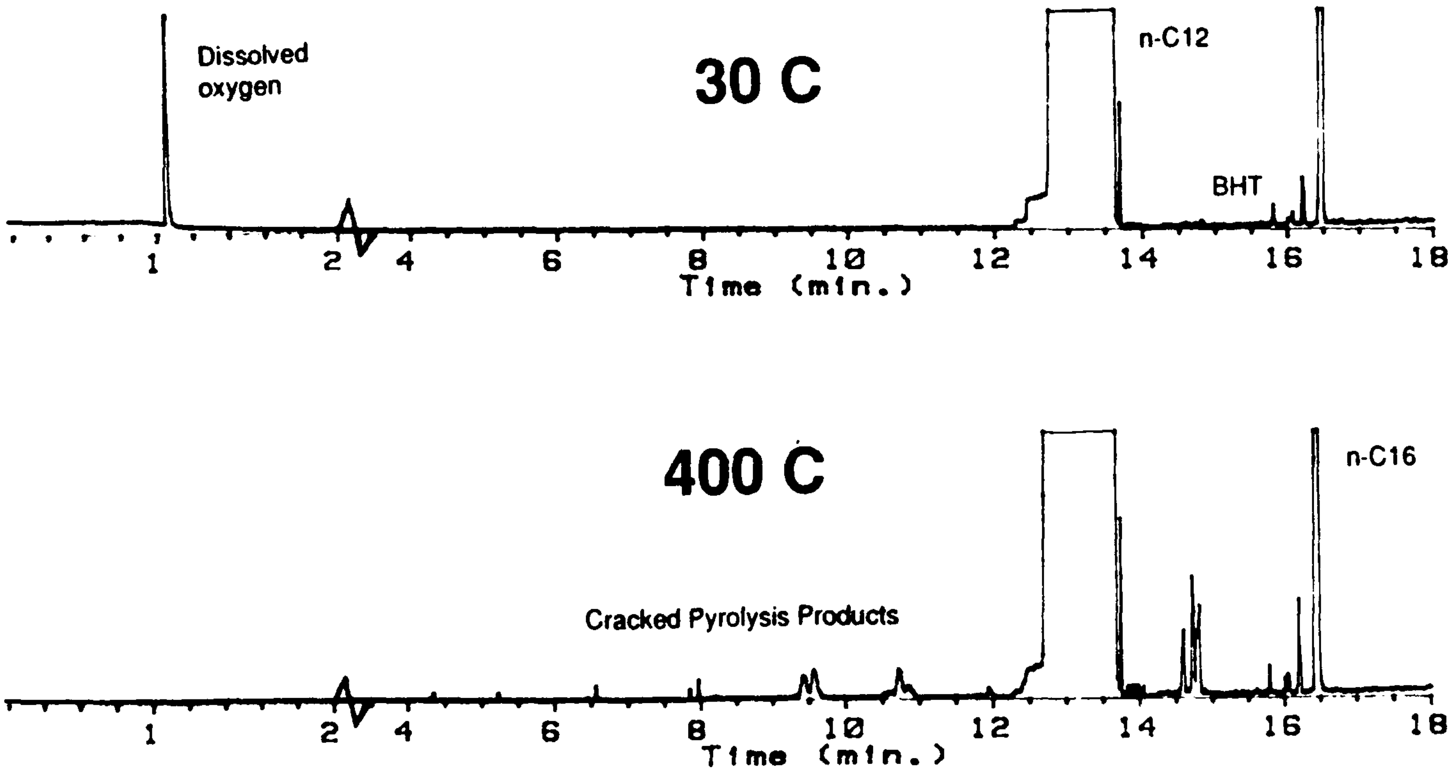


Figure 16. Degradation of Dodecane at Supercritical Conditions (Air Sparged Liquid, 500 psig, 1.0 Seconds Residence Time).

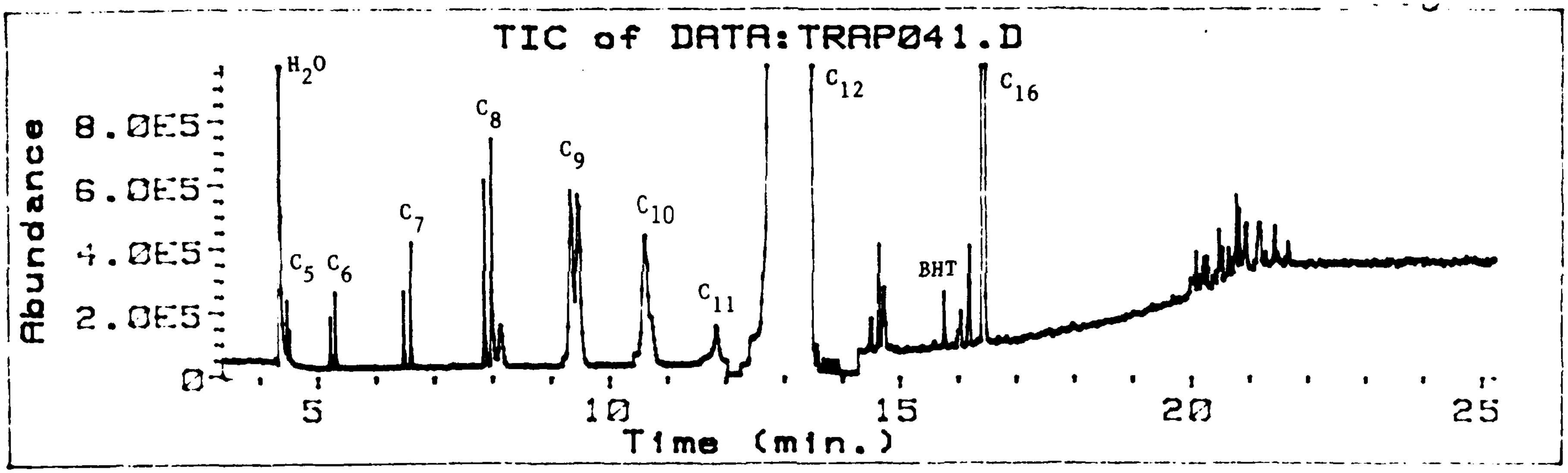


Figure 17a. Thermal Degradation of Dodecane, Hexadecane and BHT at 480°C and 500 psi.

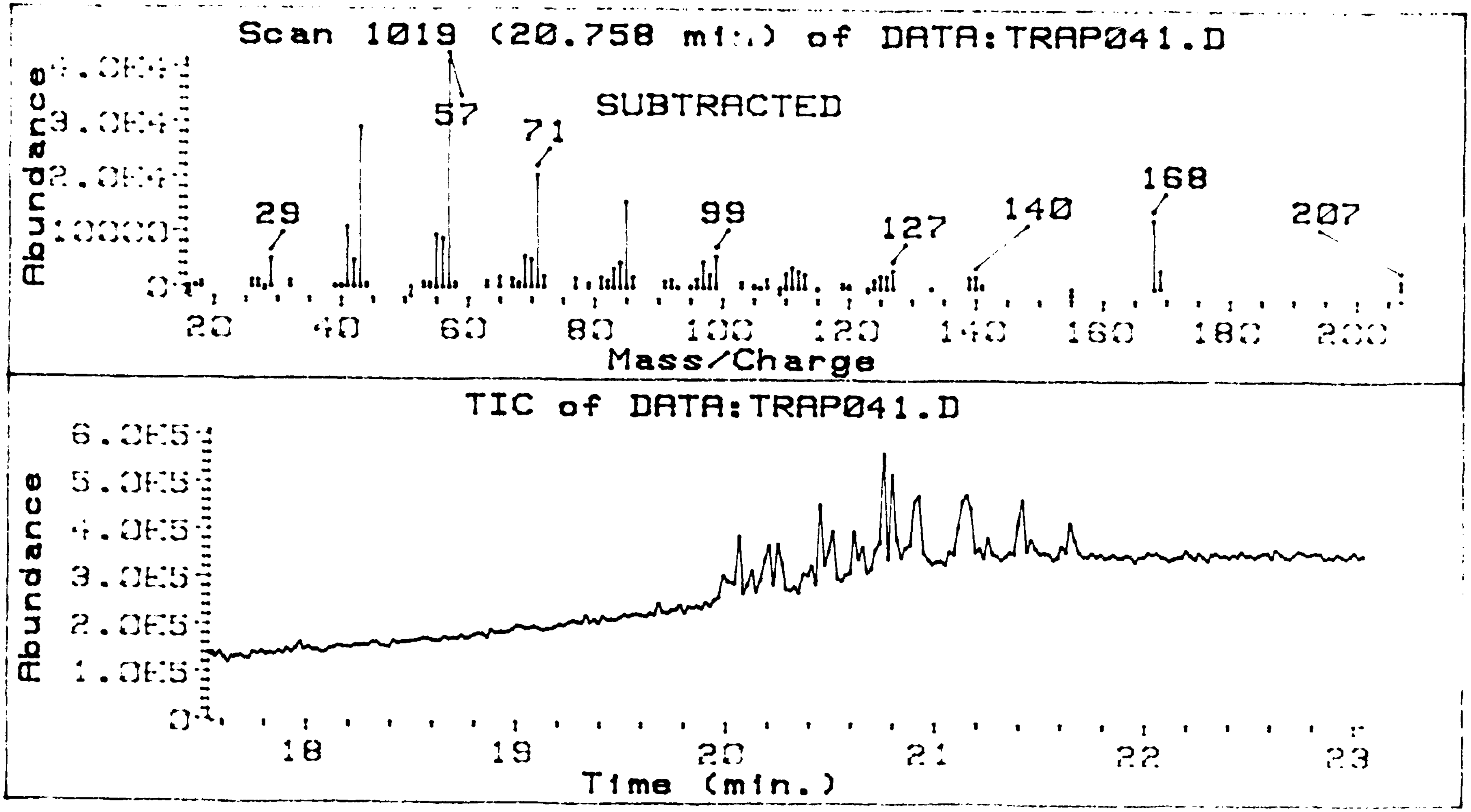


Figure 17b. Heavy Product Formation (possibly C-24) from Dodecane, Hexadecene and BHT Mixture.

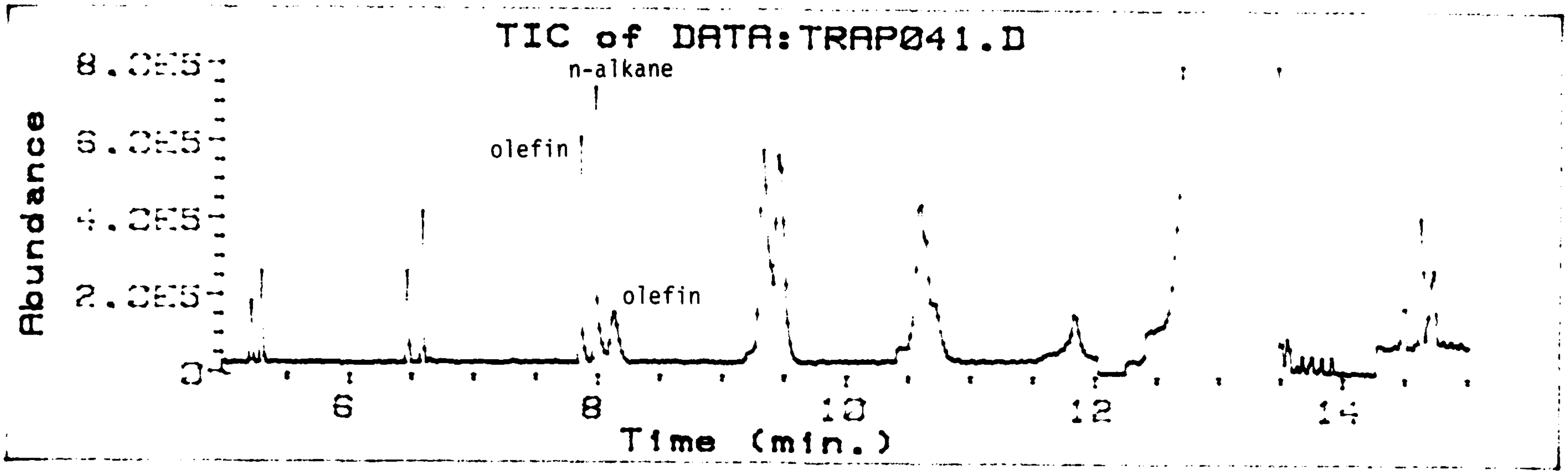


Figure 18. Normal Alkane and Olefin Formation at 480°C and 500 psi from Dodecane Mixture.

All of the dissolved oxygen was consumed at these temperatures; however, as in the 400°C analysis, there is antioxidant (BHT) present in the effluent from this analysis. Apparently, it was not successful in completely protecting this mixture from oxidation (the dissolved oxygen was used up in this reaction) or from thermal fragmentation. The BHT peak was reduced in abundance from lower temperature non-degradative experiments.

There were many compounds that could not be identified in these runs, specifically at the final portion of the 480°C experiment (see again, Figure 17b). These products are likely higher molecular weight products; their identifications may be attempted in future efforts. Attempts to identify the tallest peak in the group indicated the possibility that it may be a C24 compound, which is a chain terminating reaction in many autoxidation reactions in the literature. Further work must be performed to determine the identity of these and the other compounds in this experiment.

SECTION 5
DISCUSSION

5.1 CHARACTERIZATION OF THE REACTOR

Calculations were performed to characterize the reactor for conditions at which the CPTC was operated.

TABLE 3

Estimated Properties of n-Dodecane in CPTC Experiments

Reactor Pressure: 500 psi
Temperature: 480°C (900°F)
Flow Rate: 0.5 ml/min
Reactor Length: 4 cms
Reactor Diameter: 0.02 inch ID (0.0508 cm)
Fluid: n-dodecane
    diffusion coefficient (estimated): 1×10^{-3} cm^2/sec*
    density (estimated): 0.2007 g/ml*
    viscosity (estimated): 2.14×10^{-4} Poise*
Residence Time: 0.97 second

---

*Reid, R. L. et al., Properties of Gases and Liquids and Appendix A.

At this particular flow rate, the Reynolds numbers are well in the laminar flow region for various reactor lengths and diameters. Changing reactor lengths and internal diameter gives the Reynolds Numbers shown in Table 4. Calculation of a Vessel Dispersion Number (29) gives an indication that this reactor is near plug flow; vessel dispersion numbers below 0.1 are fairly close estimates of plug flow (20). The combination of reactor geometry and the Bodenstein Number from Table 4 indicates that an axial dispersion model can be used to calculate residence time distribution. This implies that the distribution of residence time will be an approximately gaussian function, although its distribution was not calculated for this effort.

The assumption was made that the small reactor internal diameter and small flow rate would allow the fuel to become heated to the reaction temperature very quickly. Models are available to determine the differences between bulk fuel and wall temperature

TABLE 4
Calculation of Important Reactor Parameters

Sample - n-dodecane
Temperature: 480°C
Viscosity (estimated) 0.000214 poise

Density (@ 500 psi, 480°C): 0.2007 g/ml
Schmitt No.: 1,0662681
Mean Residence Time: 0.97 sec

Mean Linear Velocity cm, sec

Length	Reactor Diameter in			
in. (cm)	0.01	0.02	0.04	0.05
1 (2.54)	2.6	2.6	2.6	2.6
2 (5.08)	5.2	5.2	5.2	5.2
3 (7.62)	7.9	7.9	7.9	7.9
4 (10.16)	10.5	10.5	10.5	10.5
5 (12.7)	13.1	13.1	13.1	13.1

Reynold's Number, dimensionless

Length	Reactor Diameter in			
in.,(cm)	0.01	0.02	0.04	0.05
1 (2.54)	62.4	124.8	249.5	311.9
2 (5.08)	124.8	249.5	499.0	623.8
3 (7.62)	187.1	374.3	748.5	935.7
4 (10.16)	249.5	499.0	998.0	1247.6
5 (12.7)	311.9	623.8	1247.6	1559.4

Bodenstein Number (ReSc), dimensionless

Length	Reactor Diameter in			
in,(cm)	0.01	0.02	0.04	0.05
1 (2.54)	67	133	266	333
2 (5.08)	133	266	532	665
3 (7.62)	200	399	798	998
4 (10.16)	266	532	1064	1330
5 (12.7)	333	665	1330	1663

Vessel Dispersion Number, dimensionless

Length	Reactor Diameter in			
in. (cm)	0.01	0.02	0.04	0.05
1 (2.54)	0.0036	0.0140	0.0556	0.0868
2 (5.08)	0.0035	0.0139	0.0555	0.0866
3 (7.62)	0.0035	0.0139	0.0554	0.0866
4 (10.16)	0.0035	0.0139	0.0554	0.0866

(30) and this analysis will be examined in future work. Other researchers (26) have estimated heat-up times for higher flow rates on similar reactor dimensions to be 20% of the residence time in the reactor.

5.2 DISSOLVED OXYGEN DISAPPEARANCE

The measurement of dissolved oxygen in the samples was consistent with previous literature studies; the oxygen peak was not observed for experiments at temperatures of 350°C and greater (see Figure 19). However, the disappearance of oxygen was not accompanied by an increase in a detectable oxygenated product of any kind, i.e., no detectable hydroperoxide formation as one of the initiation steps to the autoxidation reaction.

Detectability is probably the key to this discrepancy. The dissolved oxygen was detected by selected ion monitoring (SIM) at levels of 50 ppm and lower and the oxygen was likely used up in peroxide formation. However, given all of the intermediates and products that are probable according to the initiation, propagation, branching and termination reactions previously reported (31), the levels of any one of the oxygenated products was probably not of great enough concentration to be detected. In addition, the product analysis was performed in the scanning mode, which is at least an order of magnitude less sensitive than SIM.

Certainly, the time of reaction is an important consideration when comparing to the body of literature on autoxidation. Typical oxidation tests can run up to 4 hours and longer (31) compared to a reactor residence time in this test of 1 second. Other researchers (19) have been able to identify the autoxidation products from flowing tests with 9 seconds residence time, but only after preparation and concentration of compound classes. Future experiments will include this type of analytical work along with target analysis in the more sensitive SIM mode.

5.3 REACTION PATHWAYS FROM DECOMPOSITION DATA

Oxygen was consumed at low temperatures (i.e. 350°C) which is below the temperature necessary for pyrolytic cracking of dodecane. This implies that the oxygen is initiating decomposition in what is typically referred to as an oxidative, pyrolysis reaction scheme. In this scheme molecular oxygen may initiate degradation by abstracting H atoms. The resulting radicals may then crack following well-documented

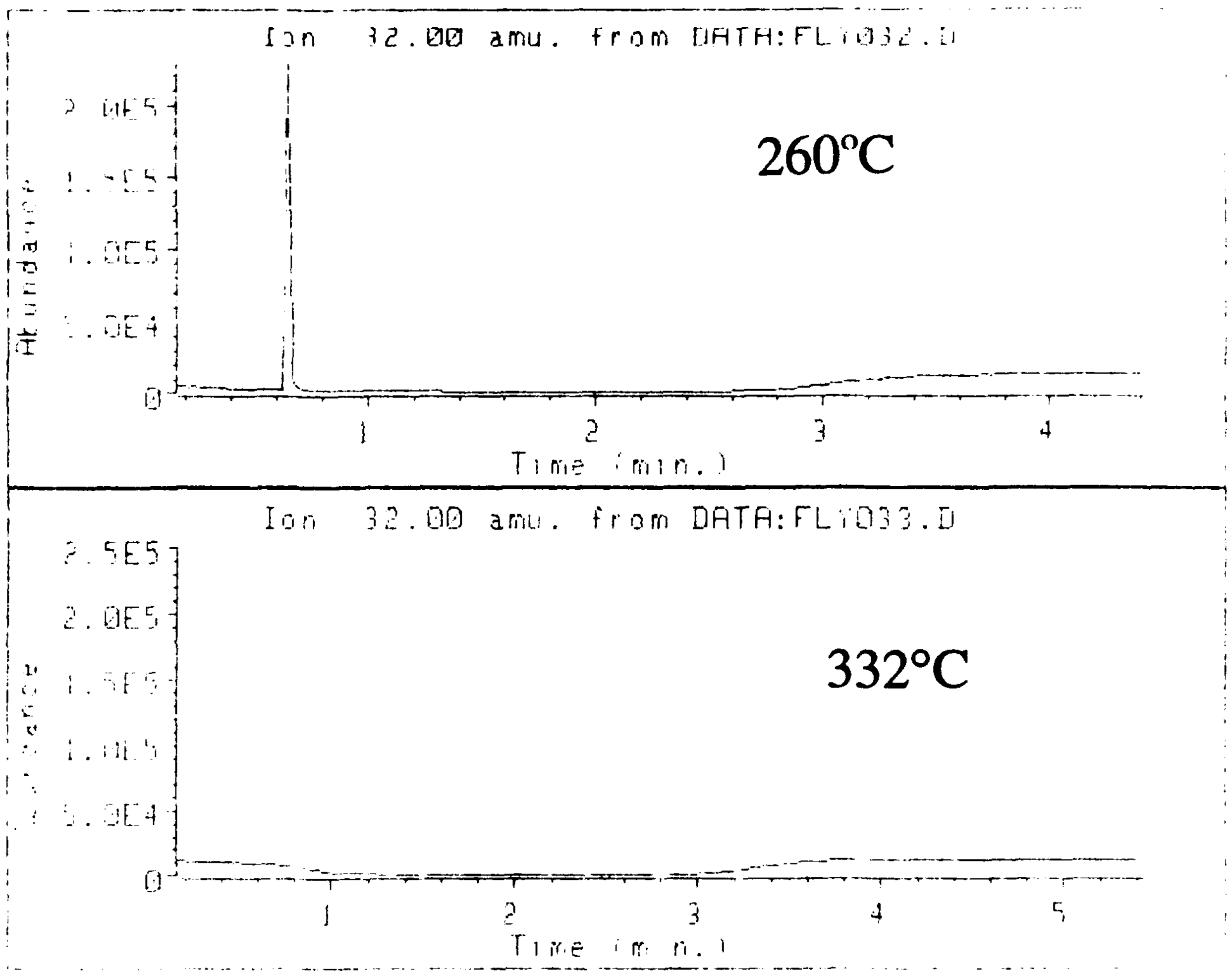


Figure 19. Dissolved Gas Detection at 260°C Compared to 332°C.

radical decomposition reactions to form stable olefins and alkanes. These were individually observed.

Because of the inability of this system to measure oxygenated products at low enough levels, little more can be said about the autoxidation mechanisms. This detection limit may be overcome by conducting experiments at longer residence times and by collecting samples for off-line analysis and extracting and concentrating the samples collected.

The pyrolysis mechanism was apparent in the experiments conducted at 480°C (900°F). The formation of homologous series of normal alkanes and 1-olefins has been demonstrated as the products of thermal decomposition for other straight chain compounds such as polyethylene (32). Product distribution in this study was very much dependent on the pyrolysis conditions. The mechanism of product formation in the experiments on the CPTC was probably similar to that in polyethylene type studies. A chain scission process and free radical formation were followed by hydrogen transfer (hydrogen abstraction) reactions to produce the alkene and the alkane. In the chromatogram for the 480°C experiment, the identity of the third peak could not be determined, but may be the diolefin as described in the reactions outlined in the literature (32). If the olefins are forming, of course, we suspect that hydrogen gas is also being produced, which is also an event well documented in literature (26). We did not attempt to measure hydrogen; the mass spectrometer was not capable of this type of measurement.

The source of the water in the 480°C run is unknown and needs further work to establish its effect. Dodecane is somewhat hydroscopic and no attempt was made to exclude water from the reactant.

5.4 THERMAL DECOMPOSITION OF SUPERCRITICAL FLUIDS

Dodecane, under the conditions of temperature and pressure that were investigated in this feasibility study, was a supercritical fluid. Its P_c value of 17.9 atmospheres and T_c of 386°C (28) were exceeded in the 400°C and 480°C experiments conducted at 500 psi. It was apparent that molecular oxygen did not survive under supercritical conditions. Although the exact temperature of oxygen depletion was not determined, it was significantly below supercritical conditions. Thus, thermal decompositions for supercritical fluids will be a combination of oxidation and pyrolysis. Flowing, supercritical experiments will continue to show time dependencies because the more the experiment is run, the more oxygen will be consumed and the greater the chance that these oxygenated products will migrate to and collect on the surface of the metal tube. Future experiments will be conducted to collect more sample off-line and to concentrate the oxygenates by liquid extraction with a suitable solvent, separating the polar compounds from the nonpolar hydrocarbons produced in the reactions.

It is possible that the supercritical nature of the reactants and products formed will allow them to migrate toward the walls of the reactor much easier than for subcritical reactions. The viscosity and diffusion coefficients for compounds under supercritical conditions would give them a greater chance for participating in wall reactions. However, in these experiments, no deposits were ever formed, even though the experiment was conducted for a matter of hours. In allowing the system to come to equilibrium, the reactor was continually exposed to these supercritical fluids, but never showed any significant pressure increases. The small diameter of tubing could have plugged easily, unless the supercritical nature of the fuel allowed the compounds produced to stay solubilized in the dodecane mixture. Compounds that were formed with high molecular weight (such as those seen in the 480°C chromatogram) may be soluble in the supercritical fluid, but may not be in subcritical fluid. More work needs to be performed to determine the identity of the heavy compounds and their solubility in supercritical fluids.

5.5 LIGHT GAS FORMATION

Although light gases (C1 through C4) were definitely formed in the high temperature experiments, there was obviously a distribution of products identified without a clear major product. Other researchers have suggested that the major product of thermal decomposition for straight chain compounds like dodecane under supercritical conditions was ethylene (33). Although the conditions described in the literature were different than those used in these experiments, we have no evidence to suspect that this was the case. We have observed that the propylene and propane seemed to predominate the light product formation at 480°C and 500 psig. Yields of heavier products (>C4) were determined in the programmed temperature GC chromatographic analysis; the C8s and C9s were the largest yields of the distribution from the C12 starting product.

5.6 GAS PHASE REACTIONS VS. CPTC EXPERIMENTS

The relationships between flowing and static tests and between subcritical and supercritical exposures of hydrocarbons are two critical issues with regard to future fuels.

An important link may exist between reactions occurring in the liquid phase at relatively low pressure (such as a flask test) and those that occur in the supercritical phase. It may be that gas phase reactions provide an important link between these two regimes. Gas phase oxidation studies, conducted in flowing air, provided some interesting results concerning the decomposition of dodecane. Figure 20 shows the oxidation products generated while performing an experiment at 350°C in air with 2.0 seconds residence time. Other than the water, which may be due to the hydroscopic nature of dodecane, oxidative reaction products included by a homologous series of acids in small concentrations (see Figure 21). These acids had a characteristic peak shape on this particular column and were, therefore, relatively easy to identify. The acetic and propanoic acids were just two of the acids identified in the gas phase oxidation experiment at 350°C.

More importantly, formation of the ketone and aldehydes in the gas phase oxidation experiments (shown in Figure 20) was documented. These same products were also products of fuel oxidation in static tests (34). Specifically, the aldehydes, ketones, alcohols and acids were all observed as the major oxidation products at temperatures of 140 through 175°C for jet fuels and jet fuel surrogates under liquid phase conditions. These same tests were extended in time to demonstrate the formation of deposits, soluble and insoluble gums from these starting materials.

Thus, from the similar product formation in the two sets of experiments, it is possible that there exists some relationship between gas phase pyrolysis and oxidation reactions and liquid phase reactions. It may also be possible that gas phase reactions, liquid phase static tests and liquid phase flowing tests may also be related and that the mechanisms of product formation may be the key to determining the relationships between this chemistry. If these mechanisms are important, the STDS and CPTC assembly will be critical tools for conducting research in this area of jet fuel thermal and oxidative stability.

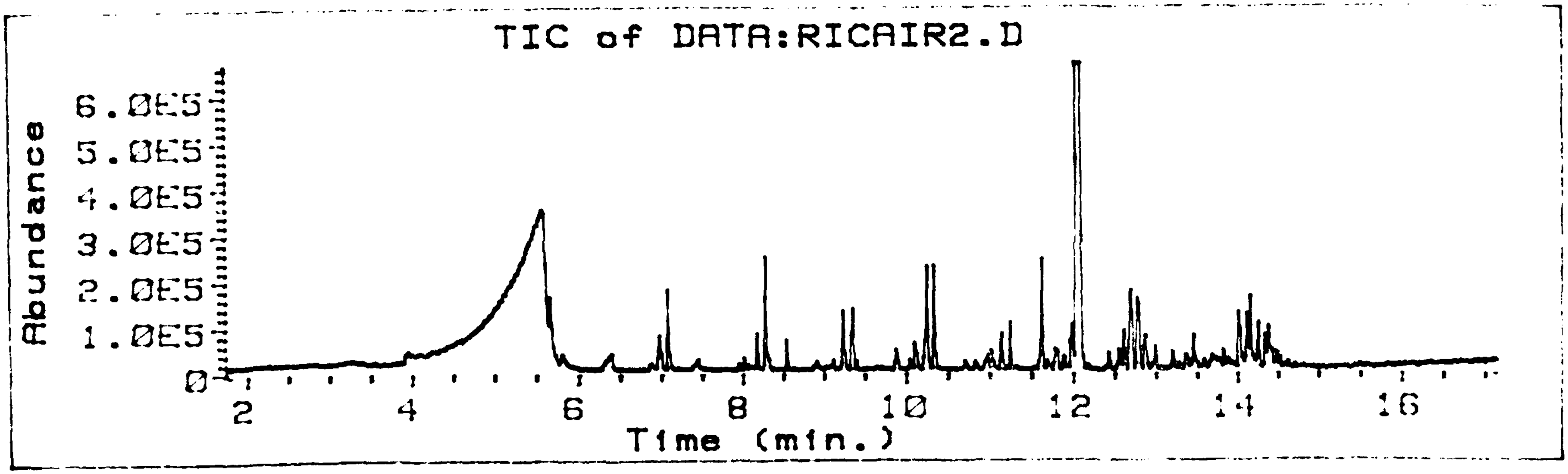


Figure 20. Oxidation Products Formed from the Gas Phase Exposure of Dodecane in Flowing Air, 2.0 Seconds Residence Time, Reactor Temperature of 350°C.

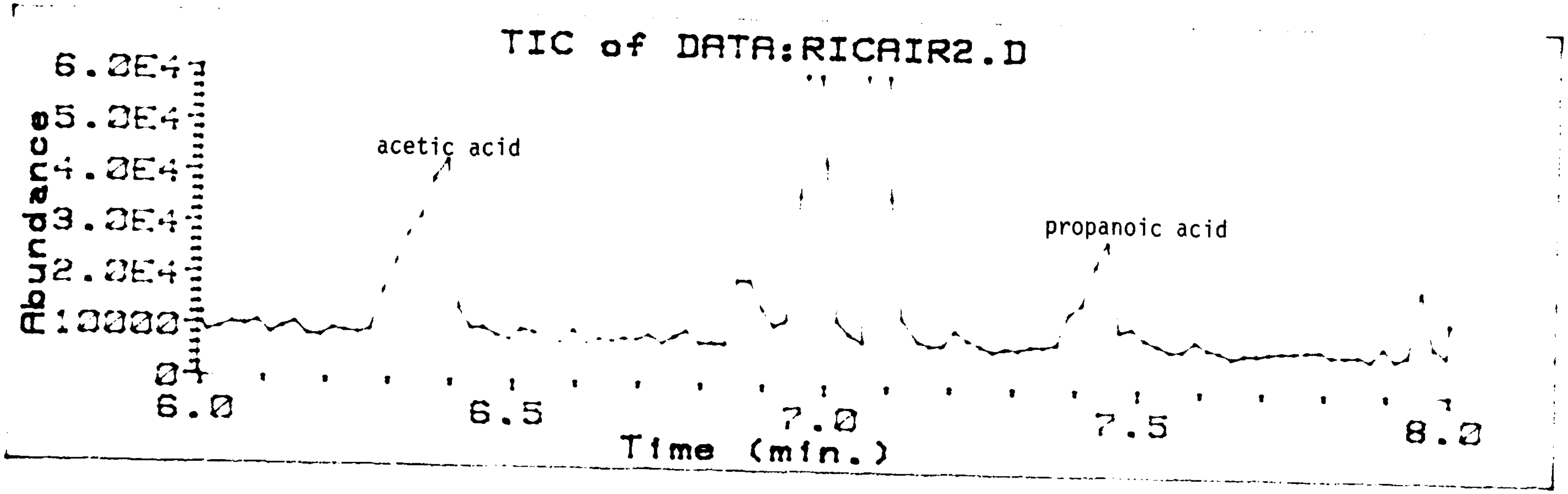


Figure 21. Small Concentrations of Acetic Acid and Propanoic Acid from 350°C Exposure of Dodecane Under Oxidative Conditions.

SECTION 6
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The CPTC was designed in a manner similar to the design of the gas phase reactor for the STDS, with precise control of residence time, reactive atmosphere (level of dissolved gases) and temperature and pressure. The overall purpose of the CPTC was to demonstrate the feasibility of conducting well controlled flowing experiments at high temperatures and pressures, to conduct analyses of the products formed from these thermal exposures, and to relate the product formation to the formation of gums and deposits. In the experiments conducted thus far, no detectable deposits have been formed, due to the low flow rates of materials through the reactor, the short residence times, and the supercritical nature of the mixtures investigated possibly tending to keep reaction products more soluble.

The GC-MS is an acceptable system for conducting the determination of dissolved oxygen in jet fuels. Because it is a universal detector, it can be used to detect any of the fixed or light gases as well as to perform product analysis on any of the parent materials or thermal decomposition products. In the scanning mode, it is not extremely quantitative; thus, GC-FID-MSD is an appropriate analytical detection method.

The valves that sample the flow stream worked quite well. However, if significant amounts of deposits are formed in the reactor, they may condense in the sampling loop and create plugging of the sample lines. However, if experiments are conducted from low temperatures to high temperatures, the analysis of the effluent will give an indication of the amount of degradation occurring in the fuel. In other words, unless products other than the feed material are detected in the bulk liquid stream, it is unlikely that any deposits are forming. Unless deposit formations were a completely surface reaction, with no dependence on the bulk fuel properties (which it does not appear to be), there should be a change in the bulk fuel composition before deposit formation begins.

This system could be an excellent tool for studying additive effectiveness. Because of the GC-MSD, additive concentration can be determined after high temperature stressing. One of the measures of additive effectiveness which has been overlooked to some extent is the actual concentration of the additive after stressing. In other words, if additive concentration is still high after significant degradation of the jet fuel or model mixture, the additive has not been very effective at deterring oxidation.

GC-MS, especially in the selected ion monitoring mode, would be an effective tool in these kinds of evaluations.

We feel that the smaller the reactor is for thermal decomposition experiments, the better experimental information can be obtained. Heat transfer problems become less important with the smaller reactor and fuel usage problems are reduced. An in-line analysis mechanism is very important in being able to determine the quantity and identity of the light and fixed gases, which are critical to understanding both the autoxidation and pyrolysis mechanisms.

Future work regarding this system has been pointed out several places in the text. Improvements in the analysis of the off-line samples could be made to obtain better and more sensitive identifications of reaction products. The effect of supercritical fluids can be investigated by conducting experiments in and around the critical point. The investigation of antioxidant effectiveness can be performed on this system using the GC-MS in the sensitive SIM mode. Long residence time and recirculation experiments (see Figure 22) can be performed by a simple redesign of the reactor assembly and/or coiling of the reactor. Certainly, pressure effects could be investigated by the addition of other back pressure regulators onto the existing regulator.

In the gas phase, experiments involving the thermal decomposition of hydroperoxides would be of interest. They should be fragmenting to alcohols, aldehydes and ketones, even in the gas phase.

The effect of surfaces could be investigated using an electroformed nickel tube which has a much smoother inner surface compared to typical extruded tubing (see Appendix B). In addition, surface coating techniques and passivation techniques may be a good way to reduce the tendency for deposits to form on a surface.

In conclusion, the CPTC can address almost any type of thermal analysis for liquids. Because of its sensitive in-line analysis capabilities and control of reactor conditions, it can address the investigations of jet fuel thermal degradation in both the subcritical and supercritical regimes.

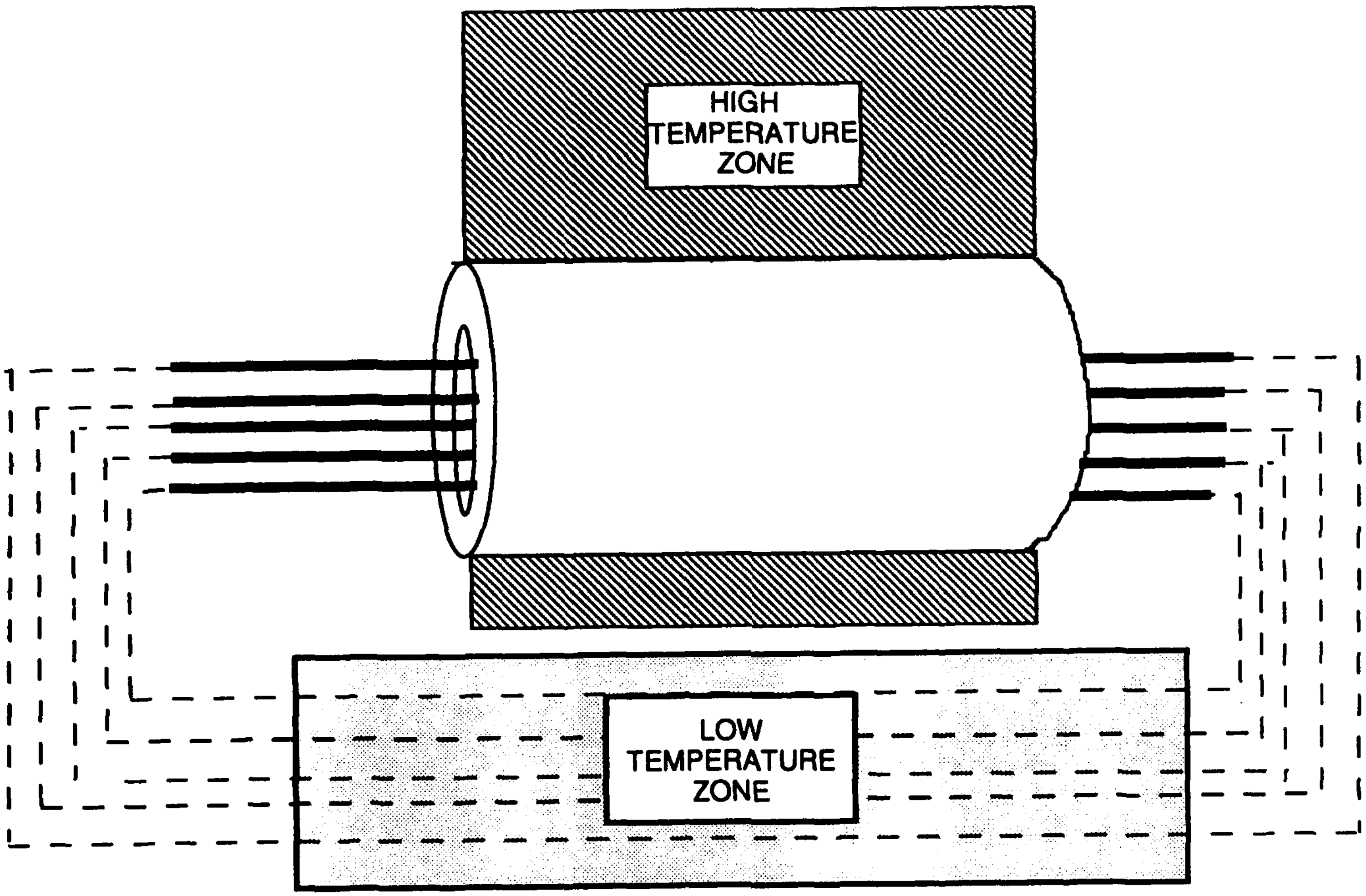


Figure 22. Conceptual Design for Conducting Recirculation Experiments Using a Modified Reactor in the CPTC Assembly.

REFERENCES

1. Technology Area Plan, FY92, Wright Laboratory, Wright-Patterson AFB OH., 1992.
2. L. E. Faith, et al., "Hydrocarbon Fuels for Advanced Systems," Technical Report AFAPL-TR-70-71, Part II, Contract F33615-70-C-1038, December 1971.
3. H. T. Henderson, et al., ACS paper, presented in New York City Meeting of ACS, September 7-12, 1969.
4. Mayo, F. R., et al., "Oxidation and Formation of Deposit Precursors in Hydrocarbon Fuels," NASA-CR-168121, Contract NAS3-22510.
5. W. F. Taylor, "Investigation and Analysis of Advanced Hydrocarbon Fluids," Final Report for Contract N00019-70-C-0340, Naval Air Systems Command, U.S. Navy, August 1970.
6. W. A. Rubey, "Conceptual Aspects of a System for Thermal Diagnostic Studies (STDS)," University of Dayton Technical Report, 1986.
7. R. C. Striebich and W. A. Rubey, "A System for Thermal Diagnostic Studies (STDS)," American Laboratory Magazine, 1989.
8. W. A. Rubey and R. A. Grant, Rev. Sci. Instrum. 59 (2), February 1988.
9. R. C. Carnes and B. Dellinger, "A Correlation of Emissions from Laboratory and Pilot Scale Thermal Decomposition of an Organic Compound Mixture," Toxicology and Environmental Chemistry, Vol. 14, p. 307.
10. D. A. Tirey, B. Dellinger, W. A. Rubey, and P. H. Taylor, "The Thermal Degradation Characteristics of Environmentally Sensitive Pesticide Products," report prepared for the US-EPA Cooperative Agreement CR-813938-01-0, May 1991.
11. P. H. Taylor, B. Dellinger, and D. A. Tirey, "Oxidative Pyrolysis of CH_2Cl_2, $CHCl_3$, and CCl_4 -I": International Journal of Chemical Kinetics, Vol. 23, p. 1051, 1991.
12. P. H. Taylor, D. A. Tirey, B. L. Fox, R. C. Striebich, and J. G. Stalter, "Evaluation of Hazardous Organic Products from the Oxidation and Pyrolysis of Creosote-Treated Wood Using a Versatile GC-MS Instrumental System," proceedings of the 39th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, February 1988.
13. P. H. Taylor and W. A. Rubey, Energy and Fuels, 2 (6) p. 723, 1988.
14. S. Zabarnick, Unpublished Data, 1992.

15. R. C. Striebich and R. Rausa, Unpublished Data., June 1990.

16. I. Glassman, Combustion, Academic: New York, p. 243, 1977.

17. R. N. Hazlett, et al., I&EC Prod R&D, 16, p. 171, 1977.

18. ASTM D3241, American Society for Testing and Materials, 1975.

19. K. T. Reddy, et al., Energy and Fuels, 2 (2), p. 205, 1988.

20. W. F. Taylor, Ind. Eng. Chem. Prod. Res. Dev., 13, p. 133, 1974.

21. W. F. Taylor, Ind. Eng. Chem. Prod. Res. Dev., 15, p. 64, 1976.

22. Taylor, W. F., Franhen Gield, J.W., Ind. Eng. Chem. Prod. Res. Dev., 17, p. 86, 1978.

23. Gield J. W. Franhen and W. F. Taylor, Ind. Eng. Chem. Prod. Res. Dev., 19, p. 65, 1980.

24. P. J. Marteney and L. V. Spadaccini, Trans. of ASME, 108, p. 648, 1986.

25. J. TeVelde, et al., AIAA-83-1143, June 1983.

26. B. M. Fabuss, et al., Ind. Eng. Chem. Proc. Des. and Dev., 1 (4), p. 293, 1962.

27. Hewlett Packard Internal Publication: "SFE: A Strategy for Successful Extractions," 1990.

28. S. Zabarnick, Unpublished Information, May 1991.

29. O. Lievenspiel, The Chemical Reactor Omniboth, OSU Press, 1989.

30. J. L. Krazinski and S. P. Vanka, "Development of a Mathematical Model for the Thermal Decomposition of Aviation Turbine Fuels," WRDC-TR-89-2139, Final Report, December 1989.

31. B. D. Boss and R. N. Hazlett, Can. Journal of Chem., 47, p. 4175, 1969.

32. M. Stevens, Characterization and Analysis of Polymers by Gas Chromatography, Marcell Dekker Publishers, New York, 1969.

33. J. P. Dworzanski, American Chemical Society, San Francisco Meeting, 1992.

34. W. Schulz, "Development of a Thermal Oxidative Stress Test for Elucidating Fuel Chemistry and Determining Additive Effectiveness," USAF Final Report Contract F33615-87-C-2714, 1991.

Appendix A

Calculations for estimates of density, viscosity and diffusivity for normal C_{12}

Reichenberg Method in Reid, The Properties of Gases and Liquids:Viscosity of Dense Gases :

$$\frac{\eta}{\eta^{o}} = 1 + Q\frac{AP_r^{3/2}}{BP_r + (1 + CP_r^{D})^{-1}}$$

where η = viscosity, μP

η^{o} = low pressure viscosity at system temperature

Q = 1.0 for non-polar compounds

P_r = reduced pressure

and:

$$A = \frac{1.982x10^{-3}}{Tr}\exp(5.2683xTr^{-0.5767}) = 0.22796$$

$$B = A(1.6552Tr - 1.2760) = 0.14025$$

$$C = \frac{0.1319}{Tr}\exp(3.7035Tr^{-79.8678}) = 0.11545$$

$$D = \frac{2.9496}{Tr}\exp(2.9190Tr^{-16.6169}) = 3.54997$$

$$Tr = \frac{T}{Tc} = \frac{480 + 273}{659K} = 1.1426$$

$$\Pr = \frac{P}{Pc} = \frac{34.0136}{17.8912} = 1.9011$$

$$\frac{\eta}{\eta^{o}} = 1 + \frac{(0.22796)(1.9011)^{3/2}}{(0.14025)(1.9011) + (1 + .11545(1.9011)^{3.54997})^{-1}}$$

$$= 1 + \frac{.59754}{.73624} = 1.81161 = \frac{\eta}{\eta^{o}}$$

For non-polar gases (Thodos et al.)

$$\eta^{o}(\mu\mathrm{P}) = \frac{4.610Tr^{.618} - 2.04e^{-.449Tr} + 1.94e^{-4.058Tr} + 0.1}{Tc^{1/6}M^{-1/2}Pc^{2/3}}$$

T_c - critical temp, K = 659K
M = molecular weight 170.34 for $C_{12}H_{26}$
P_c = critical pressure (atm) = 17.8912 for $C_{12}H_{26}$

$$\eta^{o} = \frac{5.00587 - 1.22131 + 0.018798 + .1}{(2.94995)(0.0766199)(0.146186)} = \frac{3.90336}{0.033042}$$

$$\eta^{o} = 118.13\mu\mathrm{P}$$

$$\eta = \eta_{o} x 1.81161$$

$$\eta = 214.0\mu\mathrm{P} * \frac{1mP}{1000\mu\mathrm{P}} * \frac{1cP}{10mP} = 0.214cP$$

$$\rho_{JP-7}(900F, 500psi) = 12.517 * \frac{454g}{10^{6}ml} = 0.2007\frac{g}{ml}$$

$$D_{C_{12}H_{26}}\ estimate\colon 1x10^{-3}cm^{2}/\sec$$

Appendix B

Use of electroplated nickel tubing to investigate surface effects due to roughness

April 9, 1991

Mr. Richard C. Striebich
The University of Dayton
Research Institute
300 College Park
Dayton, Ohio 45469-0001

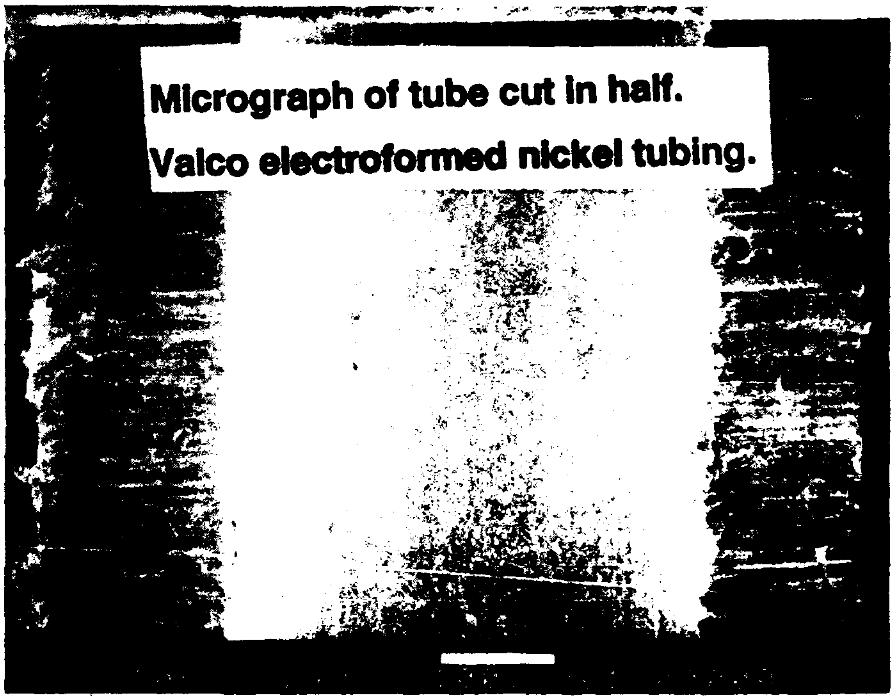
Dear Mr. Striebich:

At the recent PittCon you requested some samples of the new Valco electroformed nickel tubing and copies of the micrographs of the surfaces of the electroformed tubing. Enclosed are two eight inch pieces of electroformed nickel tubing (both 1/16 inch od 1 mm id and 1/32 inch od 0.5 mm id). These tubes were cut with an electrochemical tube cutter, the ends were electropolished, and were cleaned with high pressure steam. Also are enclosed micrographs of the inside surfaces of the Valco electroformed tubing, Handy & Harmon extruded nickel tubing, and Handy & Harmon extruded SS 316 tubing.

Sincerely yours,

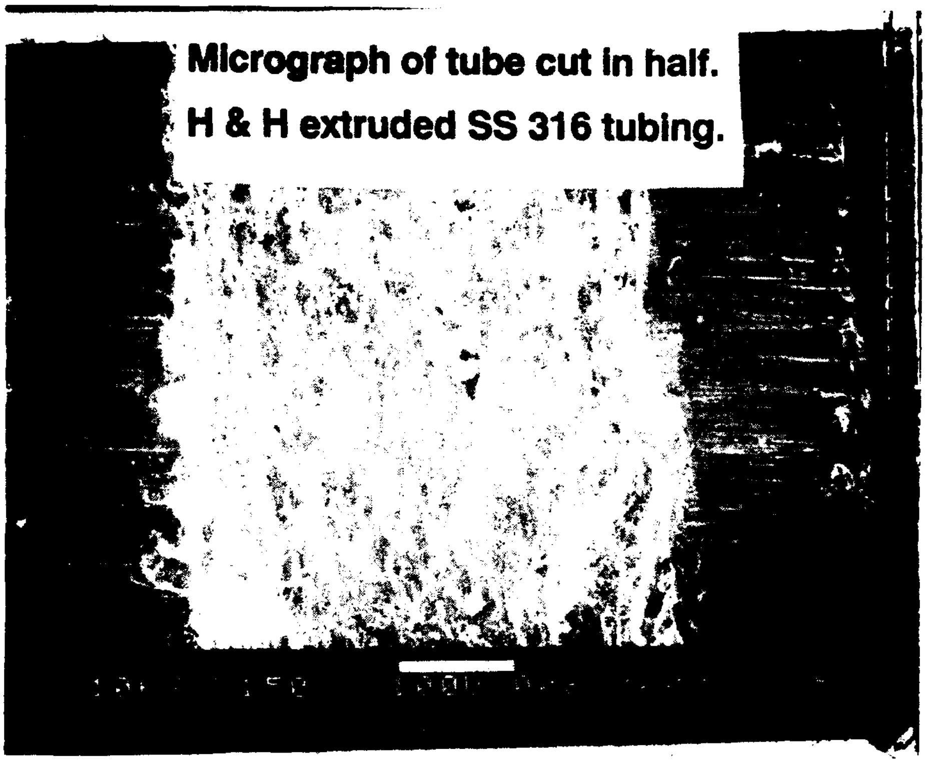
Mack C Harvey

Mack C. Harvey

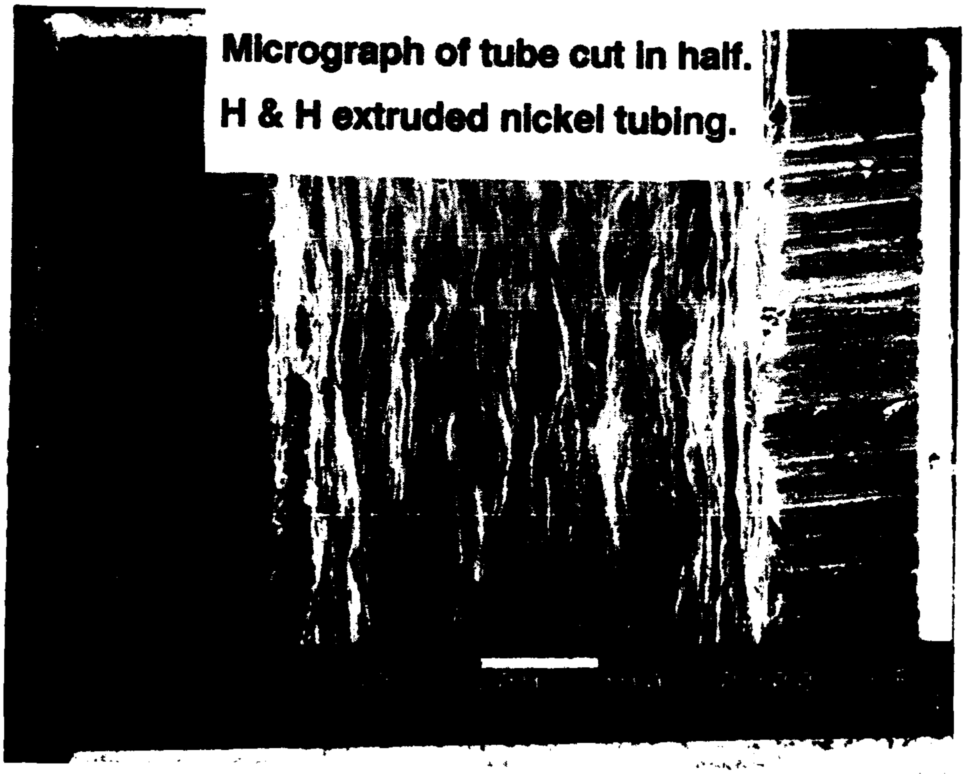


Micrograph of tube cut in half.

Valco electroformed nickel tubing.



Micrograph of tube cut in half.
H & H extruded SS 316 tubing.

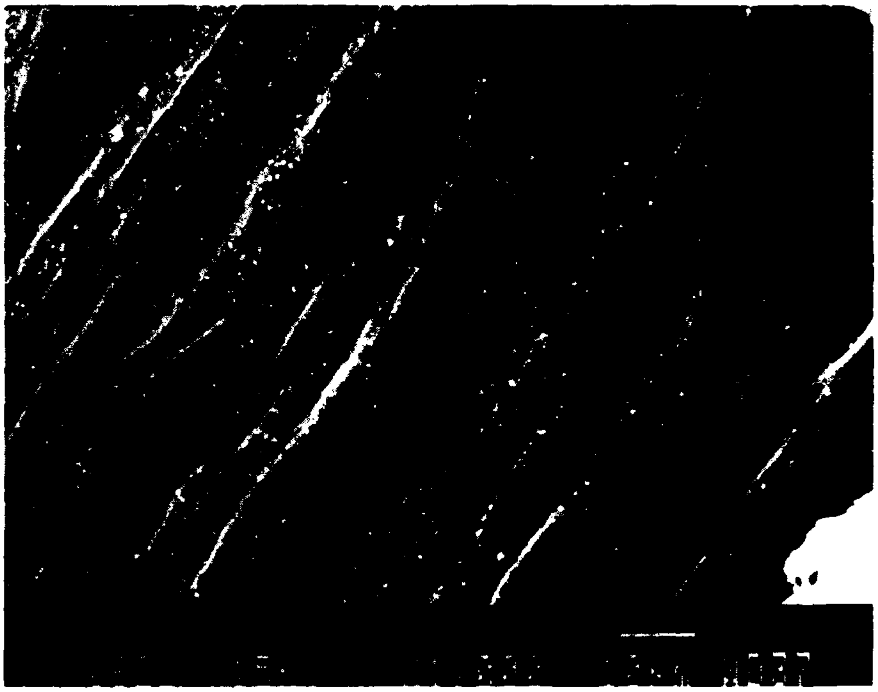


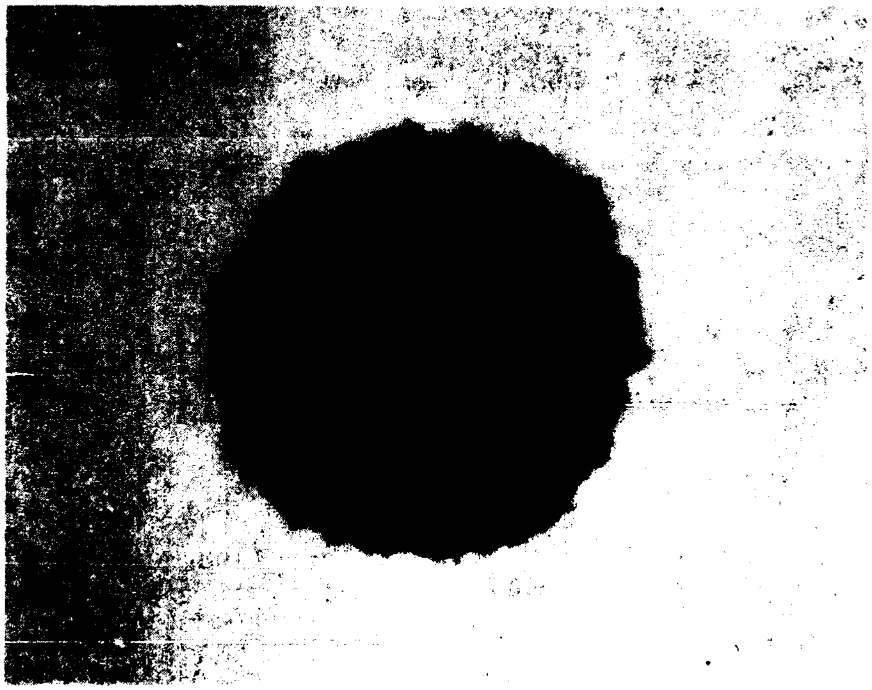
Micrograph of tube cut in half.
H & H extruded nickel tubing.

Page: 1

OBJECTS PARAMETER LIST

Job name : 910462
Date : 08/07/1991
Time : 12:31:32
Objects : 1
Units : microns
Microscope mag. : 100.0





U.S. GOVERNMENT PRINTING OFFICE 750-113