APL TDR 64-100 Part I September 1964

ERRATA - November 1964

The following corrections are applicable to APL-TDR 64-100 Part I. Vaporizing and Endothermic Fuels for Advanced Engine Application, September, 1964:

Page 97; Table 28

The heat sinks for n-dodecane at 1022°, 1112°, and 1202°F read 615, 685 and 755; the corrected values are 751, 826 and 918 Btu/lb.

Page 104; Table 35

The total heat sink values for n-dodecane in Columns 1 through 6 read 750, 699, 735, 720, 685, 652; the corrected values are 886, 835, 916, 883, 826 793 Btu/lb.

Page 54; Table 19

The total heat sink for n-dodecane reads 685; the corrected value is 826 Btu/lb.

NOTICE

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FOREWORD

This report was prepared by Shell Development Company under U.S. Air Force Contract No. AF 33(657)-11096. The contract was initiated under Project No. 3048, Task 304801. The work was administered under the direction of the AF Propulsion Laboratory, Research and Technology Division, Mr. J. R. Fultz, Project Engineer.

This report covers work for June 1963 to June 1964.

ABSTRACT

Studies leading toward the development of specifications for heat sink fuels for hypersonic aircraft are reported. Consideration of the effect of design parameters on the conditions under which endothermic reactions can be carried out has led to the conclusion that space velocities of 50 or higher would be necessary due to volume limitations in high-speed aircraft.

Rate considerations favor catalytic reactions. Preliminary studies of the dehydrogenation of propane to propene and methylcyclohexane to toluene have been made, and dehydrocyclization of various paraffins attempted. Conditions include temperatures to 1300°F, pressures to 10 atmospheres and space velocities to 100. Using a platinum on alumina catalyst, almost complete conversion of MCH was achieved with a maximum heat sink of 2000 Btu/lb at 1300°F. Chromia on alumina was a less successful catalyst but with propane it yielded a total heat sink at 1200°F of 1600 Btu/lb.

A literature survey in this field is being made which will be issued in the form of a special report and a set of machine sortable cards.

Thermal stability studies include the modification of two types of cokers to minimize contamination possibilities and improve reproducibility. Fuels may be tested at temperatures up to at least 1000°F. The thermal stabilities of samples of n-dodecane, toluene and methylcyclohexane decreased in the order named.

A 25 gal/hr fuel system simulation test rig which will be used for determining heat transfer coefficients, heat sinks and product compositions has been designed.

This report has been reviewed and is approved.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Contd)

ILLUSTRATIONS

ILLUSTRATIONS (Contd)

TABLES

TABLES (Contd)

TABLE PAGE

VAPORIZING AND ENDOTHERMIC FUELS FOR ADVANCED ENGINE APPLICATION

Part I. Preliminary Studies of Catalyzed Reactions and Thermal Stabilities of Hydrocarbon Fuels

Introduction

The present report relates the status of this investigation at the end of the first year of a three-year study.

The objective of the study is to develop specifications for hydrocarbon fuels which will be capable of absorbing the aerodynamic heat generated by aircraft operating in the Mach 3 to 6+ range. It is intended that the fuel absorb the heat by virtue of its sensible and latent heat and its endothermic reaction capability. This requires that the fuel have excellent thermal stability at temperatures up to its reaction temperature and that it then react rapidly and cleanly to give products which can serve as fuel for the engines. Previous work has served to demonstrate the general feasibility of the endothermic aproach, but many details as to specific application remain to be established. It is intended to resolve as many of these uncertainties as possible in the present work. To this end we intend to follow a number of different approaches: to carry out a thorough study of the pertinent literature, to apply the most sophisticated methods for evaluating and improving thermal stability, to examine both catalyzed and thermal endothermic reactions of possible fuels by laboratory methods, to determine the realizable heat sink capacities and heat transfer parameters of selected fuels in a fuel system simulation rig, to construct a mathematical model of the fuel system for correlation and extrapolation, and to determine the combustion properties of the reaction products produced by the endothermic reactions.

Program

The aim of previous work has been primarily to determine physical and chemical properties of fuels and their total heat sink capacities below some arbitrary upper temperature limit. These past efforts have shown the possibilities of the endothermic fuel concept. Less emphasis has been placed on the manner in which this heat sink capacity is distributed over the temperature interval. However, in the selection of a fuel and the design of an aircraft cooling system, the temperature levels at which heat generated by the several sources in the aircraft must be transferred to the sink are of primary importance. The study of the factors which determine or can modify this distribution of heat sink capacity over the available temperature range is an important aim of the present work.

The factors which are expected to be most significant are: the type of fuel - paraffinic, naphthenic, or mixed; the type of endothermic reaction to be performed - cracking, dehydrogenation, dealkylation, dehydrocyclization, depolymerization; and the means of carrying out the reaction - thermal or catalytic.

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To minimize the use of auxiliary refrigeration cycles and hence the total heat load, it is desirable to make as large as possible a fraction of the heat sink capacity of the fuel available at low temperature. Thermal reactions generally occur at fairly high temperatures; the use of catalysts for the endothermic reactions of the fuel is a means of effecting a major reduction in the temperature at which reaction can be carried out. A program of screening catalytic reactions of the fuels chosen for study and determining catalytic reaction rates for the most promising catalyst-fuel combinations is included in the present program.

The major portion of the program comprises selection, evaluation and establishment of specifications for fuels that are promising both from the standpoints of performance and availability. Sufficient studies will be carried out to allow a satisfactory engineering design of a prototype cooling system utilizing these fuels. The areas being emphasized in the experimental studies of these fuels are divided as follows:

1. Engineering Data

Although existing correlations of heat transfer coefficients and friction factors are applicable to much of the cooling system, further studies for the specific fuels will be required. These include heat transfer and pressure drop in flow through those sections of the system where vaporization (or rapid change of fuel density with temperature in the case of supercritical fluids) and reaction take place.

2. Thermochemical Data

Results of prior investigations provide a useful and fairly comprehensive background of such data for pure hydrocarbon types and a few fuel mixtures. However, for the specific fuels chosen, heat of reaction, vaporization and heat capacities may have to be confirmed experimentally.

3. Chemical Reaction Rates

The open literature and considerable proprietary information provides a useful background for both thermal and catalyzed endothermic reactions of hydrocarbons. However, the selected fuels are being studied individually under conditions sufficiently close to those anticipated, to allow accurate extrapolation or interpolation.

4. Thermal Stability

The importance of thermal stability for the satisfactory performance of jet fuels is amply demonstrated by the attention this subject is receiving in connection with present and SST fuels.20-28) Information accumulated in these investigations will be of great benefit, but in the present connection even higher standards of thermal stability may be necessary. Accordingly, test methods are being refined and improved to provide better discrimination

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20) See References.

between candidate fuels and to provide reliable tests for specification purposes. In this category also falls the evaluation of the effect of storage, contaminants, additives and minor components.

5. Combustion Properties

The application of the vaporizing and endothermic principle of cooling means that the fuel will be fed into the engine in the form of vapor containing different molecular species than those present in the tank fuel. For instance, the dehydrogenation of a naphthene will result in the formation of an aromatic and hydrogen. The combustion properties of such mixtures will be established by means of empirical tests in small scale combustors.

Present Status and Future Projection

Design Parameters

Continued exploration of the literature and contacts with engine and air frame manufacturers are serving to bring various aspects of the problem into sharper focus. Efforts to accumulate additional information and opinions will be continued in the future. Considerations of times, temperatures and volumes which can be expected in supersonic aircraft have led to some tentative conclusions with respect to operating conditions that will be practical in high speed aircraft. At the present time we can anticipate that space velocities must be in excess of 20 and temperatures in the neighborhood of 1200°F. With conventional combustion chambers a pressure of at least 150 psi must be maintained in the reaction zone, but with hypersonic ramjet engines lower pressure could be tolerated.

Reaction Studies

The promising results that have been obtained on the dehydrogenation of methylcyclohexane over Pt/Al_2O_3 catalyst at space velocities up to 50 and total heat sinks of 2000 Btu/lb at 1340°F augurs well for the utility of this type of reaction. Essentially the same results were obtained with both a special laboratory catalyst and one commercially available. With such a catalyst it will probably be possible to use a variety of naphthenic materials as fuels viz: single pure naphthenes such as MCH or decalin; a mixture of pure naphthenes, such as MCH, decalin, di- and trimethylcyclohexanes and mono-, di- and trimethyldecalins; a refinery cut with high naphthene content (which could be augmented by hydrogenation of aromatics and extraction of n-paraffins with urea or mol sieves); a feed produced from selected refinery cuts by dehydrogenation, extraction of aromatics followed by complete hydrogenation of the extract to naphthenes. Some of these possibilities will be explored. However, the most important consideration with this feed/catalyst system is to increase the allowable space velocity without loss in heat absorption, to improve the activity/weight ratio of the catalyst and to increase its heat conductivity. The effect of one feed component on the reactivity of another must be assessed as well as the effect of minor components, impurities and fuel additives.

The preliminary examination of propane using a chromia on alumina catalyst at space velocities up to 50, temperatures up to 1290°F and pressures up to 10 atm, showed that total heat sinks of 1365 to 1600 Btu/lb can be achieved. Coke formation and cracking reactions have prevented the attainment of the complete potential of this fuel. The desirability of developing a more active catalyst for this reaction has become evident. The achievement of maximum heat sinks with propane is limited to relatively low pressure by equilibrium considerations. The chrome/alumina catalyst was found to be less active for the dehydrogenation of MCH than Pt/Al_2O_3.

A variety of paraffins in the C_7 to C_{16} range has been tested for dehydrocyclization over the chromia on alumina catalyst, and in a few cases with Pt/Al_2O_3, but with poor success because of the higher rate of cracking compared to the desired reaction. It is evident that improved catalysts must be developed for this type of reaction.

The work to date has established the desirability of utilizing catalytic dehydrogenation as a heat sink reaction but has pointed up the necessity for a considerably more intensive effort on the development of new and improved catalysts than will be possible under the present contract. In connection with the interpretation of the laboratory results, it has become evident that a more sophisticated method of treating the data might yield more comprehensive results. To this end an existing computor program is being modified to simulate the laboratory equipment and to extend the conditions into the regions of higher mass flow rates in longer reactor tubes to determine the limiting space velocities at which the reactions will give practical conversions.

Thermal Stability Studies

The types of cokers (Modified Erdco and SD) being used for thermal stability evaluation have been modified to decrease fuel holdup in the system and limit sources of contamination. A detailed analysis of the effect of various parameters on the operation and response of cokers has revealed the need for stringent control to achieve meaningful results. Comparative experiments suggest that the SD (recycle) coker provides a more severe test of filter plugging tendencies with preheater deposit tendency being roughly comparable. It is expected that some further modifications will be made in the future. Consideration is being given to improving the methods of evaluating tube deposits by using a radiation technique. The method gives promise of being of value in the whole problem of the relationship between heat transfer rate and deposit thickness and if successful will be explored more extensively.

Other areas in which work is going on or will be initiated include: simpler methods of predicting thermal stability related to the fundamental susceptibility of fuels to oxidative attack and, assessment of the effect of normal storage on the thermal stability of candidate endothermic fuels. These studies will include the effect of additives, impurities and minor components on thermal stability and endothermic reactivity.

Literature Survey

A method of presenting the results of the literature survey involving the transfer of references and abstracts to a machine-sortable IBM card, which will also be utilized for assemblage of the data in report form, has been devised. This method of presentation of the data has the additional advantage that the survey can be kept up to date with a minimum of difficulty. The survey will be issued as a special report and a set of cards.

Fuel System Simulation Test Rig

Modification of the laboratory in which the 25-gal/hr fuel system test rig will be installed has been completed. Most of the equipment is now on hand, and it is anticipated that construction will be completed by about the end of July. The initial fuels to be tested will include propane, methylcyclohexane, decalin, n-dodecane, and stable paraffinic and naphthenic jet fuels.

Combustion Studies

Existing small-scale equipment for carrying out combustion studies on endothermic fuels and their reaction products has been made available for use in this project. It is expected that some preliminary experiments with this equipment to determine its suitability will be done early in the next contract year.

Design Parameters Affecting Applications

The total problem of the effect of design parameters on the application of the vaporizing and endothermic hydrocarbon fuels has not been resolved and we do not intend to attempt it here. However, some speculations about the nature of the constraints imposed by the requirements of a supersonic vehicle may be helpful. The major concern is, of course, the constraints placed on the system by the temperature levels to which the aircraft is subjected. The variation of temperature with Mach number is illustrated in Figure 1 as presented by Duggar.1) This shows the increase in inlet air temperature, the temperature of the engine combustor under two conditions of stoichiometry while burning kerosene, and the equilibrium temperature of longitudinal surfaces. It is assumed that the aircraft operates at sufficient elevation to maintain a pressure of 350 psfa in the inlet air. It is seen that the inlet air temperature rises rapidly from 600°F at Mach 3 to 1100°F at Mach 4, 2800°F at Mach 6, and more than 6000°F at Mach 10. If we assume that the combustion in the engine takes place under subsonic conditions, practically all of this thermal energy is released between the inlet and the combustion chamber with the consequence that the combustion chamber temperature also increases with Mach number (the full complement of the increased temperature would not, of course, be realized if combustion were to take place under supersonic conditions). The temperature of bluff surfaces will become equal to that of the stagnation temperature of the air. Thus, leading edges and noses will require cooling above about Mach 4-5 depending on the particular types of materials used for construction. However, longitudinal surfaces (because of inefficiencies in the transfer of energy to the surface and loss of energy by radiation) will come to equilibrium at a lower temperature than that of the stagnated inlet air. As shown in Figure 1, this will level off above about Mach 6 at around 1000°F. The exact value of this temperature will, of course, depend on the emissivity of the material used for the aircraft, whether it is in sunlight or dark, and also the radiation reflective characteristics of the surface that it is facing. However, the temperature will be sufficiently low that cooling of all surfaces will not be required. Nevertheless, it is evident that whatever the properties of the fuel, it will have to be confined within insulated tanks in order to minimize to the greatest degree the flow of heat into the fuel from the hot skin surface at the higher Mach numbers. It also appears evident that above about Mach 4 the utilization of wings for the storage of fuel in integral tanks must be abandoned. Even at Mach 3 great difficulty has been experienced with the development of suitable sealants for fuel tanks as the temperatures climb into the range of 500°F.2) In any event, the requirement of reducing the thickness of wings in high-speed aircraft will not only decrease the volume available in the wings but also make its utilization less desirable from economic and maintenance considerations. The necessity of carrying all the fuel essentially within the fuselage seems inevitable.

Heat Sink Required

The actual magnitude of the heat sink which will be required in any particular case will be a function not only of Mach number but also of engine design and operating conditions. Drake3) shows the effect of operating conditions, engine structural materials, and regenerative cooling on the limiting Mach number. Figures 2 and 3 show that the upper limiting flight speed increases: (1) with altitude, (2) with decreasing pressure in the engine, (3) with improved structural materials, and (4) with regenerative cooling. Without a particular engine design specified, it is impossible to set precise limits on the amount of heat sink required at the different Mach numbers. Information obtained by discussions with representatives of engine manufacturers suggests that a value of 1000 Btu/lb of fuel would be required at Mach 4-5 and a value of about 1600 in the 6-7 Mach number region. From information given by Conners and Obery,4) one may roughly estimate that a hypersonic ramjet with a 6-foot inlet diameter and an overall length of about 40 feet would require a heat sink at Mach 7 of about 1800 Btu/lb of fuel at a fuel consumption of 100,000 lb/hr assuming a wall temperature of 2000°R. It is considered that most of the heat sink would be required by the engine because of necessity of keeping the combustion chamber walls below about 1800°F and the large amount of heat liberated in that area.

Heat Sinks Available

Thermal Reactions

Apart from sensible and latent heat, heat sinks can be provided by hydrocarbon fuels through endothermic reactions, which may be either catalyzed or uncatalyzed. Thermal reactions, of course, have the advantage that no catalyst need be provided to stimulate the reaction in the cooling zone. However, they have the disadvantage that the maximum heat sink that is

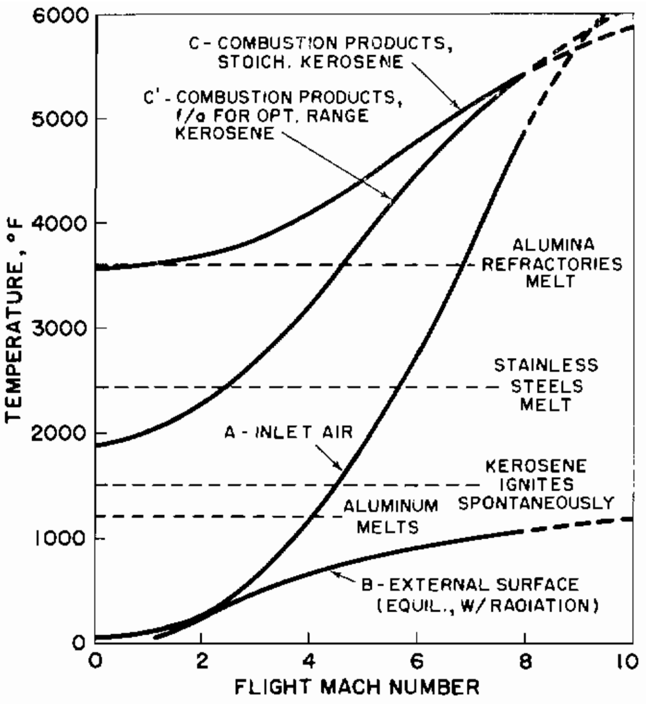

Figure 1. TEMPERATURES WHICH MAY BE TYPICAL IN RAMJET ENGINES AT SUPERSONIC AND HYPERSONIC SPEEDS
Altitude Assumed to Increase with Mach Number to Maintain Constant Free Stream Dynamic Pressure of 350 psfa1)

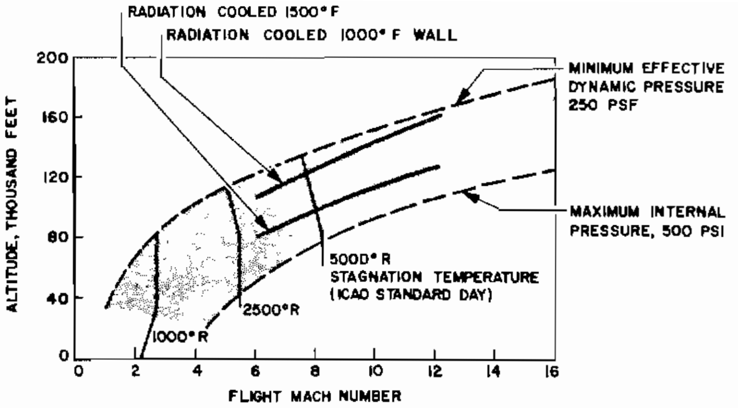

Figure 2. RAMJET FLIGHT ENVELOPE[3)]

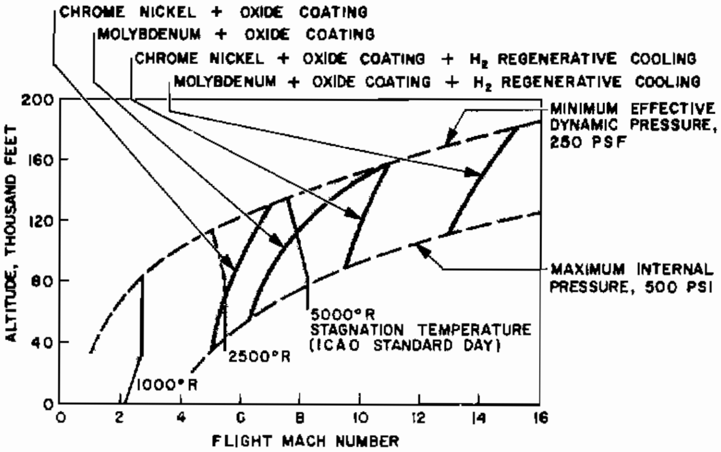

Figure 3. STRUCTURAL MATERIAL LIMITS[3)]

available is limited by secondary reactions which come more and more prominently into play at higher conversions. Thus, Monsanto reports5) that a maximum heat sink of about 1200 Btu/lb is achieved at about 60% conversion with only about 400 Btu/lb contributed by the reaction. As the reaction is carried further and further towards 100% conversion, the available heat sink decreases, presumably because of hydrogenation of reaction fragments from thermal cracking, so that at 100% conversion the reaction is close to thermal neutrality. A second limitation of thermal reactions arises from the high temperature that is required to achieve sufficient reaction to make the heat sink available within the reaction time which can be permitted by the physical limitations of heat exchanger size. Thus, if we accept the rate constants given by Smith et al5) and assume that space velocitiesa) above 20 are required by limitations in heat exchanger volume, it is seen from Figures 4 and 5 (plotted from the data in Table 24 in the Appendix) that temperatures must be above 1100-1200°F unless pressure is very high. (Note the contact times indicated in Table 24 are maximum values since the increase in volume caused by the products of reaction has been ignored.) Comment along this same general line has been made by Kutzko6) as a result of his study of fuel/air heat exchange. He states "The rate at which heat can be absorbed by the thermal cracking reactions is so slow that practical rates of heat transfer cannot be maintained". Although it must be conceded that the particular design of heat transfer equipment utilized could have a bearing on the question, the fact that the heat flux is a function not only of the heat transfer coefficient but also of the temperature difference between the fluids makes it highly desirable to carry out the reaction at as low a temperature as possible.

Catalytic Reactions

There are advantages and disadvantages, of course, to the use of catalysts; and, although we have an incomplete understanding at the present time, it may be instructive to delineate those features which now seem apparent. The great advantage to the use of catalyst is the higher rate of reaction and the greater selectivity that can be obtained and the consequent greater control over the products which will result from the reactions. Hence, the more thermally desirable dehydrogenation reactions can be achieved by catalysis, resulting in higher heat sinks and a more desirable product distribution. Because of the high proportion of molecular hydrogen in the reaction products they should have better burning qualities, which could be critical in high performance ramjet engines. Because of the lower temperature at which the reactions can be carried out, a better temperature approach is available in the heat exchange process resulting in the possibility of smaller heat exchangers. Since high-speed aircraft will probably be volume limited, this could be a very desirable characteristic. Of course, the simple necessity of providing a catalyst for the reaction is undesirable in itself and particularly so if it is a solid catalyst which means that it is going to occupy space as well as have weight. The interrelationship between fuel flows, space velocity, heat exchanger volume and catalyst weight can be illustrated by simple calculation. For instance, if an engine has a fuel flow of 100,000 lb/hr (approximately

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a) This refers to liquid hourly space velocity, the number of volumes of the fuel calculated as liquid passing through the reaction zoner per hour.

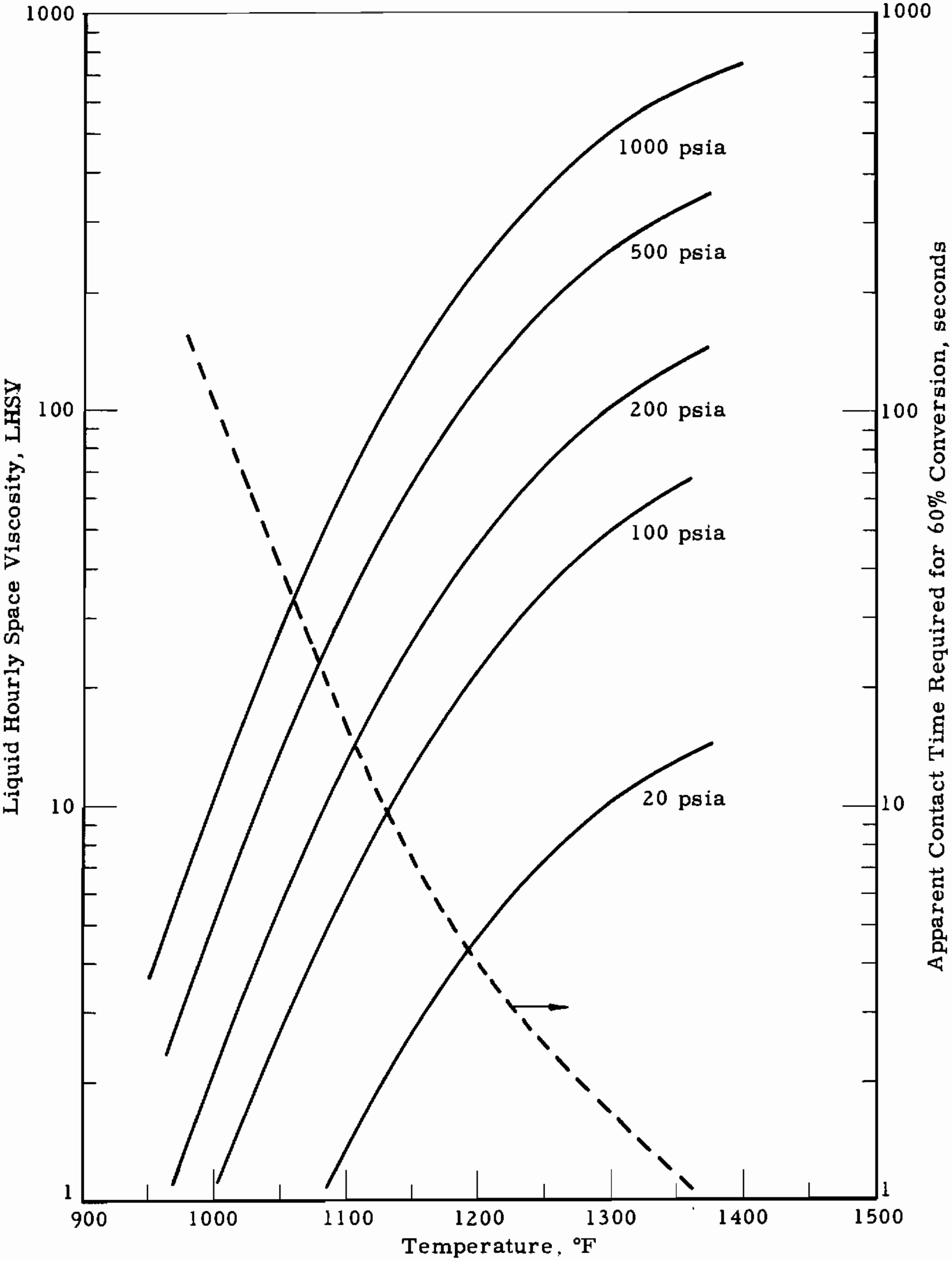


Figure 4. THERMAL CRACKING OF CETANE
Calculated Relation Between Temperature Space Velocity and Contact Time for 60% Conversion (See Table 24)[5)]

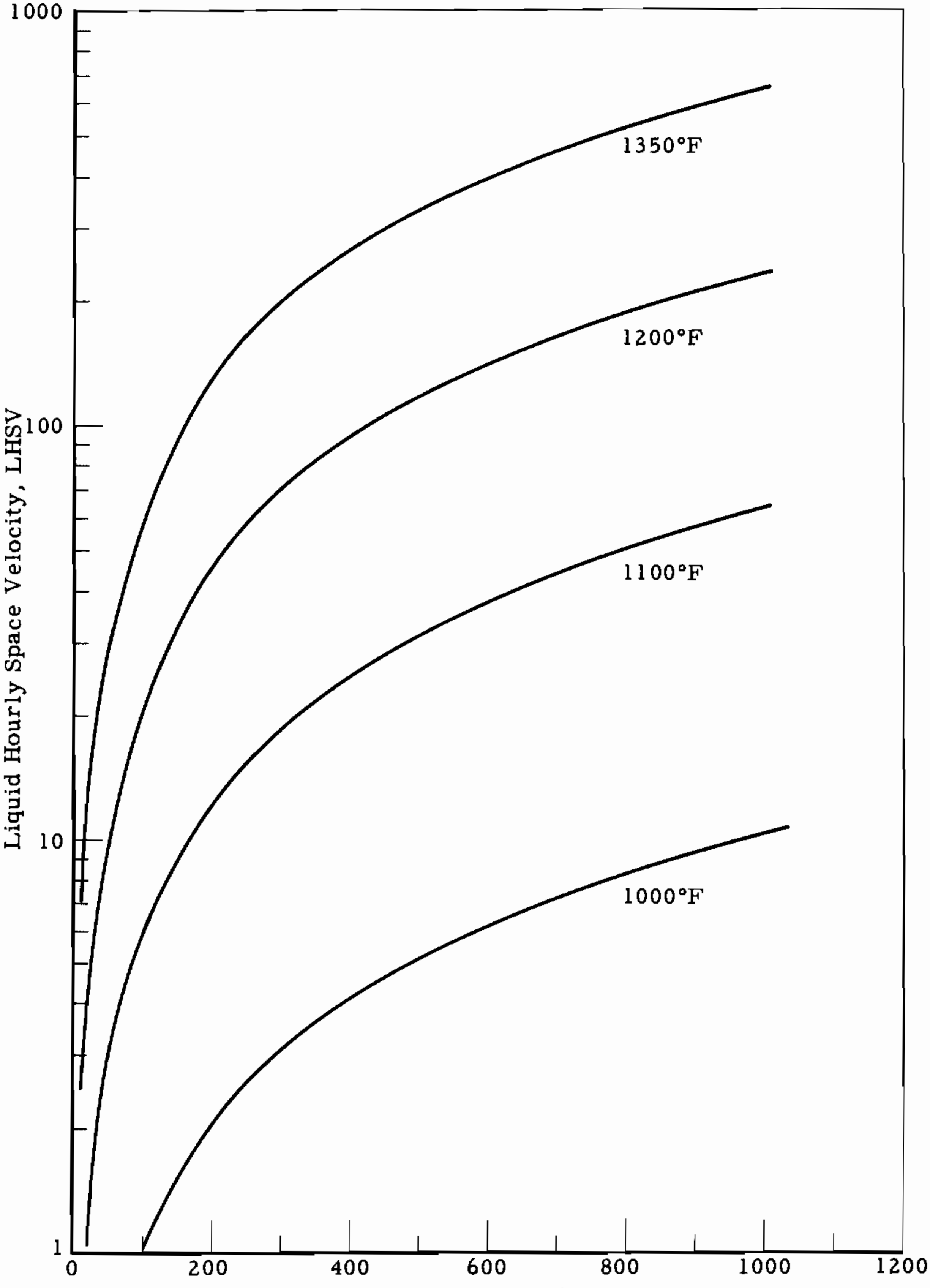


Figure 5. THERMAL CRACKING OF CETANE
Calculated Relation Between Pressure and Space Velocity for 60% Conversion (See Table 24)[5)]

2,000 cu ft feed volume) a space velocity of 50 would require a heat exchanger (reactor) volume of 40 cu ft on the fuel side. If a solid catalyst of the type described later were used, this would have a weight of about 2,000 lb. Alternatively, if a longer contact time were required for the reaction so that a space velocity of only 20 were possible, the volume required would be 100 cu ft with a catalyst weight of 5,000 lb. It will probably be necessary to develop special types of catalysts to provide low weight, minimum pressure drop and high heat conductivity into the center of the packed reactor tubes. Arrangements would also have to be made to either remove the catalyst for regeneration or regenerate in place on the ground between flights or after every several flights. This would necessitate a more complex plumbing system. However, if it is possible to operate the catalytic system at the desired low temperatures, deposition of coke on heat exchanger walls due to thermal reactions would be minimized. This would minimize the decrease in heat transfer coefficients with time.

Space Time Limitations

As mentioned above, the necessity of minimizing the volume occupied by the cooling equipment will severely tax the efficiency of the heat exchanger equipment. Another difficulty arises from the high heat transfer rates which must be achieved within the engine itself in order to maintain the engine structure below the maximum allowable temperature. With present metallurgy this appears to be in the neighborhood of 1800°F. Figure 6 represents an evaluation made by Conners and Obary4) (vide supra) in which they estimate heat transfer rates in a hypersonic ramjet engine operating at Mach 7 with a wall temperature of 2,000°R It is noted that high heat transfer rates occur at the throat inlet, in the combustion chamber, and particularly at the exhaust nozzle throat where the rate rises to 400 Btu/sq ft/second. This will necessitate extremely efficient heat transfer conditions, although the authors point out that the maximum rate is only about 25% of the heat transfer rate currently being handled successfully in regenerative rocket motors. It should be noted that the average heat transfer rate across the engine from Conners and Obery's figure amounts to about 60 Btu/sq ft/second. The authors also stress the considerable effect that engine design has upon the load on the engine. This is illustrated in Figures 7 and 8. In the latter an attempt has been made to increase the radiating surface of the engine and restrict the cooling load simply to the blind portion of the combustion chamber. They conclude that the asymmetric external compression expansion circular combustor (Type B) is the design to be favored because it results in minimal internal (non-radiating) combustion chamber surface. They also point out that the larger the engine, the easier it is to cool.

Another approach to the cooling problem has been discussed by Duggar1) who remarked:

> "A better way to push back the structural temperature limitation on ramjet engine flight speed might be to turn the engine inside out, so that all of the compression-heat addition-expansion cycle is carried out on external surfaces, which are free to radiate to the atmosphere. Thus, the all-external engine (ERJ) is simply a

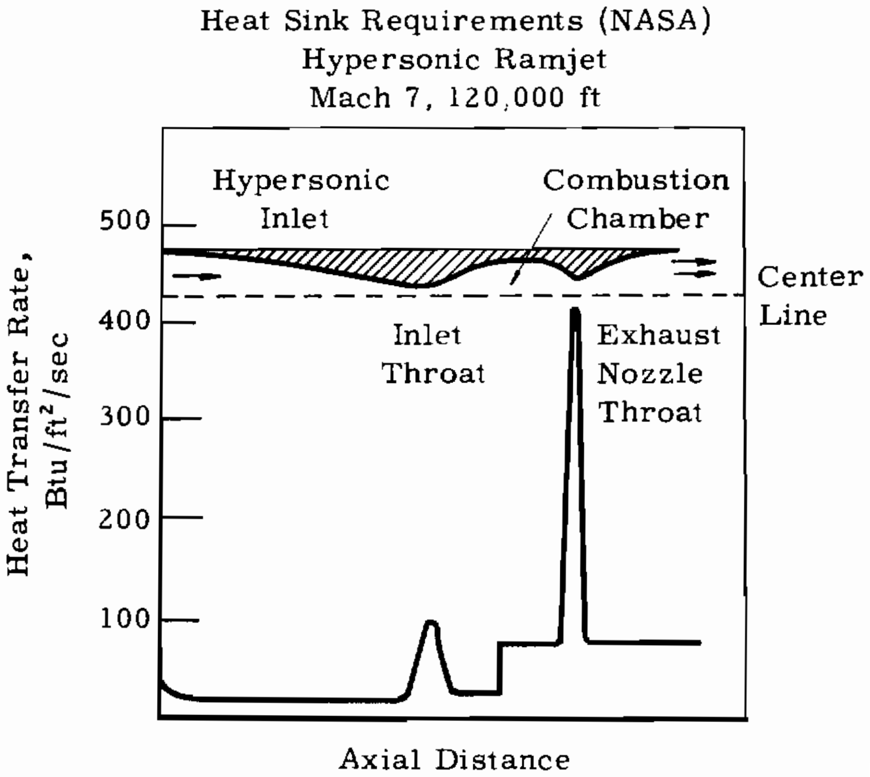


Figure 6. ESTIMATED HEAT TRANSFER RATES
(After Connors and Obery)[4)]

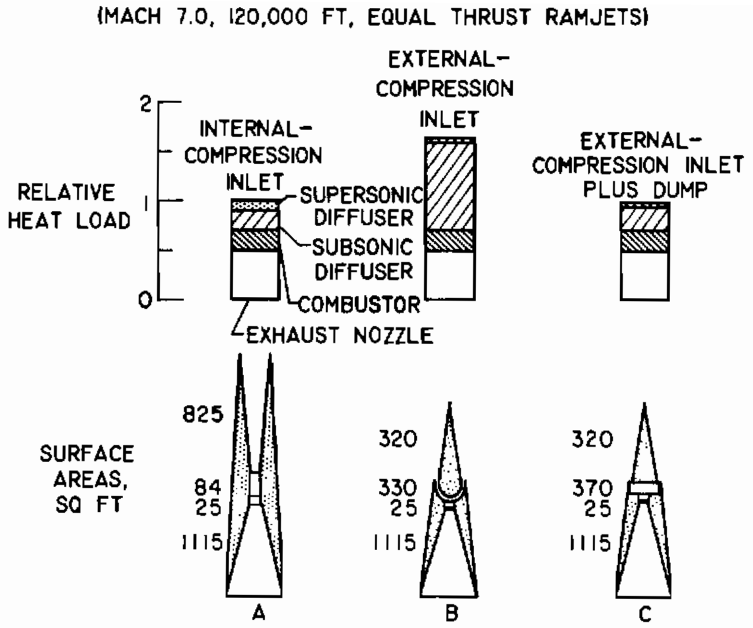
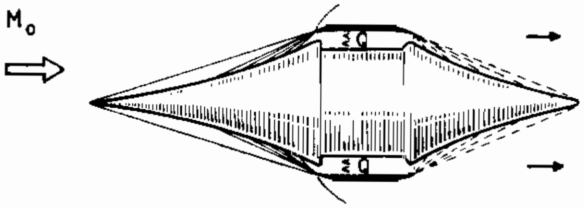
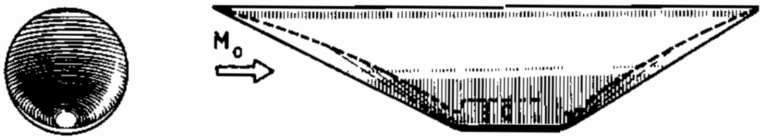


Figure 7. TOTAL HEAT LOADS WITH VARIOUS INLETS[4)]



(A) AXISYMMETRIC PLUG-INLET-EXIT ANNULAR COMBUSTOR



(B) ASYMMETRIC EXTERNAL-COMPRESSION-EXPANSION CIRCULAR COMBUSTOR

Figure 8. EXTERNAL-COMPRESSION-EXPANSION HYPERSONIC RAMJET DESIGNS[4)]

> supersonic wing beneath which mass and heat are added by injecting fuel into the supersonic air stream. The addition of mass and heat beneath a wing causes the supersonic air stream reaching the heat addition region to be deflected away from the wing, and increases lift in much the same way that an increased angle of attack would increase lift. If the heat or mass addition is concentrated under the rear part of the wing, where the increase in surface pressure will serve to reduce drag, then the maximum lift to drag ratio may be increased by a factor of 2 or more. If the pressure rise under the rearward-facing surface is great enough, the "wing" will have a net thrust, and it becomes a "propulsive wing" or "engine". Luidens and Flaherty (see reference 7) estimate that a simple wedge air-foil of small thickness to chord ratio and large rear to fore angle ratio could become more efficient than a conventional ramjet engine plus wings at speeds greater than about Mach 8."

A sketch of an ERJ type of engine is given in Figure 9. Although all surfaces are external and hence free to radiate, it would be necessary to cool the rearward-facing surface since it would be facing the fuel combustion zone.

The amount of heat sink capacity which can be carried on board a particular aircraft will depend on two factors: the amount of space available for the fuel and the amount of fuel which has to be carried in order to accomplish a certain mission. These factors can be judged from the volumetric heat sink (e.g., thousands of Btu/cu ft of fuel) and the heat sink as a proportion of the heat of combustion. These factors are given in Table 1 which is selected from information given in Table 3. This table presents the calculated values for a number of possible fuel types and types of heat sink reactions. It also includes hydrogen which is often mentioned as a possible fuel for high Mach number vehicles. It will be noted that there is an extremely wide range of volumetric heat sink capacity varying from about 31 K-Btu/cu ft for liquid hydrogen up to about 109 K-Btu/cu ft for normal octane when dehydrocyclized and dehydrogenated to styrene and hydrogen. This latter reaction also gives the highest heat sink in terms of percent of the heat of combustion.

It may be instructive to compare the normal octane with hydrogen. This has been done in a preliminary way in Table 2 for various considerations with respect to the use of the two fuels. It is obviously premature to regard this as any sort of definitive analysis but it does point out a weakness of hydrogen as a fuel for high-speed volume limited aircraft, namely the large amount of fuel tank volume that would have to be provided. The comparison in the table is made on the basis of carrying the same amounts of fuel in terms of energy content with no correction for boil-off and assumes that the octane is dehydrocyclized to styrene and hydrogen.

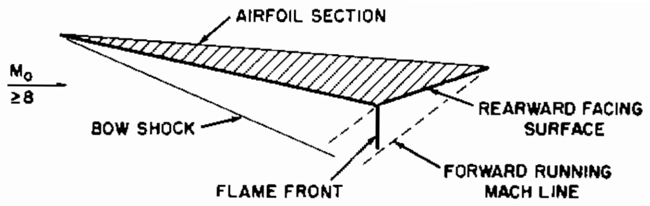


Figure 9. "PROPULSIVE WING," OR EXTERNAL RAMJET (ERJ)
After (4)

TABLE 1
ENDOTHERMIC CAPACITIES OF SOME FUELS

Fuel	Type[a] Reaction	Products	Equil. Conv., %	Heat Absorbed (1340°F, 10 atm)				
				Btu/lb			Total as	
				Chemical	Physical	Total	K-Btu/ft³	% of ΔH_c
Methane	none	-	-	-	1460	1460	41.6	6.8
Propane	DH	C_3H_6, H_2	40	510	1240	1750	78.9	8.9
Propane	Cr	C_2H_4, CH_4	95	740	1240	1980	89.2	10.0
n-Hexane	DHC	C_6H_6, H_2	99	1250	1030	2280	94.3	11.9
n-Octane	DHC	C_8H_{12}, H_2	99	970	1030	2000	88	10.5
n-Octane	DHC-DH	C_8H_{10}, H_2	99	1440	1030	2470	109	13.0
MCH[a]	DH	C_7H_8, H_2	99	940	1016	1956	94.1	10.5
Prop. tet.[a]	DP	C_3H_6	99	630	945	1575	74.8	8.3
H_2	none	-	-	-	6500	6500	30.8	12.8

a) Key DH = dehydrogenation; Cr = cracking; DHC = dehydrocyclization; DP = depolymerization; MCH = methylcyclohexane; Prop. tet. = propylene tetramer.

TABLE 2
COMPARISON OF HYDROGEN AND A HYDROCARBON AS A FUEL FOR HIGH SPEED AIRCRAFT

Properties	Hydrogen	n-Octane
Volume	3.5	1
Heat sink capacity	1	1
Weight	0.373	1
Cost[a)]	3-4	1
Combustion characteristics	superior	
Thermal stability	superior	
Handling		easier
Storage		easier
Application[b)]	less difficult	
Fuel tank construction		simpler

a) Based on using n-octane (dehydrocyclized to styrene and H_2) at 4¢/lb, hydrogen at 25-35¢/lb, and carrying the same thermal value of each fuel.

b) Aircraft heat exchanger complexity.

Thermodynamic Calculations

Two general types of thermodynamic calculations were carried out - first, those to aid in selecting fuels which would have promisingly high capacities to absorb heat both by virtue of heat capacity and by endothermic reaction; second, those to aid in interpreting the results of experiments in the small-scale catalytic reactor tests. In this second category, calculations were purely thermochemical. The sensible and latent heat absorbed in going from ambient temperature liquid to vapor fuel at the final temperature was calculated. The heat of reaction of the vapor fuel at the final temperature to the observed products of reaction (determined by analyzing the reactor effluent stream) was calculated and added to the sensible and latent heat to derive the total indicated heat absorption for the fuel under the experimental conditions. For these calculations, enthalpy data have been available from the tables of API Project 44 for all systems considered thus far. The calculated results are reported along with the experimental results of the catalytic studies.

In the screening calculations in the first category mentioned above, additional assumptions and calculations were required to specify the product composition after reaction and hence the heat absorbed by the endothermic reaction. For these calculations a single reaction was considered (100% selectivity to the specified product) and it was assumed that reaction proceded to equilibrium at a total pressure of 10 atm and at the upper limit temperature specified. The total endothermic capacity of the fuel was then calculated as the sum of the heat of vaporization, the sensible heat from the lower temperature (either the fuel freezing point or 77°F), to the upper limit temperature, (calculations were made for 620°F and 1340°F as upper temperatures for each fuel) and the heat of reaction for equilibrium conversion to the product indicated. In addition to fuels which can undergo endothermic reaction, such calculations were also made for some non-reacting "cryogenic" fuels: methane, ethane, and liquid hydrogen.

A summary of the most pertinent results is given in Table 3. At the lower temperature, 620°F, conversion of light paraffins by dehydrogenation or of heavier paraffins by dehydrocyclization is not favored. Hence, the paraffin fuels have available at this temperature endothermic capacities of 455 to 935 Btu/lb or 2.4 to 4.4% of their heats of combustion. In the cases of propane and butane, cracking reactions are favored thermodynamically and when these are taken into account these fuels can have endothermic capacities of 5-5-1/2% of their heats of combustion. However, to make use of these potential reactions would require development of suitable catalysts for cracking at this temperature. Such catalysts are not known in the present technology. The depolymerization of olefins and dehydrogenation of naphthenes to aromatics can go nearly to completion at 620°F. At this temperature the latter fuels have the highest endothermic capacities among those investigated, 6-7% of the heat of combustion.

At the higher temperature, except for the dehydrogenation of light paraffins, all reactions studied can go to conversions of 95% or higher. At this temperature, 1340°F, the fuels having highest endothermic capacities are

TABLE 3
ENDOTHERMIC CAPACITIES OF SOME HYDROCARBON FUELS[d]

Reactant Fuel	Freezing Point, °F	Net Heat of Combustion, KBtu/lb[c]	Density[a] lb/ft^3	Products of Reaction	At 620°F (600°K)						At 1340°F (1000°K)					
								Total Capacity						Total Capacity		
					Equilib. Conv. at 10 atm, %	Heat of Reaction, Btu/lb	Sensible + Latent Heat,[b] Btu/lb	Btu/lb	KBtu/ft^3	% of Net Heat of Combustion	Equilib. Conv. at 10 atm, %	Heat of Reaction, Btu/lb	Sensible + Latent Heat,[b] Btu/lb	Btu/lb	KBtu/ft^3	% of Net Heat of Combustion
CH_4, methane	-296	21.46	28.4	None			935	935	26.5	4.35			1460	1460	41.5	6.8
C_2H_6, ethane	-298	20.38	41.1	None			790	790	32.5	3.9			1270	1270	52.2	6.2
C_3H_8, propane	-306	19.75		C_3H_6, propylene; H_2, hydrogen	negl.		770	770	34.7	3.9	40	510	1240	1750	78.8	8.9
C_3H_8, propane	-306	19.75	45.1	C_2H_4, ethylene; CH_4, methane	30	230	770	1000	45.1	5.1	95	740	1240	1980	89.2	10.0
C_4H_{10}, butane	-217	19.48	47.5	C_4H_8, butylene; C_4H_6 butadiene; H_2	negl.		695	695	33.0	3.6	52	540	1150	1690	80.2	8.7
C_4H_{10}, butane	-217	19.48	47.5	C_3H_6, propylene; CH_4, methane	82	390	695	1085	51.5	5.6	99	480	1150	1630	77.4	8.4
C_6H_{14}, n-hexane	-139	19.21	41.4	C_6H_6, benzene; H_2	negl.		455	455	18.8	2.4	99	1350	1030	2380	98.5	12.4
C_6H_{12}, cyclohexane	44	18.68	48.86	C_6H_6, benzene; H_2	73	880	430	1310	63.8	7.0	99	1125	1000	2125	104	11.4
C_8H_{18}, n-octane	-70	19.08	44.1	C_8H_{12}, ethylbenzene; H_2	80	750	450	1200	52.9	6.3	99	970	1030	2000	88.	10.5
C_8H_{18}, n-octane	-70	19.08	44.1	C_8H_{10}, styrene; H_2	negl.		450	450	19.8	2.4	99	1440	1030	2470	109	13.0
C_7H_{14}, methyl-cyclohexane	-196	18.64	48.27	C_7H_8, toluene; H_2	80	770	430	1200	58.0	6.1	99	940	1010	1950	94.1	10.5
C_8H_{16}, di-isobutylene	-150	18.99	44.9	C_4H_8, butylene	99	350	440	750	33.6	4.0	99	295	990	1285	57.6	6.8
$C_{12}H_{12}$, propylene tetramer	-28	18.87	47.5	C_3H_6, propylene	99	615	440	1055	50.0	5.6	99	630	945	1575	74.8	8.3
$H_2(\ell)$, liquid hydrogen	-434	51	4.74	None			4000	4000	19.0	7.8			6500	6500	30.8	12.8

a) At freezing point for H_2, and C_1-C_4; at 70°F for higher hydrocarbons.
b) From freezing point for H_2 and C_1-C_4; from 70°F for higher hydrocarbons.
c) At 70°F, fuel in liquid state.
d) Based on data from tables of API Project 44.

the C_6-C_8 paraffins and naphthenes which can be converted to aromatics with total endothermic capacities in the range 10-14% of the heat of combustion. It should be noted that for the C_6 and higher fuels no allowance has been made for possible precooling of the fuel. If this were practiced it could add as much as 200 Btu/lb in some cases.

The fuel system pressure, 10 atm, for which calculations were carried out was selected somewhat arbitrarily, on the assumption that combustion chamber pressure would be in the range of 50-100 psi. If the combustion chamber pressure could be lowered and the fuel system operated at 5 or even 2 atmospheres, the equilibrium conversions possible for some of the reactions would be increased. At 620°F, lowering the system pressure would permit only slight increases in the endothermic capacity of the C_6 and C_8 naphthenes since conversions are relatively high for these compounds at 10 atm. The dehydrogenations of paraffins and dehydrocyclization would remain negligible at any practical pressure. Only in the case of cracking of propane would a significant gain be made at this temperature. At the higher temperature, 1340°F, lower pressures would have a significant effect only on the dehydrogenations of propane and butane, since all other reactions considered can go nearly to completion at 10 atm.

For comparison with the numbers given in Table 3 for hydrocarbon fuels, corresponding endothermic capacities for liquid hydrogen fuel at these two temperatures have been calculated. Taking into account the sensible heat from the freezing point and the relatively minor contributions of the heat of vaporization and the ortho-para conversion, hydrogen has an endothermic capacity to 600°K of 4000 Btu/lb (7.7% of the heat of combustion) and to 1000°K of 6500 Btu/lb (12.5% of the heat of combustion). Thus, compared on the basis of the fraction of the heat of combustion available as endothermic capacity, the best of the hydrocarbons listed in Table 3 are practically equivalent to hydrogen as an endothermic fuel. This is particularly true if precooling of the hydrocarbon fuel is practiced and mixtures of hydrocarbons are used to lower the freezing point.

Reaction Studies

Although thermal reactions are not being neglected, the major effort in this phase of the investigation involves catalytic dehydrogenation. Catalytic reactions have the advantage of generally proceeding at lower temperatures and for some reactions, of proceeding more cleanly than uncatalyzed reactions. These reactions have not been studied previously in connection with the selection of fuels for multi-Mach flight, and an important aspect of the present program is to study the possibility of utilizing catalysts in heat sink reactions. While there is a tremendous body of literature dealing with endothermic catalytic reactions of hydrocarbons such as dehydrogenation of paraffins and naphthenes,8)9)10)11)12)13)14) in practice these reactions have been studied at low conversions and space velocities, in the presence of hydrogen and with respect to useful product material, rather than for maximum energy absorption during reaction. In the present research, laboratory studies are being carried out to determine conditions under which heat can be absorbed in quantities sufficient to satisfy the cooling requirements of multi-Mach flight speeds. As pointed out above, total heat sinks of 1800-2000 Btu/lb will be needed. Latent and sensible heats obtainable from most hydrocarbons are 1000-1200 Btu/lb at 1340°F (when the starting material is at the freezing point). Thus, to be useful, a catalytic reaction should contribute at least 800 Btu/lb to the total heat sink.

Vapor phase catalytic dehydrogenation of methylcyclohexane and ethylcyclohexane were studied over laboratory and commercial platinum on alumina catalysts and over a commercial potassium promoted chromia on alumina catalyst. Propane dehydrogenation and dehydrocyclization of six normal and branched higher hydrocarbons (C_7-C_{18}) were studied over the chromia catalyst only. Tests were for 90-minutes duration and were carried out at 1-10 atm pressure, 1022-1283°F and LHSVs of 5-100 in the absence of hydrogen. Product material was analyzed by mass spectrometry (gas products) and by gas-liquid chromatography, from which conversions and selectivities to desired products were calculated. Amounts of coke or polymer formed during reaction (generally minor) were neglected and were not included in the conversion computations. (However, a method for measuring coke formed from product distribution for the dehydrogenation of propane reaction is given in the Appendix.) Heat sinks produced were not measured directly but were calculated from thermodynamic heats of reaction based on the experimental conversions and product distributions and from sensible and latent heats for the various hydrocarbons. The bulk of the study was carried out with methylcyclohexane and with propane.

Experimental

The apparatus used for the reaction studies consisted of two identical reactor units, each with a hot tube reactor and with conventional devices for measuring feed flow rates and for collecting and measuring reaction products. A schematic of one reactor unit is shown in Figure 10; photographs of the complete dual reactor assembly are shown in Figures 11 and 12.

The reactor was a furnace-heated stainless steel tube (1/2-inch IPS) 33 inches long. (A few experiments were done with a Vycor tube of about the same dimensions.) The catalyst bed (ca 5 inches long) was located in the lower portion of the tube; the top portion served as a preheater. For thermal reaction studies, a bed of quartz was used instead of catalyst. The non-hydrocarbon gases (used for catalyst regeneration), were metered through conventional rotameters and entered the reactor at the top. Liquid hydrocarbon feed was forced from a liquid reservoir through a rotameter by means of argon pressure. The feed was then vaporized in a heated line and entered the reactor as a vapor through a separate tube that terminated just above the catalyst bed. The hot exit gases from the reactor passed through a condenser and then a liquid-gas separator. The liquid was collected in a Jerguson gauge; the gas products were passed through a Grove pressure regulator, a wet test meter and then were vented. Gas samples were taken upstream from the wet-test meter. A thermowell entered the reactor from the bottom end and served to contain the thermocouples used for measuring bed temperatures.

The procedure used in the experimental work and the method of calculating conversions, selectivities and heat sinks are given in the Appendix.

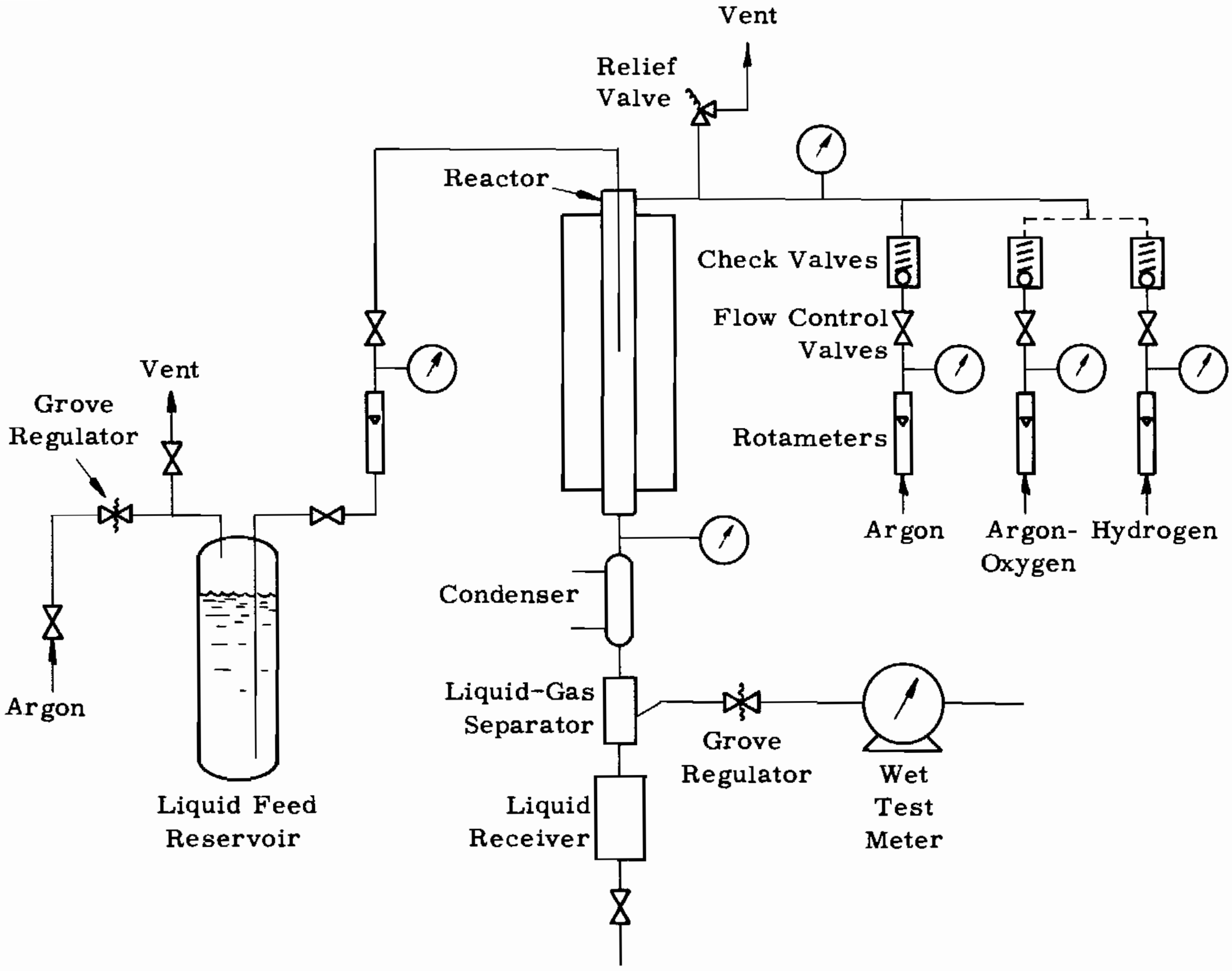


Figure 10. DIAGRAM OF CATALYTIC REACTOR SYSTEM

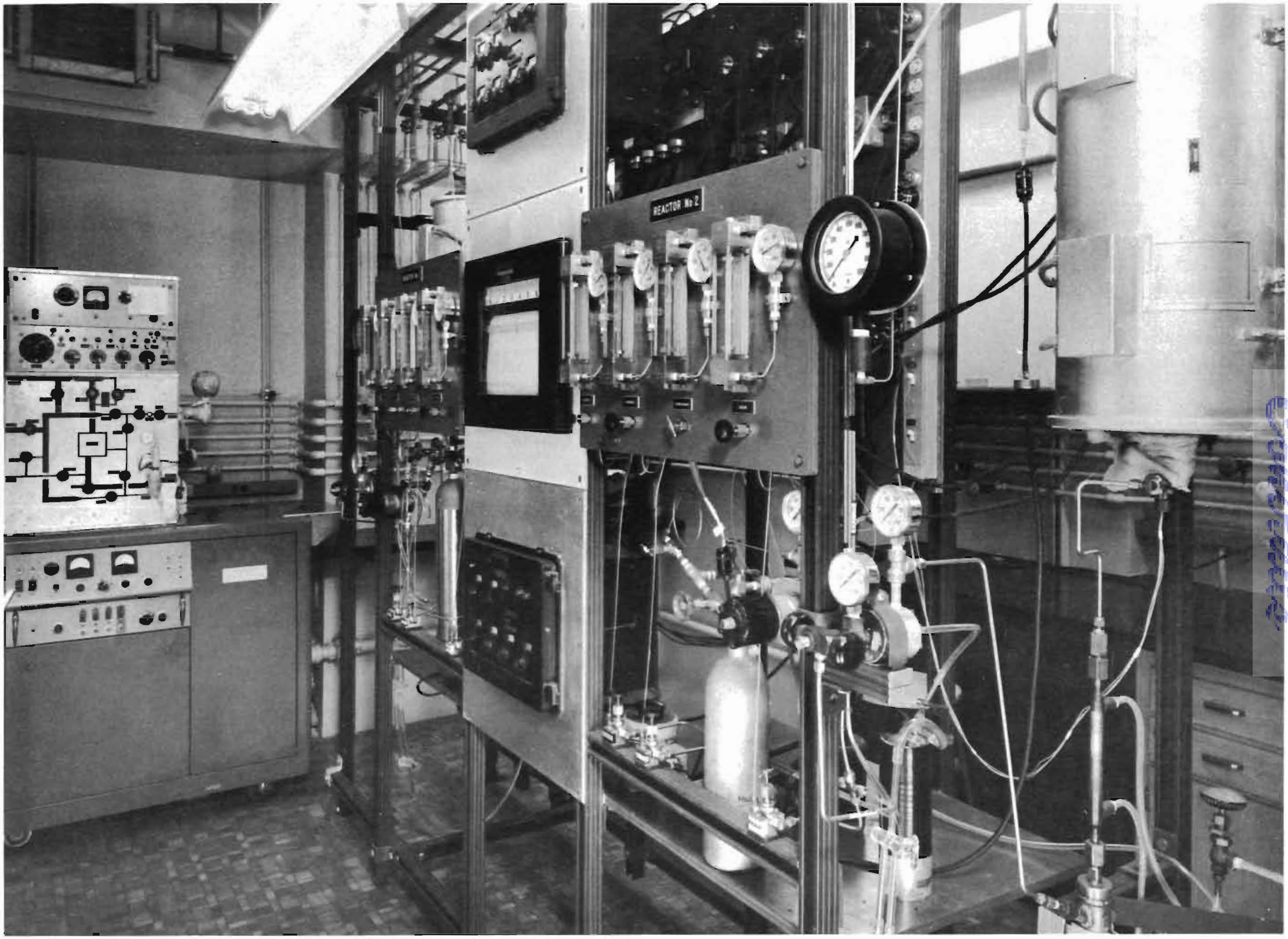


Figure 11. DUAL CATALYTIC REACTOR SHOWING MASS SPECTROMETRIC ANALYSER

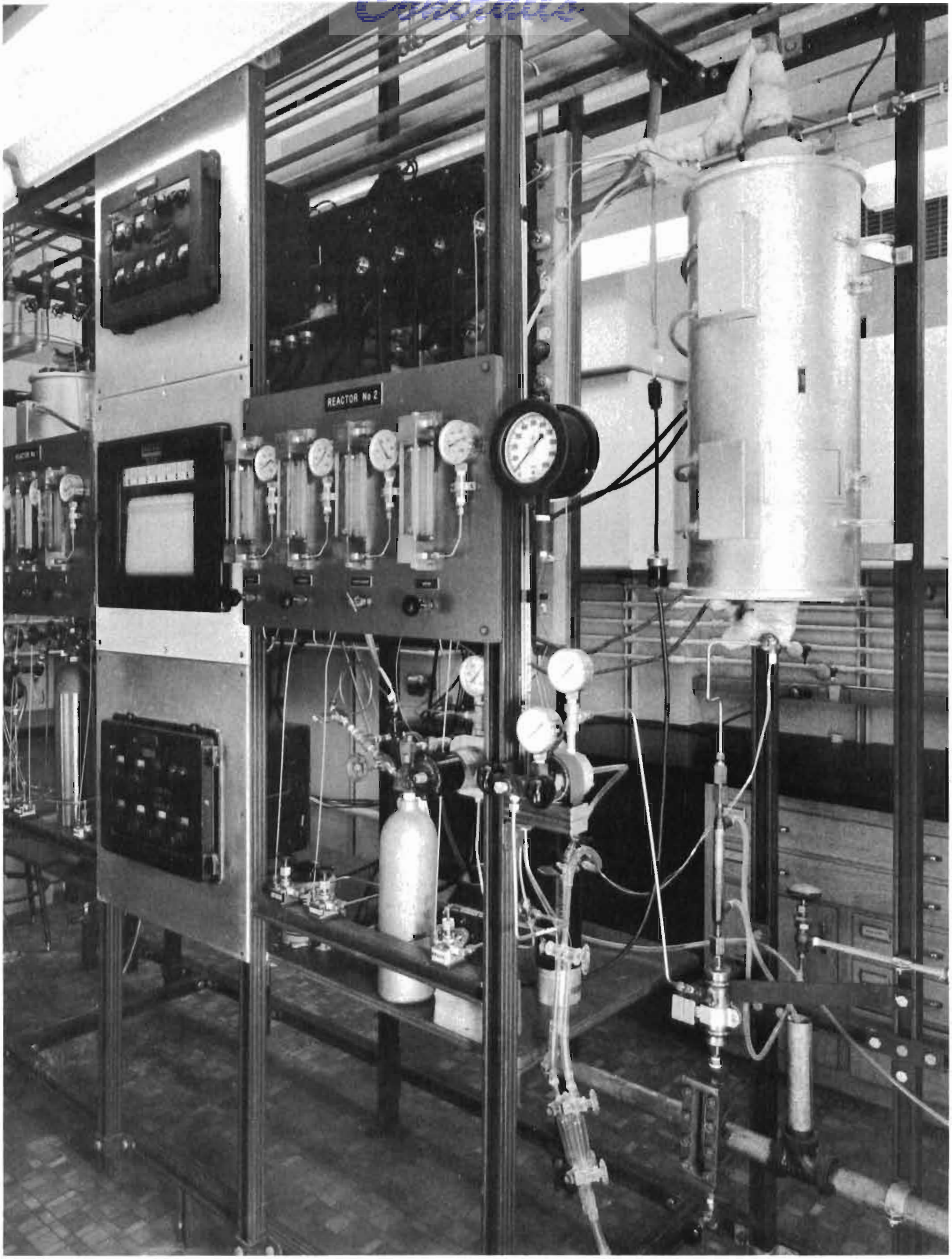


Figure 12. DUAL CATALYTIC REACTOR SHOWING REACTOR NO. 2 AND PRODUCT SAMPLING SYSTEM

Thermal Decomposition of Methylcyclohexane

Methylcyclohexane (MCH) reacted thermally in the metal tube reactor to give toluene, cracked products and intermediate dehydrogenation products such as methylcyclohexenes and methylcyclohexadienes. At 10 atm pressure and 1283°F, extensive reaction occurred with over 50% of the MCH fed being converted (Table 4). At this temperature and pressure the reaction products were principally cracked material with lesser amounts of dehydrogenation products. Lower conversions and lower selectivity for cracked products were observed at lower temperatures and lower pressures (Table 4).

Dehydrogenation of Methylcyclohexane

The dehydrogenation of methylcyclohexane (MCH) to toluene and hydrogen was studied over platinum on alumina and potassium-promoted chromia on alumina catalysts at 1-10 atm pressure, 846-1283°F and at LHSV's of 20-100. The reaction is not equilibrium limited in these regions and conversions of 99+% are theoretically possible (see Appendix). This corresponds to an endothermic heat of reaction of about 940 Btu/lb and total possible heat sinks of 1860 and 2060 Btu/lb when the final temperatures of the reaction products are 1112° and 1340°F, respectively.

Platinum on Alumina Catalysts

Platinum on alumina catalysts were the most active of the catalysts tested thus far. With this catalyst conversions and heats of reaction that were 90% to 97% of theoretical were obtained at 10 atm pressure, LHSV's of 20-50 and at 846-1112°F (Table 5). The reaction was highly selective for toluene (97+%) so that a total heat sink of 1816 Btu/lb was obtained at LHSV of 50 at 1112°F (Table 5). This would correspond to a total heat sink of 2016 Btu/lb if the reaction products were brought to 1340°F. Catalyst stability was excellent and little or no decline in activity (i.e., conversion) was observed during the 60-90-minute reaction periods. Equally high conversions, selectivities for toluene, catalyst stabilities and heats of reaction were obtained at lower temperatures and lower space velocities. The data for conversions, selectivities and heats of reaction after 30-minutes reaction time are presented in Table 5. The data for the complete runs are given in the Appendix (Table 37). The clean nature of the reaction is well shown by the simplicity of the product GLC curve (Figure 13).

With the platinum catalyst, the catalyst bed temperatures were considerably lower than the block temperatures (ΔT = ca 350° to 450°F). Presumably, these large temperature differences were due to a combination of high catalyst activity and the inherently poor heat conductivity of the catalyst granules. This suggested that higher conversions at a given space velocity and block temperature would be possible if heat could be transferred more rapidly from the reactor walls to the catalyst bed. This was achieved by diluting the catalyst bed with copper shot and also by making the catalyst bed longer and thinner (i.e., by reducing the annular dimension of the catalyst bed). For example, at 1112°F and LHSV of 50 an MCH conversion of 97% was obtained when the catalyst bed was diluted with copper (7-ml catalyst,

TABLE 4
THERMAL REACTION OF METHYLCYCLOHEXANE[a)]

Product Distribution

Reaction Time:	20 min
Catalyst:	Quartz chips
Catalyst Vol:	20 ml
Reactor:	Stainless Steel

Run No. 8277-	24	25	27	57	58-1	58-2
Temperature, °F	1112	1202	1293	1112	1202	1283
Pressure, atm	1	1	1	10	10	10
LHSV[b)]	5	5	5	20	20	20
MCH conversion, %	0.4	3.2	14.0	11.2	26.3	51.1
Product Components, %						
Methylcyclohexane	99.6	96.8	86.0	88.8	73.7	48.9
Toluene	0.1	0.2	2.5	0.2	0.6	2.2
Benzene	-	0.1	1.5	0.1	0.9	3.5
1-Methylcyclohexene	0.1	0.6	1.5	0.7	1.9	2.3
3-Methylcyclohexene	-	-	1.9	1.5	4.1	4.6
4-Methylcyclohexene	0.1	1.8	2.5	0.6	1.8	2.3
Cyclohexadienes	-	-	-	-	0.6	1.3
Heavier than toluene	-	-	-	-	0.9	1.3
Cracked	0.1	0.4	4.0	8.2	16.4	35.3

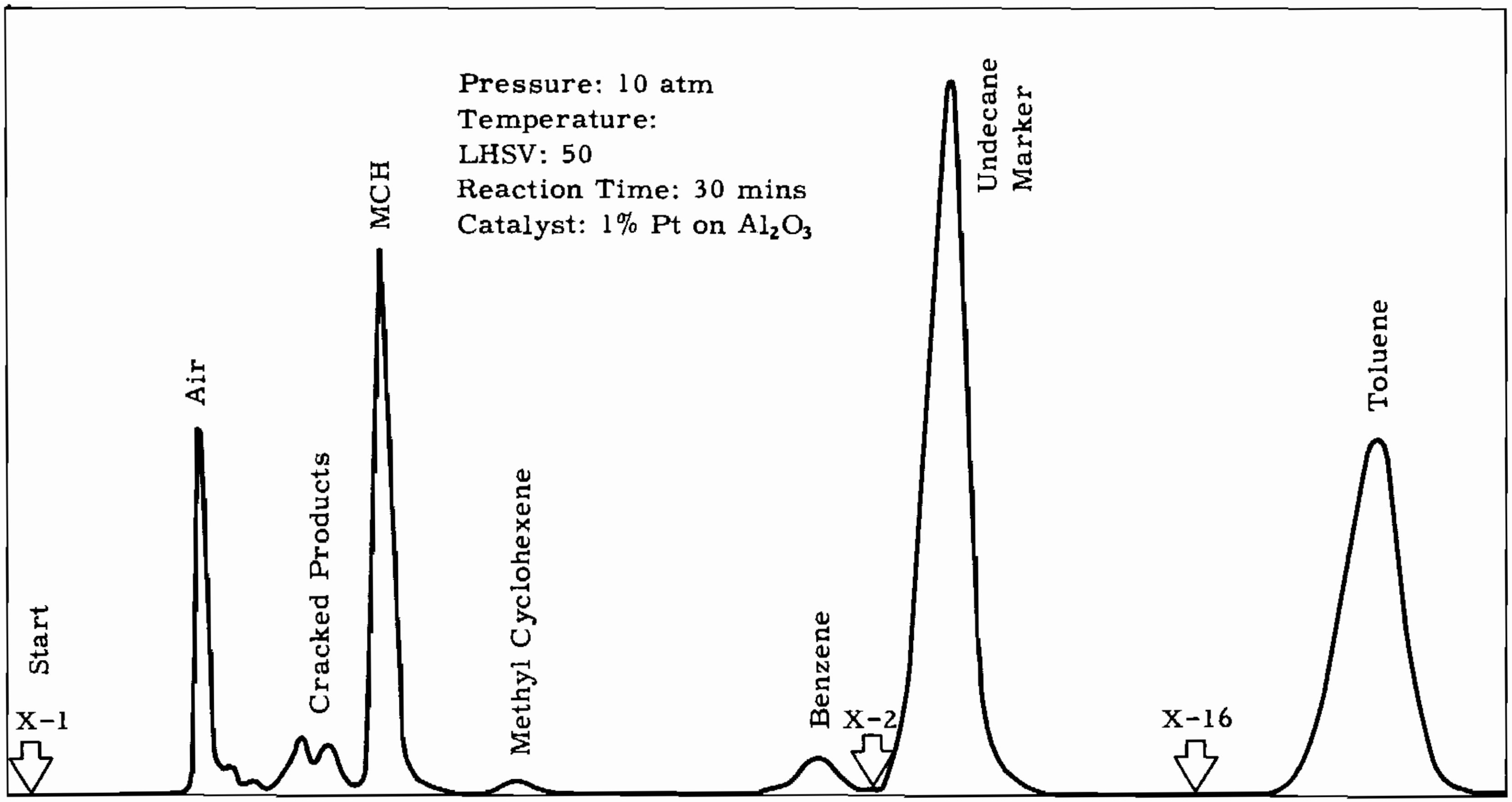
a) Phillips Petroleum "Pure" grade; 99.8%m, 0.2%m lighter than MCH by GLC analysis.

b) LHSV calculated basis 20 ml volume.

TABLE 5
DEHYDROGENATION OF METHYLCYCLOHEXANE OVER PLATINUM ON ALUMINA CATALYSTS

Pressure: 10 atm
Reaction time: 30 minutes
Feed: pure MCH
For more complete data, cf
Table 37 (Appendix)

Run No. 8277-	Catalyst	Catalyst Volume, ml	Feed	LHSV	Reaction Temp, °F		MCH Conv., %	Selectivity for Toluene, %	Heat Sink, Btu/lb	
					Block	Catalyst			Reaction	Total at Block Temp
68	1% Pt; No. 7947-60	20	Pure Grade	20	1022	640	91.1	99.2	856	1706
69	1% Pt; No. 7947-60	20	Pure Grade	53	1112	649	60.4	99.4	565	1485
73	1% Pt; No. 7947-60	20	Pure Grade	53	1202	718	65.0	99.1	607	1597
79	1% Pt; No. 7947-60	20	Pure Grade	30	1202	750	85.7	98.3	806	1796
95	0.7% Pt; UOP-R8	20	Pure Grade	20	1022	626	91.8	98.8	862	1712
97	0.7% Pt; UOP-R8	20	Tech. Grade	20	1022	626	87.9	96.8	800	1650
98	0.7% Pt; UOP-R8	20	Comm. Grade	20	1022	682	87.3	97.6	617	1467
Catalyst bed diluted with copper shot (volume copper/catalyst = 1.86)										
100	1% Pt; No. 7947-60	7	Pure Grade	20	842	646	97.0	99.4	912	1692
101	1% Pt; No. 7947-60	7	Pure Grade	50	1112	838	97.2	98.0	896	1816
103	1% Pt; No. 7947-60	7	Pure Grade	100	1202	918	63.9	97.8	588	1578
Thin catalyst bed										
92	1% Pt; No. 7947-60	7	Pure Grade	20	842	690	96.0	99.2	900	1680
	1% Pt; No. 7947-60	7	Pure Grade	50	1022	684	69.5	99.3	654	1504



Pressure: 10 atm
Temperature:
LHSV: 50
Reaction Time: 30 mins
Catalyst: 1% Pt on Al_2O_3

Figure 13. GLC CURVE. PRODUCT ANALYSIS OF RUN 8277-101-1

13-ml copper shot; bed temperature was 848°F), while only 60% conversion was obtained with an undiluted catalyst bed (bed temperature was 648°F; cf runs 101 and 69, Table 5). With a thin catalyst bed, in which the annular distance between the reactor wall and the thermowell was about 1/16 inch or about the diameter of the catalyst granules, 96% conversion was observed at a block temperature of 842°F (bed temperature = 690°F) while with the normal catalyst bed (3/16-inch thick) only 91% conversion was observed at a block temperature of 1022°F (bed temperature 640°F; cf runs 92 and 68, Table 5). Thus, high conversions at space velocities higher than 50 in the temperature region of 934 to 1022°F appear feasible, possibly by using a thin, diluted, catalyst bed.

The majority of the work with platinum was done with a laboratory prepared catalyst (1% Pt on alumina). This catalyst was designed to minimize cracking reactions and contained no halogen. However, comparable results were obtained with a commercial platforming catalyst (UOP-R8) which contained about 0.7% halogen and 0.76% Pt (cf runs 95 and 68, Table 5). Apparently at 1022°F the acidity effect of the halogen in the platforming catalyst does not catalyze the cracking reaction to any appreciable extent.

Several grades of MCH feed were tested using the platforming catalyst. Highest conversions and selectivities were obtained with Phillip's "Pure" grade. Slightly lower conversions and selectivities were obtained with "Technical" and "Commercial" grade MCH (runs 95, 97, 98, Table 5). However, the "Commercial" grade contained only 75% MCH; hence, the heat of reaction per pound of feed was low. More complete analyses of the feedstocks are given in the Appendix.

Regeneration of the used platinum catalysts was not carried out in this work. However, the catalyst has been regenerated in the laboratory after other dehydrogenation studies, using techniques developed for regenerating platforming catalysts (i.e., carbon burnoff in air followed by chlorination and subsequent steam stripping of the chloride from the catalyst).

Chromia on Alumina Catalysts

The chromia catalyst was considerably less active than the platinum catalyst and MCH conversions of only 70-80% were possible only at the higher temperatures (1202-1283°F). Under these conditions selectivities for toluene plus benzene, heats of reaction and catalyst stabilities were only fair. For example, at 1 atm pressure, LHSV of 5 and at 1283°F, 81% conversion, 73% selectivity and a heat of reaction of 562 Btu/lb for a total heat sink of 1627 Btu/lb was observed. Considerable cracking was observed at this temperature with about 20% of the MCH fed being converted to cracked products. Catalyst activity declined about 18% during the 90-minute process period. Lower heat sinks, less MCH cracking and somewhat better catalyst stabilities were observed at lower temperatures.

The experimental data for runs with the chromia catalyst at various temperatures, pressures, and space velocities are tabulated in Table 6. The initial heat sinks based on conversions and selectivities at 30-minute reaction

TABLE 6
DEHYDROGENATION OF METHYLCYCLOHEXANE OVER CHROMIA ON ALUMINA CATALYST

Catalyst:	2% K_2O, 8% Cr_2O_3, 90% Al_2O_3
Catalyst Wt:	13.3 ± 0.2 g
Catalyst Volume:	20 ml
Feed:	Pure Methylcyclohexane

Run No. 8277-	Pressure, atm	LHSV	Block Temp, °F	Catalyst Bed Temperature, °F			Methylcyclohexane Conversion, %			Selectivity for Toluene + Benzene, %		
				30 Min	60 Min	90 Min	30 Min	60 Min	90 Min	30 Min	60 Min	90 Min
Stainless Steel Reactor												
29	1	5	1022	930	938	938	41.0	42.0	39.3	99.0	99.6	99.9+
31	1	5	1112	1000	1008	1013	61.2	57.6	56.9	95.7	98.4	92.8
32	1	5	1202	1096	1108	1116	70.3	-	53.5	91.1	-	91.1
65	1	5	1283	1182	1199	1206	81.3	69.2	66.4	73.5	68.1	61.6
Vycor Reactor												
40	1	5	1112	986	990	998	55.6	52.4	44.6	99.9+	99.9+	99.9+
Stainless Steel Reactor												
43	10	20	1022	923	934	943	21.2	20.0	16.8	75.6	91.5	88.1
45	10	20	1112	948	954	959	35.4	35.3	34.2	93.0	91.0	87.4
48	10	20	1202	1042	1049	1058	50.1	47.0	46.2	72.4	72.3	67.8
52	10	20	1283	1141	1168	1168	69.9	62.7	60.6	48.1	29.6	20.9

times are presented in Table 7. Product analyses are given in Table 8. The data are further summarized in Figure 14 which shows MCH conversion and total heat sinks at 1 and 10 atm pressure as function of reaction temperature. The solid lines refer to MCH conversions, the broken lines are the corresponding heat sinks. The unusual shapes of the conversion curves in which the conversion values at 1283°F are higher than would be expected from extrapolation is attributed to thermal reaction occurring simultaneously with the dehydrogenation reaction at the higher temperature.

With increased pressure, lower heat sinks, lower MCH conversions, more cracking and somewhat enhanced catalyst stability were observed (Tables 6 and 7). Thus, at 10 atm pressure, 1283°F and LHSV = 20 a total heat sink of only 1380 Btu/lb at 70% MCH conversion was found. During the 90-minute run the catalyst activity declined by 13%. At this pressure the thermal reaction was even more evident and at 30 and 90-minute reaction times 27% and 39.2% of the MCH fed was converted to cracked products. At lower temperature, lower heat sinks, lower conversions, and less cracking was observed (Tables 6 and 7, Figure 14).

The used catalysts were readily regenerable with 5% oxygen in argon at 1022°F.

Reaction products from the dehydrogenation reaction were mainly toluene with small amounts of benzene and methylcyclohexenes. Of the cyclohexene isomers the 4-methyl appeared most abundant (Table 8). Further, the 3-methyl isomer appeared to be a product of the thermal reaction (cf runs 65, 52, and 52A in Table 8 with 58-1, 58-2, and 27 in Table 4). More cyclohexenes were produced at the higher reaction pressure (cf runs 40 and 45, Table 8). Typical GLC curves of product analyses are shown in Figures 15 and 16. The greater complexities of the curves reflect the greater tendency for cracking to occur over the catalyst.

Dehydrogenation of Ethylcyclohexane

The dehydrogenation of ethylcyclohexnne (ECH) was tested over the platinum on alumina catalyst (1% Pt) at 10 atm pressure, 1202°F and LHSV of 20. Total heat sinks of only 906 to 955 Btu/lb were observed (calculated from observed conversions) although the reaction has a potential total heat sink of over 2000 Btu/lb when the starting material is dehydrogenated to styrene. Under our test conditions the reaction products were principally cracked material (Table 9). Why this reaction is so much less selective than the dehydrogenation of methylcyclohexane is not immediately evident. It is suspected that one or more of the reaction products, probably styrene, is thermally unstable giving rise to an exothermic secondary reaction. This could occur through the formation of its unstable isomer, cyclooctatetracene.

TABLE 7
HEAT SINKS GENERATED FROM DEHYDROGENATION OF METHYLCYCLOHEXANE

Run No. 8277-	Pressure, atm	LHSV	Block Temp, °F	MCH Conv., %	Heat Sink,[b] Btu/lb		
					Catalytic Reaction	Total	Total Equil.
29	1	5	1022	41.0	381	1231	1790
31	1	5	1112	61.2	550	1470	1860
32	1	5	1202	70.3	600	1590	1930
40[a]	1	5	1112	55.6	522	1442	1860
34	1	5	1283	81.3	562	1627	2005
43	10	20	1022	21.2	182	1032	1790
45	10	20	1112	35.4	310	1230	1860
48	10	20	1202	50.1	340	1330	1930
52	10	20	1283	69.9	315	1365	2005

a) Vycor reactor.

b) Total heat sinks were calculated from experimental conversions and heat capacity and heat of reaction data.

TABLE 8
DEHYDROGENATION OF METHYLCYCLOHEXANE OVER CHROMIA ON ALUMINA

Product Distribution

Reaction time: 30 minutes

Run No. 8277-	29	31	40[a)]	32	65	43	45	48	52	52A[b)]
Temperature, °F	1022	1112	1112	1202	1293	1022	1112	1202	1283	1283
Pressure, atm	1	1	1	1	1	10	10	10	10	10
LHSV	5	5	5	5	20	20	20	20	20	20
Product Components, %										
Methyl-cyclohexane	59.0	38.8	44.4	29.7	18.7	78.8	64.6	49.9	30.1	39.4
Toluene	40.5	57.6	56.0	60.5	54.2	16.7	32.6	134.2	27.5	8.0
Benzene	0.1	0.9	0.7	3.5	5.5	0.1	0.4	2.3	6.1	4.8
1-Methyl-cyclohexene	0.8	0.6	0.5	0.7	1.0	1.2	1.3	1.5	1.1	2.8
3-Methyl-cyclohexene	-	-	-	-	0.2	-	-	-	1.1	3.1
4-Methyl-cyclohexene	0.9	1.1	1.0	1.4	0.9	1.2	1.3	1.8	1.5	2.3
Cracked	0.1	0.3	0.4	1.2	19.8	0.4	0.8	6.0	27.2	39.2

a) Vycor reactor.
b) After 90 minutes reaction time.

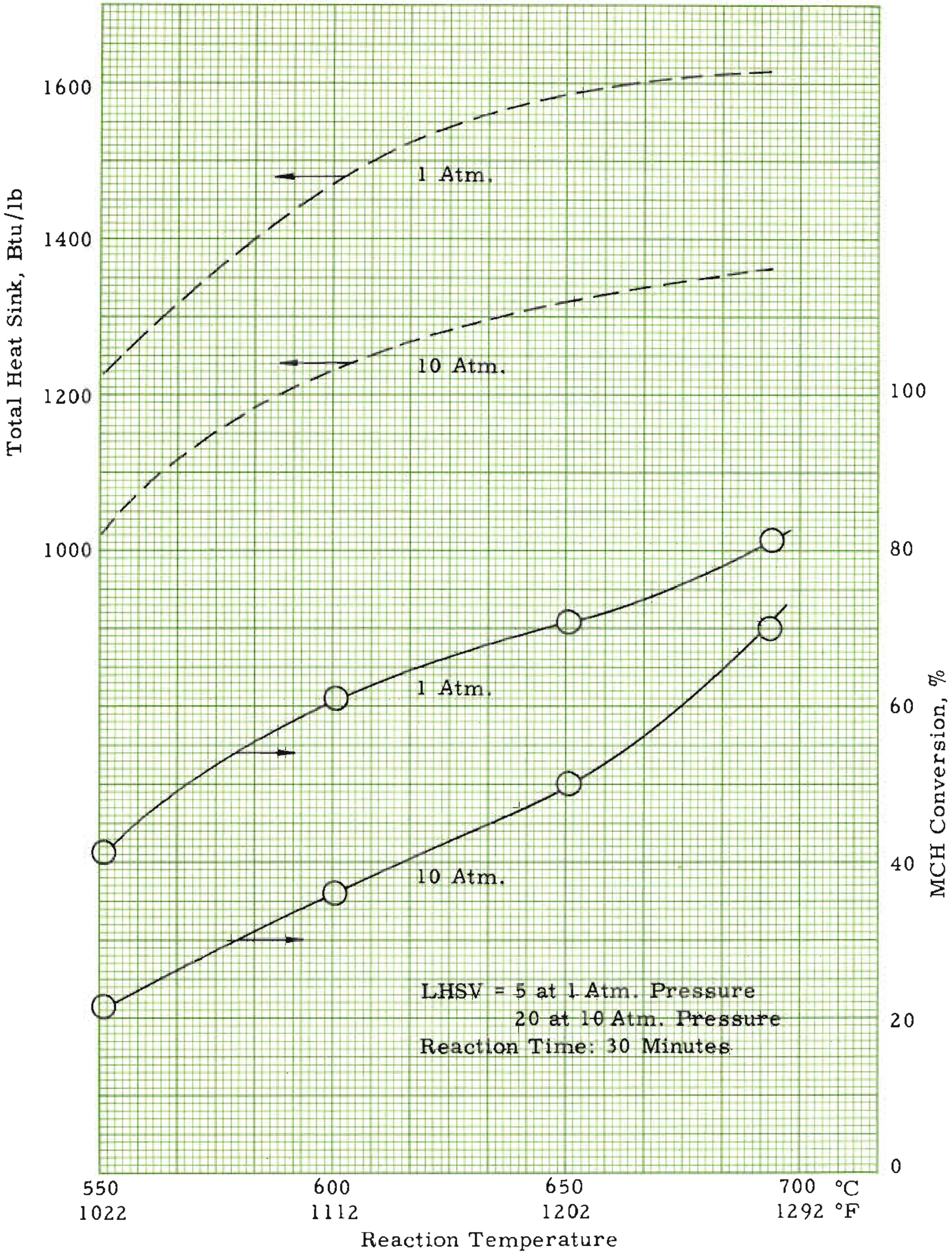


Figure 14. DEHYDROGENATION OF METHYLCYCLOHEXANE OVER CHROMIA ON ALUMINA CATALYST

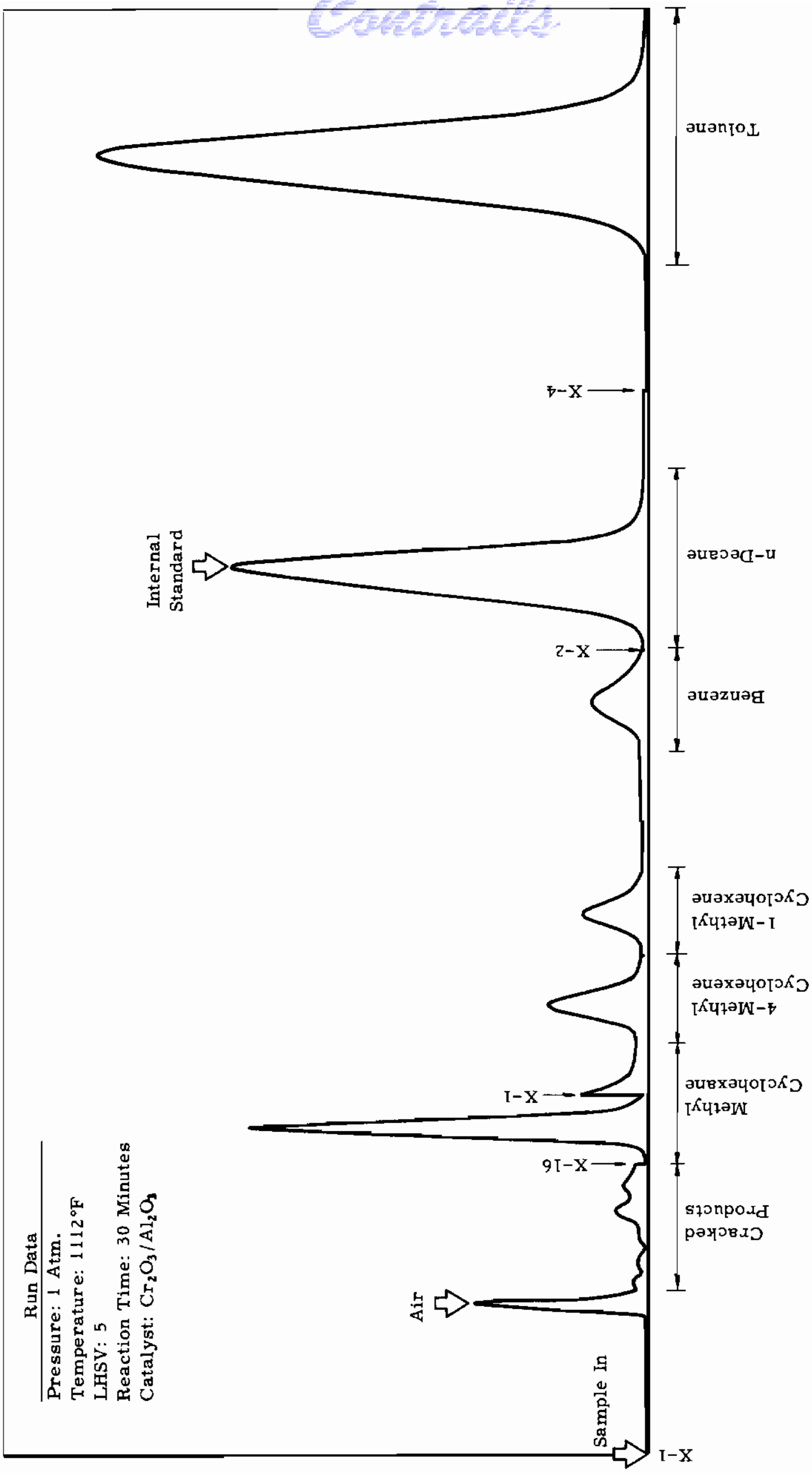


Figure 15. GLC CURVE PRODUCT ANALYSIS OF RUN 8277-40-1
Dehydrogenation of Methylcyclohexane

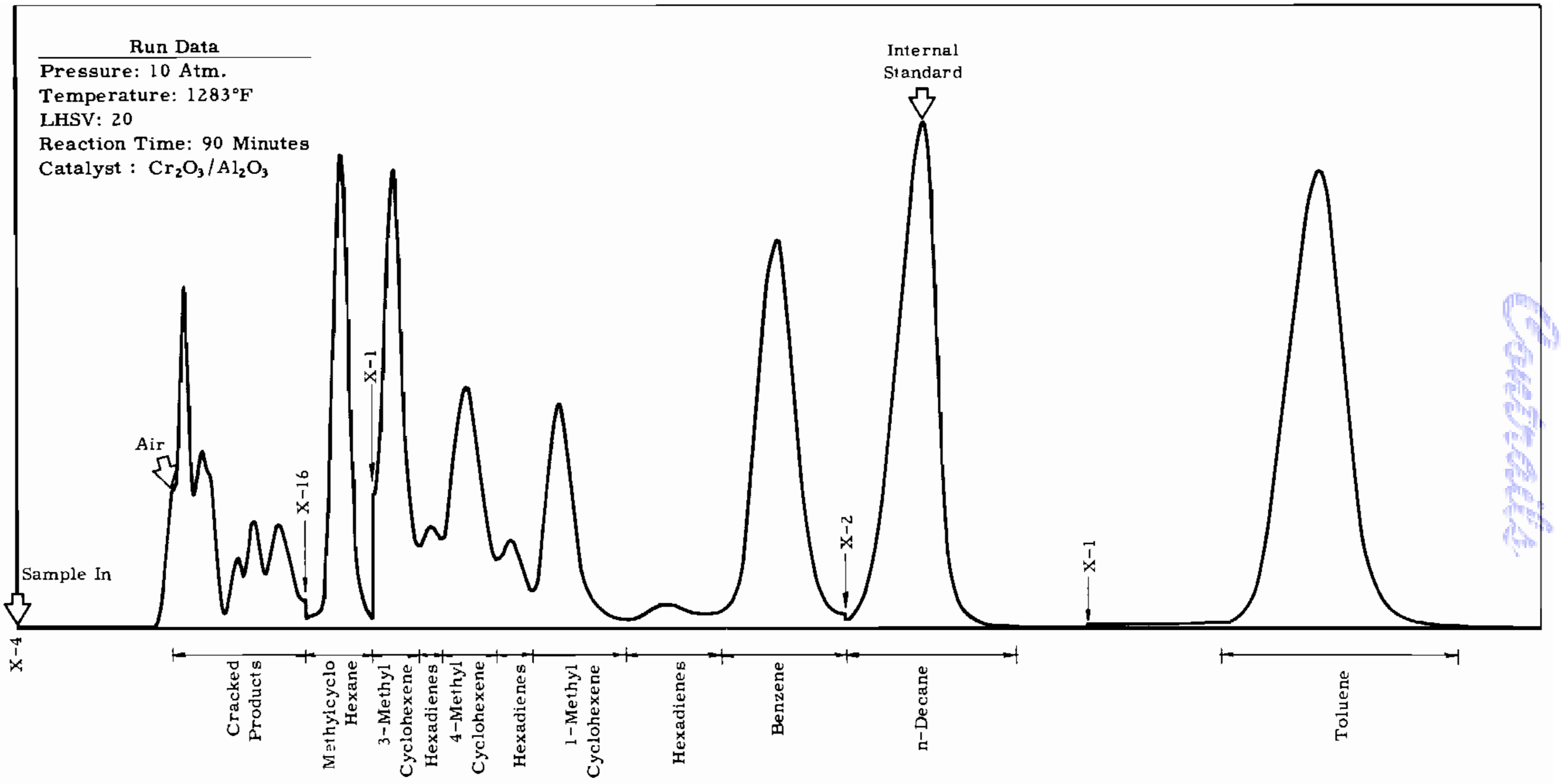


Figure 16. GLC CURVE PRODUCT ANALYSIS OF RUN 8277-53-1
Dehydrogenation of Methylcyclohexane

TABLE 9
DEHYDROGENATION OF ETHYLCYCLOHEXANE OVER PLATINUM ON ALUMINA CATALYST

Catalyst:	1% Pt on Al_2O_3
Pressure:	10 atm
LHSV:	20
Block temperature:	1202°F

Run No. 8277-	85	
Reaction time, min	30	90
Catalyst temperature, °F	1116	1122
<u>Product Analysis, %</u>		
Ethylcyclohexane	40.9	45.3
Ethylcyclohexene	0.6	0.6
Benzene	5.8	4.6
Toluene	3.5	2.5
Xylene	1.7	1.6
Ethylbenzene	7.4	4.0
Styrene	0.4	0.2
Cracked products	39.7 a)	41.2 b)
Ethylcyclohexane conversion, %	59.1	54.7
<u>Heat Sink, Btu/lb</u>		
Reaction	66	17
Total	955	906

a) Cracked products were 45.0% liquid, 55.0% light gas.

b) Cracked products were 56.7% liquid, 43.3% light gas.

Dehydrogenation of Propane

With the dehydrogenation of propane reaction (chromia on alumina catalyst) at 1202°F and 1 atm pressure, a total heat sink of 1580 Btu/lb of hydrocarbon was obtained, of which the catalytic reaction contributed about 29%. This heat sink was 85% of theory[a)] and was the highest obtained thus far from this reaction. Higher heat sinks are possible at higher temperatures but catalyst stability will be poor, presumably because of catalyst coking. Indeed, at 1202°F a 30% decline in catalyst activity over the 90-minute process period was observed. In a similar reaction period at 1112°F only an 11% decline in activity was observed. At this lower temperature a heat sink of 1510 Btu/lb was obtained (93% of theory). The reaction was quite selective with selectivities for propylene of 89% and higher being observed. The data for conversions, propylene selectivities and coke formed at various temperatures, pressures and space velocities[b)] are tabulated in Table 10. The corresponding heat sinks generated are presented in Table 11. The data are further summarized in Figure 17, which shows conversion and heat sink generated as a function of space velocity at several temperatures. In this figure the solid lines and circle points refer to conversion; the broken line and square point refers to the heat sink.

With increased pressure lower heat sinks were obtained primarily due to equilibrium limitations on the dehydrogenation reaction (Figure 28, Appendix). Thus, at 10 atm pressure, 1202°F and LHSV 20, a total heat sink of only 1343 Btu/lb was observed which was 93% of theory (Table 11). At this temperature catalyst activity declined by about 35% during the 90-minute process period (Table 10). At 1112°F a still lower heat sink of 1211 Btu/lb was obtained (95% of theory). However, at this temperature the catalyst stability was good with only a 5% decline in catalyst activity during the 90-minute process period (Table 10). The effect of pressure on propane conversion and heat sink generated at constant temperature and contact time is shown by Figure 18. In this figure, the solid lines show experimental conversions and corresponding heat sinks at 1112°F and 0.75-second contact time. The dotted lines are the corresponding equilibrium values. Also shown are the points for 1112°F, LHSV = 20, and for 1202°F, LHSV = 20 (triangles; open and shaded diamonds).

Reaction products from the dehydrogenation reaction were mainly propylene and hydrogen. At comparable conversions increased pressure gave more cracked products and more coke. Typical product analyses are shown in Table 12.

The used catalyst was completely regenerable by treatment with 5% oxygen in argon at 1022°F. These results show that in order to obtain heat sinks of 1500 Btu/lb or greater from the dehydrogenation of propane reaction, the reaction must be carried out at 1202°F or higher. Thus, a catalyst with less coke-forming properties than our standard chromia catalyst must be developed. This is discussed in greater detail in the section on "Coke Formation".

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a) Based on thermodynamically possible value.

b) Space velocity = liquid hourly space velocity = LHSV. This is the number of volumes of liquid feed per hour per volume of catalyst.

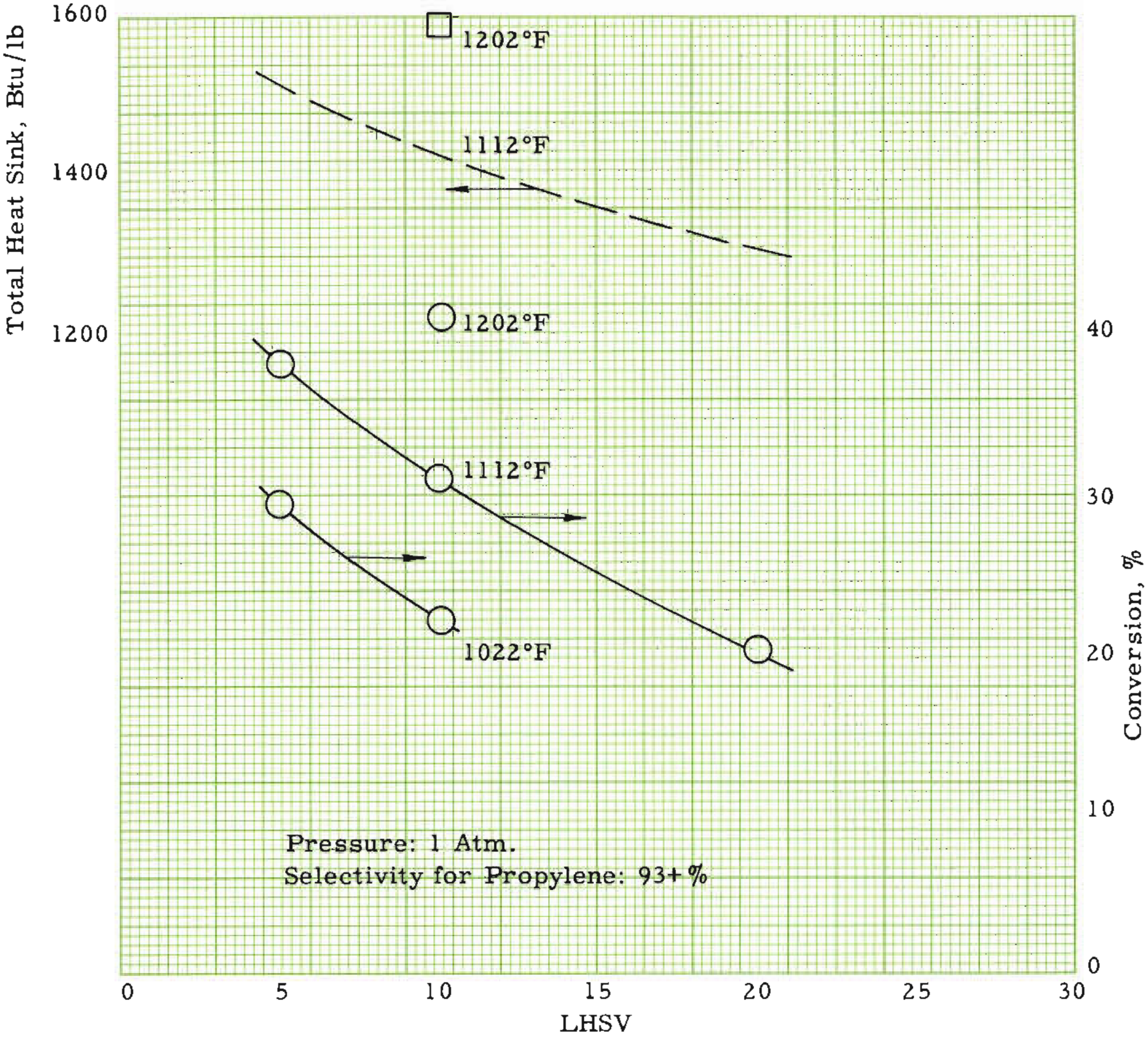

Figure 17. DEHYDROGENATION OF PROPANE AS A FUNCTION OF SPACE VELOCITY

TABLE 10
DEHYDROGENATIONS OF PROPANE OVER CHROMIA ON ALUMINA CATALYST

Catalyst: 2% K_2O, 8% Cr_2O_3, 90% Al_2O_3
Catalyst Weight: 13.3 ± 0.2 g
Catalyst Volume: 20 ml
Feed: Pure propane

Run No. 8219-	Press., atm	LHSV	Contact Time, sec	Block Temp, °F	Catalyst Bed Temp, °F			Propane Conversion, %			Selectivity for Propylene, %			Propane Converted to Coke, %
					30 min	60 min	90 min	30 min	60 min	90 min	30 min	60 min	90 min	
Stainless Steel Reactor														
92[b]	1	5	0.79	1022	968	970	972	28.5	27.5	25.6	94.5	94.5	95.0	0.2
93[b]	1	10	0.40	1022	946	944	948	22.1	20.6	19.5	94.0	97.7	97.6	0.1
59[a]	1	10	0.40	1022	928	932	937	22.5	21.5	21.0	94.5	94.4	94.1	0.7
94[b]	1	5	0.75	1112	1044	1047	1048	37.7	35.5	33.5	93.5	93.4	97.2	1.0
101[b]	1	10	0.38	1112	1002	1033	1034	30.6	26.0	23.6	94.7	95.2	92.0	0.9
61[b]	1	20	0.19	1112	977	982	988	19.0	17.5	17.0	98.7	98.7	96.5	0.1
105[a]	1	10	0.35	1202	1085	1105	1125	41.5	33.9	29.0[c]	89.0	85.4	75.8[c]	1.7
62[b]	1	20	0.18	1202	1035	1053	-	27.0[d]	25.5[e]	-	89.5[d]	80.0[e]	-	2.1
Vycor Reactor														
131[a]	1	20	0.19	1112	977	990	997	20.6	18.5	16.5	97.7	96.2	97.2	0.0
Elevated Pressure; Stainless Steel Reactor														
94[b]	1	5	0.75	1112	1044	1047	1048	37.7	35.5	33.5	93.5	93.4	97.2	1.0
144[a]	4	20	0.75	1112	979	986	990	19.9	18.0	17.0	90.9	94.0	93.1	0.5
145[b]	6	30	0.75	1112	1009	1017	1019	9.3	9.3	7.8	91.9	89.4	93.1	0.4
148[b]	8	40	0.75	1112	981	985	989	10.1	10.0	9.7	95.6	95.5	94.5	0.3
151[a]	10	50	0.75	1112	939	943	-	8.2	8.0	-	93.4	94.5	-	0.6
153[a]	10	20	1.87	1112	1000	998	998	15.7	15.0	14.8	76.2	80.9	81.8	1.0
155[a]	10	20	1.77	1202	1092	1101	1112	24.6	20.1	16.0	73.0	73.5	68.6	0.4
158[a]	10	50	0.71	1202	1033	1033	-	12.9	12.5	-	90.5	88.9	-	0.0

a) Fresh catalyst.
b) Regenerated catalyst.
c) Pressure = 20 psig.
d) Pressure = 25 psig.
e) Pressure = 65 psig.

TABLE 11
HEAT SINKS GENERATED FROM DEHYDROGENATION OF PROPANE

Run No. 8219-	Press., atm	LHSV	Block Temp, °F	Propane Conv., %		Heat Sink, Btu/lb		
				Exp	Equil.	From Catalytic Reaction, Exp	Total Exp	Total Equil.
92	1	5	1022	28.5	29	339	1339	1365
93	1	10	1022	22.1	29	262	1262	1365
94	1	5	1112	37.7	43	444	1504	1640
101	1	10	1112	30.6	43	365	1425	1640
61	1	20	1112	19.0	43	236	1296	1640
105	1	10	1202	41.5	60	466	1583	1873
144	4	20	1112	19.9	26	228	1288	1375
145	6	30	1112	9.3	22	108	1168	1337
148	8	40	1112	10.1	19	122	1182	1299
151	10	50	1112	8.2	17	95	1155	1274
153	10	20	1112	15.7	17	151	1211	1274
155	10	20	1202	24.6	26.5	226	1343	1441

TABLE 12
DEHYDROGENATION OF PROPANE

Product Distribution

Temperature: 1112°F
LHSV: 20

Run No.	8219-61	8219-153
Pressure, atm	1	10
Product Components, %		
H_2	16.2	16.2
CH_4	0.4	2.3
C_2H_4	-	0.1
C_2H_6	0.1	1.8
C_3H_6	15.8	9.9
C_3H_8	67.6	69.7

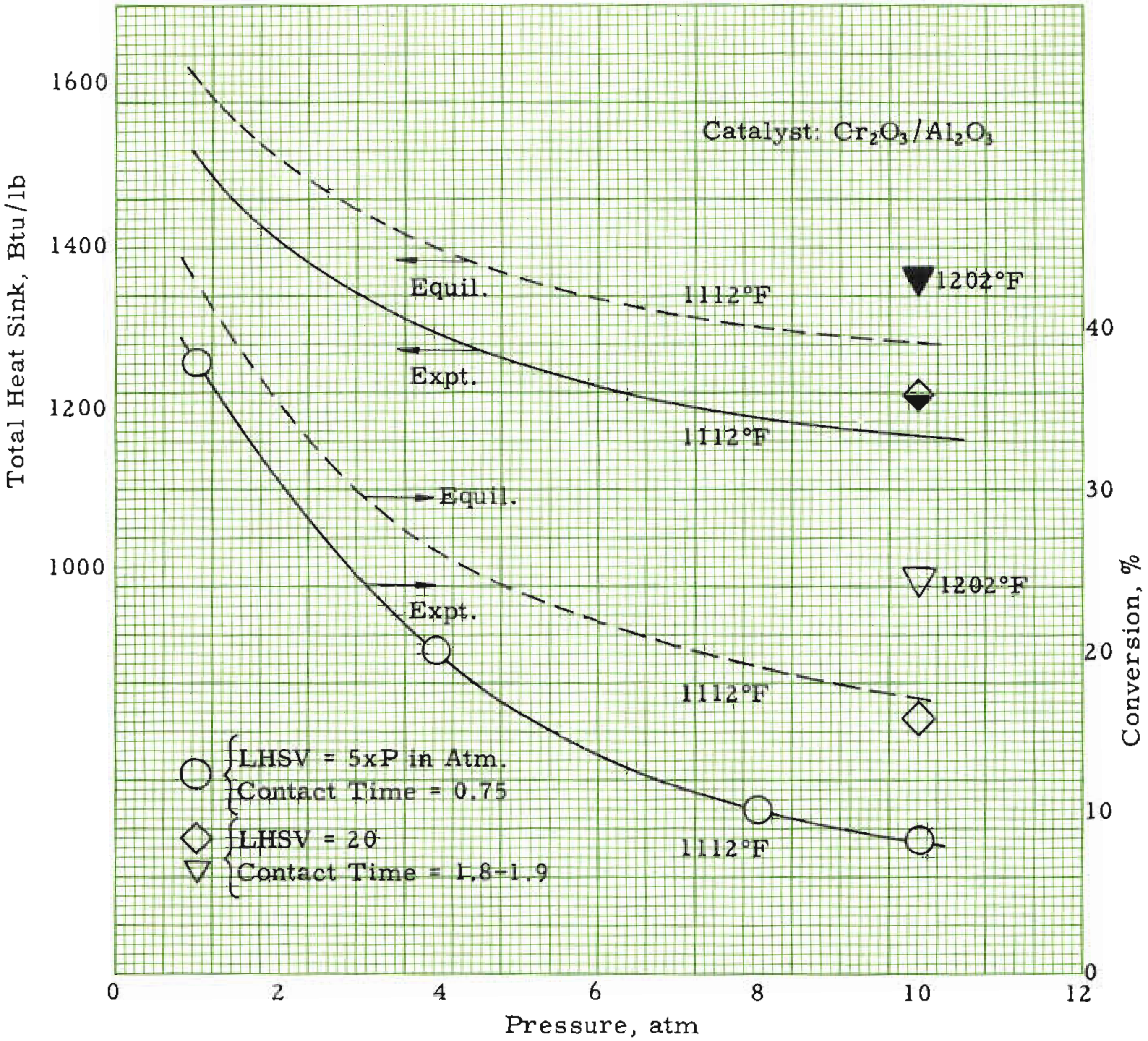

Figure 18. DEHYDROGENATION OF PROPANE AS A FUNCTION OF PRESSURE

Coke Formation

Coke formation on the catalyst is one of the main factors that limits the usefulness of the propane dehydrogenation reaction. For example, considerably greater heat sinks would be obtained if the propane dehydrogenation could be carried out at 1283°F where at equilibrium conversion the heat sink generated is 1607 Btu/lb. With the present catalyst this is not possible due to rapid coke deposition at the higher temperatures. With an aim toward elucidating the mechanism of coke formation a brief study was carried out to determine possible coke precursors.

In the metal reactor coke was deposited not only on the catalyst bed but also on the walls of the reactor and on the metal spacers just below the catalyst bed. Independent experiments, however, had shown that both propane and propylene were thermally stable in the metal reactor as well as in the Vycor reactor under comparable conditions (1112°F, 1 atm, LHSV = 20; Table 13). This suggested that coke was being formed from thermally unstable propylene reaction products. The view that propylene reacts further over the catalyst to form coke was also supported by the observation that the catalyst regeneration periods were 5-10 times longer when the catalyst was contacted with propylene than when contacted with propane (Table 14).

The most logical secondary reaction products from propylene appeared to be allene or methylacetylene. Indeed, when mixtures of 5 or 10% allene in argon were passed through the metal reactor at 1112°F with no catalyst present, conversion of allene to coke and cracked products was almost 100% (Table 15). Under the same conditions in the Vycor reactor allene appeared to polymerize to a yellow-green liquid that collected in the cool part of the tube (Table 15). A similar polymer deposit was observed in lesser amounts when propane or propylene was passed over the chromia catalyst in the Vycor reactor (Table 14). In the Vycor reactor coke was observed only on the catalyst particles.

Thus, it appears that one main source of coking in the propane dehydrogenation reaction is from secondary propylene dehydrogenation products, presumably allene or methylacetylene. These products form polymers that are unstable on both the catalyst and the stainless steel in the reactor. This suggests that less coking might be obtained by using a catalyst that contains very large pores.[a] Further, it is quite possible that coking may occur primarily on sites of high surface energy where propane is held very tightly to the surface until it reacts to form allene. Thus, reduced coke formation might be achieved by moderating the catalyst surface with promoters to eliminate the high energy sites, or by addition of small amounts of foreign material in the feed that would preferentially adsorb on sites of highest energy. The checking of these possibilities would require a considerable catalyst development program. Another important aspect which would have to be investigated is the effect of reactor material on coke formation - stainless steel promotes coke formation, Vycor does not.

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a) It has been shown by Wheeler[15] (p. 317) that for consecutive reactions of the type A ⟶ B ⟶ C the selectivity for the intermediate B will be greater with catalysts with larger pores.

TABLE 13
THERMAL REACTION OF PROPANE AND PROPYLENE IN THE VYCOR REACTOR

Pressure:	1 atm
Feed:	Pure propane
Reaction Time:	20 min

Run No. 8219-	Feed	Block Temperature, °F	LHSV	Propane Conversion, %
127	Propane	1112	5	1.1
	"	1112	10	0.7
	"	1112	20	0.0
128	"	1202	5	6.1
	"	1202	10	4.4
	"	1202	20	2.6
129	"	1283	5	25.5
	"	1283	10	17.0
	"	1283	20	9.5
124	Propylene	1112	5	0
	"	1112	10	0
	"	1112	20	0
	"	1202	5	0.5
	"	1202	10	0
	"	1202	20	0
	"	1283	5	1.1
	"	1283	10	0.6
	"	1283	20	0.1

TABLE 14
REACTION OF PROPANE, PROPYLENE AND ALLENE OVER CHROMIA ON ALUMINA CATALYST

Temperature: 1112°F
Pressure: 1 atm
LHSV: 20

Run No. 8219-	Feed	GHSV	Reaction Time, min	Catalyst Temp, °F	Feed Conv., %	Reaction Products	Regeneration Time, min
			Vycor Reactor				
131	propane	5960	90	977	20.6	97.7% propylene[a)] 2.3% cracked products	65
132	propylene	5960	90	1108	0.6	cracked products[a)]	600
135	5% allene in argon	1500	30	1114	100	68% to coke or polymer[a)] 32% to cracked products	127
136	10% allene in argon	1500	30	1175	100	66% to coke or polymer 34% to cracked products[a)]	-
			Metal Reactor				
61	propane	5960	90	982	19.0-17.0	96-98% propylene 4-2% cracked products	105
108	propylene	5960	90	1090	1	Coke plus cracked products	510

a) Considerable polymeric material collected in cool part of tube with allene feed. Polymer in lesser amounts was also observed with propylene and propane feeds.

TABLE 15
THERMAL REACTION OF ALLENE

Pressure: 1 atm
GHSV: 1500
Feed: Allene in argon

Run No. 8219-	Reaction Time, min	Block Temp, °F	Catalyst Temp, °F	% Allene in Feed	Allene Conv., %	Reaction Products
			Stainless Steel Reactor			
113	30	1022	1035	5	89.7	Coke and cracked material
	30	1022	1036	10	95.6	" " "
	30	1112	1125	5	100	" " "
			Vycor Reactor			
116	20	1022	1024	5	14.0	Polymer plus coke
	20	1022	1024	10	23.5	" " "
	20	1112	1123	5	10.2	" " "
	20	1112	1117	10	22.8	" " "
	20	1202	1207	5	20.0	" " "
	20	1202	-	10	36.0	" " "
	20	1202	-	10	23.0	" " "
	20	1202	-	5	26.0	" " "
	20	1202	-	10	44.0	" " "

Thermal Cracking of Propane

The extent of the non-catalytic thermal decomposition of propane at 1 atm pressure, 850-1290°F and LHSV of 1 to 40 was determined with quartz chips (20-ml volume; 10-20 mesh) substituted for catalyst. At an LHSV of 1 essentially no propane conversion was observed at 1074°F or lower, but at 1282°F about 33% was converted to cracked products. At LHSV of 20 propane conversions of about 0.5% or less were observed at 1157°F and about 3.5% at 1274°F. The data are recorded in Table 16, and Figure 19 is a plot of conversion as a function of temperature for various space velocities. The decomposition products were mainly propylene, ethylene and methane (Table 17).

Effect of Added Oxygen

In the thermal cracking of hydrocarbons it has been observed by other researchers[27)] that addition of small amounts of oxygen to the feed gave appreciable increase in the rate of thermal cracking. Accordingly, a propane feed containing 1% oxygen (feed: 95% C_3H_8, 0.95% O_2, 4.05% Ar, C_3H_8/O_2 = 100) was passed through the reactor at 1 atm pressure (1202-1283°F at an LHSV of 20). In the Vycor reactor at 1283°F the extent of thermal cracking of propane with 1% oxygen added was about 3.6 times greater than with no oxygen present (Table 18). This corresponded to a total heat sink of 1459 Btu/lb of propane. In the metal reactor no appreciable increase was observed at 1283°F with the oxygen-containing feed. It is probable that in the metal reactor most of the oxygen had reacted with the metal reactor before being mixed with the hydrocarbon. These results are encouraging and further study of the effect of oxygen on the rate of thermal cracking of hydrocarbons will be done in the future.

Dehydrogenation of Higher Paraffinic Hydrocarbons

Appreciable endothermic heats of reaction are possible when cyclization accompanies the dehydrogenation reaction. Even greater heats are obtained when the side chains on the cyclized products are also dehydrogenated. As noted above (Table 1) the dehydrocyclization of n-octane to ethylbenzene absorbs 940 Btu/lb while if the product is further dehydrogenated to styrene a 50% greater heat sink (1440 Btu/lb) is obtained. We have made a very brief study of seven different paraffins over the chromia on alumina catalyst with each feed and over the Pt on Al_2O_3 catalyst with n-heptane at elevated space velocities (8.7 - 22), at 10 atm pressure and in the absence of hydrogen (most of the literature data is at low space velocities and with hydrogen). Both normal and branched paraffins in the C_7-C_{16} region were tested. The results for 30-minutes reaction time are given in Table 19. The complete data are tabulated in Tables 30-36, Appendix. Data for thermal reaction is also included in these latter tables.

In general, none of these hydrocarbons gave over 25% selectivity to aromatics (30-90% conversion). As a result heats of reaction and total heat sinks/lb of feed ranged from fair to poor. Cracking appeared to be the main reaction with enhanced cracking being observed with increasing carbon number. The effect of branching on paraffin reactivity was not clearly evident from

TABLE 16
THERMAL DECOMPOSITION OF PROPANE

Pressure:	1 atm
Catalyst:	quartz chips; 10-20 mesh
Catalyst volume:	20 ml

Reaction Temperature, °F	LHSV	Propane Conversion, %	Propylene in Product, %	Specific Rate[a)] Constant, K, sec^{-1}
855	1	0.0	0.0	
855	5	0.0	0.0	
940	1	0.0	0.0	
940	5	0.0	0.0	
1036	1	0.0	0.0	
1030	10	0.0	0.0	
1130	1	0.9	0.9	
1130	5	0.2	0.2	
1125	10	0.2	0.2	
1220	1	10.0	4.7	0.029
1216	5	2.5	1.6	
1206	10	1.3	0.9	
1266	20	0.4	0.3	
1290	1	33.2	10.0	0.126
1280	5	12.2	4.7	0.192
1290	10	6.5	3.0	0.132
1265	20	3.5	2.4	
1260	30	3.2	1.4	
1240	40	3.0	1.7	

a) Assuming a first order reaction and using the apparent contact time within the quartz chips bed.

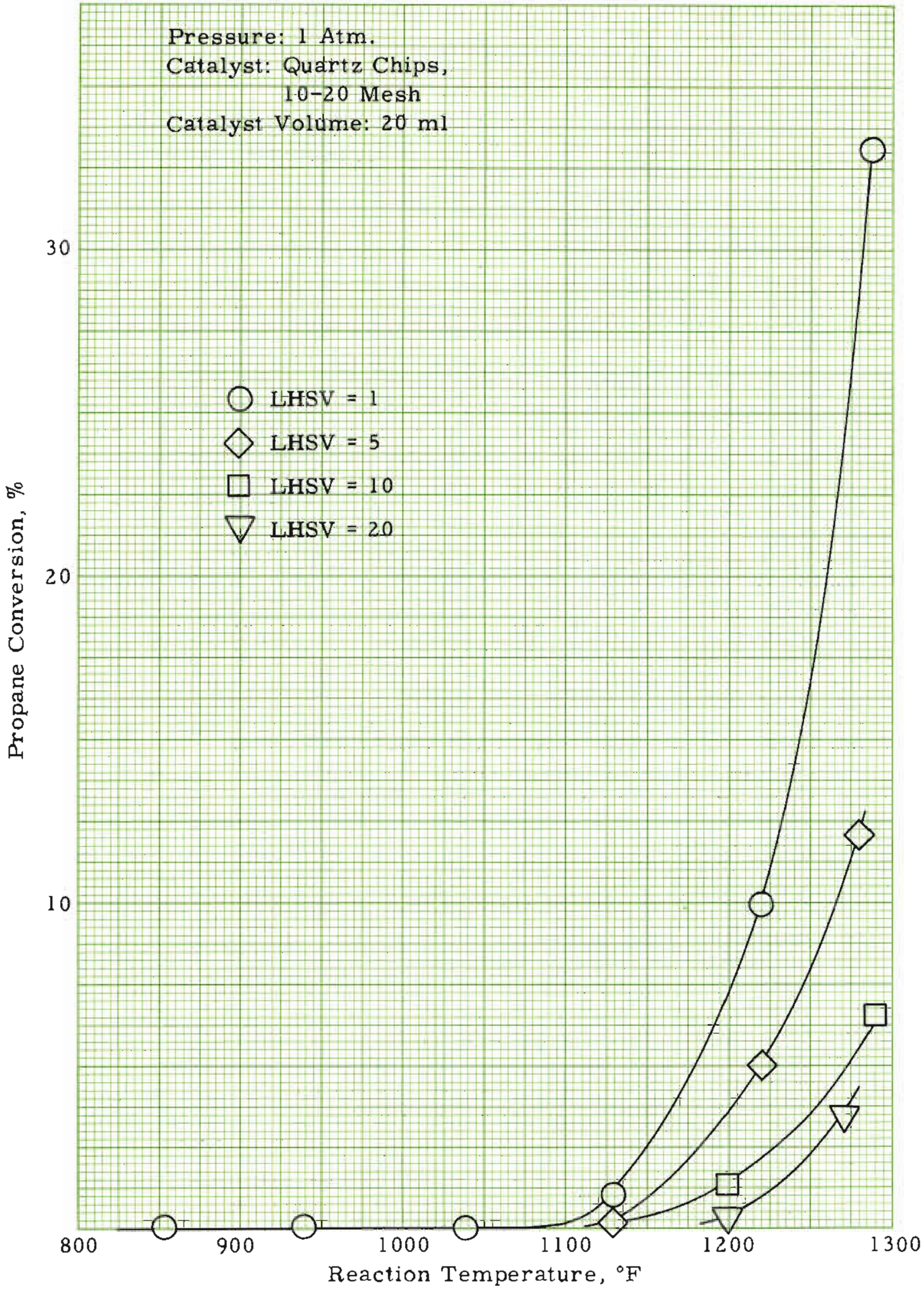

Figure 19. DEHYDROGENATION OF PROPANE
Test of Thermal Reaction

TABLE 17
THERMAL DECOMPOSITION OF PROPANE
REACTION PRODUCTS

Pressure:	1 atm
Catalyst:	quartz chips; 10-20 mesh
Catalyst Volume:	20 ml

	%m LHSV = 1 1284°F	%m LHSV = 20 1265°F
Methane	13.4	1.4
Ethane	1.1	-
Ethylene	10.3	0.1
Propane	54.8	79.5
Propylene	9.6	2.0
Hydrogen	1.9	1.3
Argon[b)]	6.7	13.0
N_2 + CO[a)]	1.9	1.9
i-Butane[a)]	-	0.2
Carbon dioxide[a)]	-	0.4

---

a) Present as impurity in propane feed.
b) Present in propane feed.

TABLE 18
THERMAL CRACKING OF PROPANE

Effect of Oxygen

Pressure:	1 atm
Reaction Time:	20 min
LHSV:	20

Run No. 8219-	Reaction Temp, °F	% O_2 in Feed	Propane Conv., %
Metal Reactor			
40	1206	0	0.4
	1265	0	3.5
160	1202	0.95	2.6
	1283	0.95	4.6
Vycor Reactor			
128	1202	0	2.6
	1283	0	9.5
162	1202	0.95	12.6
	1283	0.95	34.0

Product Distribution

Run No.	8219-162		8219-128	
Temperature, °F	1202	1283	1202	1283
% O_2 in Feed	0.95	0.95	0	0
Products Formed, %				
H_2	4.1	7.6	1.7	4.4
CH_4	4.9	8.9	1.5	4.6
C_2H_4	4.9	8.8	-	2.3
C_2H_6	-	0.5	-	0.3
C_3H_6	4.4	7.7	2.0	4.5
C_3H_8	81.9	66.5	94.8	83.7

TABLE 19
DEHYDROGENATION OF PARAFFINS OVER CHROMIA ON ALUMINA AND PLATINUM ON ALUMINA CATALYSTS

Pressure: 10 atm
Reaction Period: 30 minutes

Catalyst	Hydrocarbon	Block Temp, °F	LHSV	Conv., %	Catalyst Temp, °F	Selectivity for, %				Heat Sink, Btu/lb	
						Olefin	Diolefins	Aromatics	Cracked	Reaction	Total
Cr_2O_3/Al_2O_3[a]	n-Heptane	1112	20	31.0	973	34.8	4.5	18.1	38.7	553	1391
		1202	20	49.4	1065	11.1	3.2	10.7	68.4	413	1330
Cr_2O_3/Al_2O_3[a]	n-Octane	1202	22	53.3	1049	5.0	1.0	4.7	92.4	236	1151
Cr_2O_3/Al_2O_3[a]	i-Octane	1202	20	52.2	1096	3.1	2.1	3.7	90.1	-30	880
Cr_2O_3/Al_2O_3[a]	Mixed dimethylhexane	1112	20	42.2	972	22.2	3.0	24.9	49.0	105	940
Cr_2O_3/Al_2O_3[a]	2,2,5-Trimethylhexane	1112	20	32.8	997	15.3	2.4	13.3	74.9	-65	760
Cr_2O_3/Al_2O_3[a]	n-Dodecane	1112	20	61.2	957	9.5	4.1	5.9	81.0	2	685
Cr_2O_3/Al_2O_3[a]	n-Hexadecane	1112	8.7	92.0	1065	1.5	-	-	98.5	120	945
Pt on Al_2O_3[b]	n-Heptane	1112	22	27.4	1027	13.9	2.2	9.5	73.2	369	1207

a) 2% K_2O, 8% Cr_2O_3 on Al_2O_3.
b) 1% Pt on Al_2O_3.

the results of our experiments. In the case of n- and iso-octane (at 1112°F), the extent of reaction and the product distributions were practically the same. With n-heptane the principal aromatic product was toluene, while the mixed dimethylhexanes and the trimethylhexane gave principally meta- and para-xylenes. With n-heptane the platinum catalyst was less active and more selective for cracking than the chromia catalyst. The dimethylhexanes gave the greatest yield of aromatics. Dodecane gave mainly hexylbenzene aromatics. In the region of our study the reactivities of the various hydrocarbons appeared to increase with increasing carbon number.

Of the higher paraffins surveyed over the chromia on alumina catalyst, none appeared to give sufficiently encouraging product distributions to warrant further study with this catalyst. The cracking reaction appears to be a concurrent reaction, hence greater selectivites to the desired products may be possible with a more active catalyst that can be used at a lower temperature, assuming that the heat of activation is greater for cracking than for dehydrogenation.

Recapitulation

The prime objective of the present investigation is to develop reaction systems which will provide the highest heat sink at the lowest temperature and at the highest pressure in the shortest contact time. In order for a catalytic system to be superior to a thermal reaction the total heat sink should be above 1200 Btu/lb, the temperature preferably not above 1200°F, and the space velocity greater than 20 at a pressure of at least 10 atm. Not all these requirements can necessarily be achieved simultaneously - it may be practical to trade one consideration for another.

The dehydrogenation of methylcyclohexane to toluene and hydrogen over platinum on alumina catalysts appears to satisfy the above requirements. At 10 atm pressure and LHSV of 50 endothermic heats of reaction of almost 900 Btu/lb were obtained experimentally with this catalyst. This corresponds to total heat sinks of over 1800 and 2000 Btu/lb when the temperatures of the final products are 1112°F and 1340°F, respectively. With improved reactor design it appears that these heat sinks could be obtained at LHSV greater than 50. Catalyst stability appeared good over a 90-minute process period but should be determined for at least four to five-hour periods. For this reaction the rate of thermal reaction became appreciable above 1112°F at 10 atm pressure. Hence, it does not appear that presently available metal oxide catalysts will be suitable for use under our operating conditions due to their low intrinsic activities.

For the dehydrogenation of propane to be attractive at 10 atm pressure, the reaction would have to be carried out at 1283°F where the heat sink under equilibrium conversion is 1602 Btu/lb. To achieve this it would be necessary to moderate the chromia catalyst to reduce its coke forming properties. The adverse effect of pressure on equilibrium makes this reaction more attractive for use with engines of combustion chamber pressures of 1 atm or less, such as hypersonic ramjets. However, even for 1 atm pressure operation a more active catalyst would be needed in order to obtain a heat sink of 1800 Btu/lb at an LHSV of 20 and greater.

Dehydrocyclization reactions have not shown promise as yet. It is possible that a catalyst more active than the chromia catalyst could be developed that would promote reactions such as the dehydrocyclization of n-octane to styrene. However, this would require a more intensive catalyst development program than is contemplated under the present contract.

Calculation of Reactor Temperature and Conversion Profiles

Experiments in the small-scale catalytic reactors have been limited to relatively short beds of catalyst and relatively low values of mass velocity (mass feed rate per unit of cross-sectional area of the bed). Under these conditions, even with reasonably high values of the ratio of heat transfer surface area to volume of bed, substantial differences between the temperature at the outer wall of the reactor and the temperature at its centerline have been observed. This radial temperature difference indicates that heat transfer from the tube wall to catalyst and the radial transport of heat within the bed are limiting its effectiveness as an absorber of heat from the surroundings. Radial temperature gradients also complicate the problem of predicting the performance of catalyst beds operated with more practical values of mass velocity or with different arrangements of catalyst within the bed.

To assist in interpreting and applying these results obtained in reactors which have severe temperature gradients in both axial and radial directions we are adapting an existing computer program for simulation and design of packed bed reactors. The program solves the partial differential equations describing flow in the axial direction, with chemical reaction, pressure drop, heat and mass transport radially, and heat transfer from the tube wall to the catalyst bed. The solution is accomplished by using finite-difference approximations to the differential equations. The program is capable of dealing with systems involving up to three independent chemical reactions and up to ten chemical components. For the design or simulation of a reactor, the significant input information required includes: the reaction kinetics, stoichiometry and heat of reaction, the heat capacities of components, inlet conditions of flow, composition, and temperature and reactor operating configuration (tube size, particle size, wall temperature, etc.). Pressure drop, heat transfer coefficient and radial diffusivities are calculated by standard correlations at each point within the reactor.

In our initial application of the program we are using a trial and error process to obtain an approximate description of the kinetics of the dehydrogenation of methyl cyclohexane over a platinum on alumina catalyst. This reaction system has been the subject of our most-detailed study in the small scale catalytic reactor system. Work on the computer simulation of these experiments has just been started. When an approximate rate expression for the reaction has been derived by this trial and error simulation, further calculations will be made to predict performance of the system at higher mass flow rates in longer reactor tubes to determine the limiting space velocities at which the reaction will give practical conversions.

Thermal and Storage Stability

Stability Problems

One of the spectres that has haunted the operators of jet propelled aircraft since the fuel was first utilized for cooling purposes is that of inadequate thermal stability. It has only been through the exercise of constant vigilence and the enforcement of rigorous specifications that the problem has been kept under control. As airplane speeds have increased the potential problems have become more serious; the Air Force has attempted to keep pace by increasing the severity of the thermal stability specifications and continuing research work on the causes, detection and prevention of thermal instability.

It may be confidently expected, as aircraft speeds are increased into the Mach 6 range, that thermal stability problems will become an order of magnitude more severe and that both chemical and mechanical methods will have to be employed to overcome them. Since it is expected that heat exchange surfaces will operate at all temperatures up to 1350°F, extensive opportunity will exist for reaction and deposition to occur.

Pending preliminary airframe and engine design and selection of the type of fuel to be used there is no way of predicting the severity of the thermal stability problems that will be encountered. However, it would seem permissible to extrapolate from JP-4 through JP-6 and the SST fuel to an expectation that these problems will be exceedingly serious and troublesome. At the moment we have no way of knowing at what location in the aircraft fuel storage and delivery system they will be most damaging. High molecular weight and metallic salt contaminants will deposit out in the region where vaporization occurs (if not before), thus interfering with system cooling. At the upper temperature anticipated for this aircraft the fuel could be heated into the super critical region and lower molecular weight contaminating oxidation products, gums, and metal chelates may be transported by the fuel into higher temperature regions to deposit on heat transfer surfaces, catalysts and engine fuel nozzles.

Stability Studies

A great deal of work has been done on this problem over the last decade. Reviews and assessments of this work have been collected in the Appendix together with statements as to the present status of the problem. It is obvious from these presentations that the thermal stability problem is far from being solved. An extensive effort is being sponsored by RTD, in house, through contracts and through the CRC, as well as being pursued independently by various aircraft and petroleum industry members. This is in part in connection with the SST program and partly arises from problems encountered with JP-6 fuel. Close contact is being maintained with this effort.

The studies which are being done under the present contract are for the purpose, mainly, of ensuring that the conclusions reached in other aspects of the work are not vitiated by poor stability, and for the purpose of assessing the stability properties of candidate fuels. For this purpose, chief reliance is being placed on the SD fuel coker, shown schematically in Figure 20 and photographically in Figure 21. This is essentially the design originally developed by Lusebrink and Sorem 16) 17) but has been modified by introducing a continuous supply of air into the fuel reservoir and coating the reservoir with black paint to avoid photochemical effects. In its present form (the M-6) this apparatus is capable of stressing fuels to a temperature of 950°F and operates normally on 125 to 150 ml of fuel. This latter feature is important when utilizing rare or specially purified fuels. Since it will be impossible to use aluminum as the sole heat exchange surface in the projected aircraft, the test apparatus will also use other metals such as stainless steel and titanium as preheater surfaces. This will enable the upper limit of fuel temperature to be raised into the 1300°F range. In some instances, fuels will be prestressed by heat soaking in an autoclave, in a similar manner to the Texaco method. 18) In some instances, results obtained with the SD/M-6 Fuel Coker will be cross-checked with results derived with the ASTM-CRC Coker and the model 02FC-381 Erdco high temperature coker.

When prototype fuels are available their performance in the fuel coker both before and after aging in the presence and absence of air will be tested. The effect of common contaminants, possible impurities and fuel additivies will also be determined. At the same time significant changes in other properties of the fuels, such as steam jet gum, chromatogum, GLC analysis, IR spectra, peroxide content, acid content, color, particulate matter, metal content, etc. will be ascertained as seems desirable.

Characteristics of High Temperature Cokers

The detailed features of the SD/M-6 and Erdco Cokers, their similarities and their differences are outlined in the Appendix. Included are the modifications which have been made on the Erdco coker, wherein it now differs from the original model 02FC-381 as purchased. Further modifications of both cokers may necessarily be made as our work progresses.

Fuel Testing Results

Much of our fuel testing until now has been to check and evaluate performance of the test equipment. These preliminary tests resulted in many of the modifications which have already been discussed, plus improvements in operating and cleaning procedures and precautions in fuel handling. Although some further modifications are yet planned, a satisfactory degree of test reproducibility and freedom from equipment contamination sources generally has been achieved, and attention is being turned to objective areas of investigation. These include the following:

a) Comparison of preheater tube and filter ratings of the M-6 and high temperature Erdco cokers at comparable temperature, pressures and fuel flows.

b) Rating of available jet fuels which represent presently high state of the art materials. These fuels serve as standardization materials

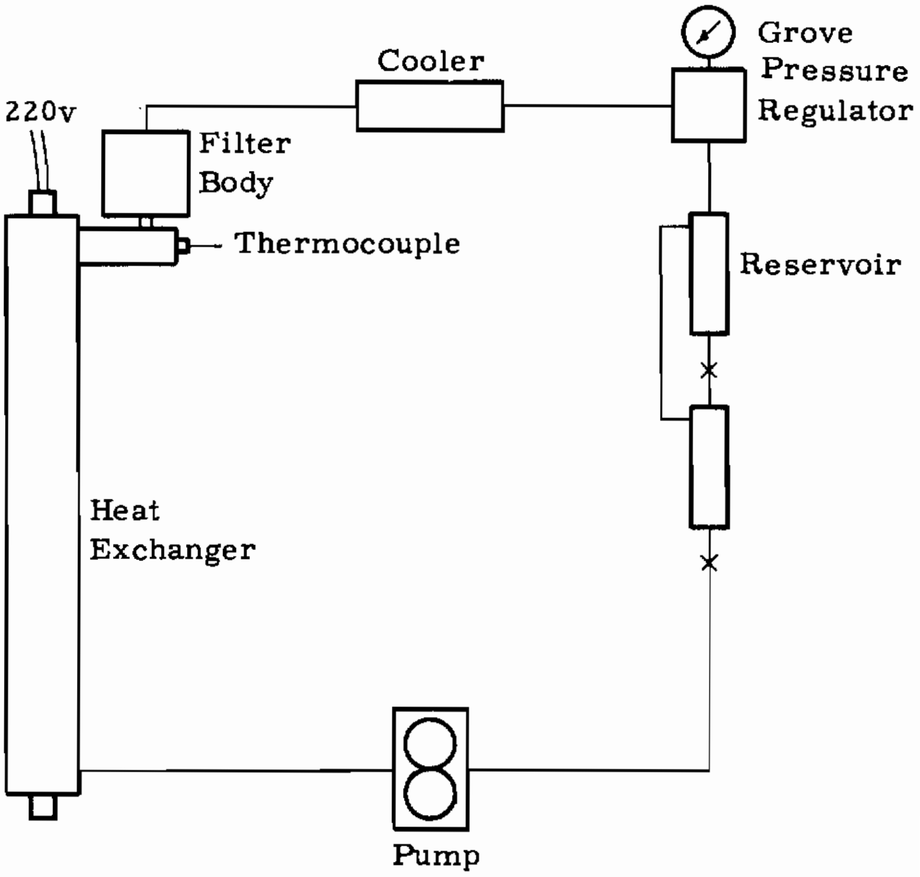

Figure 20. SCHEMATIC DIAGRAM OF SD/M-6 HIGH TEMPERATURE FUEL COKER

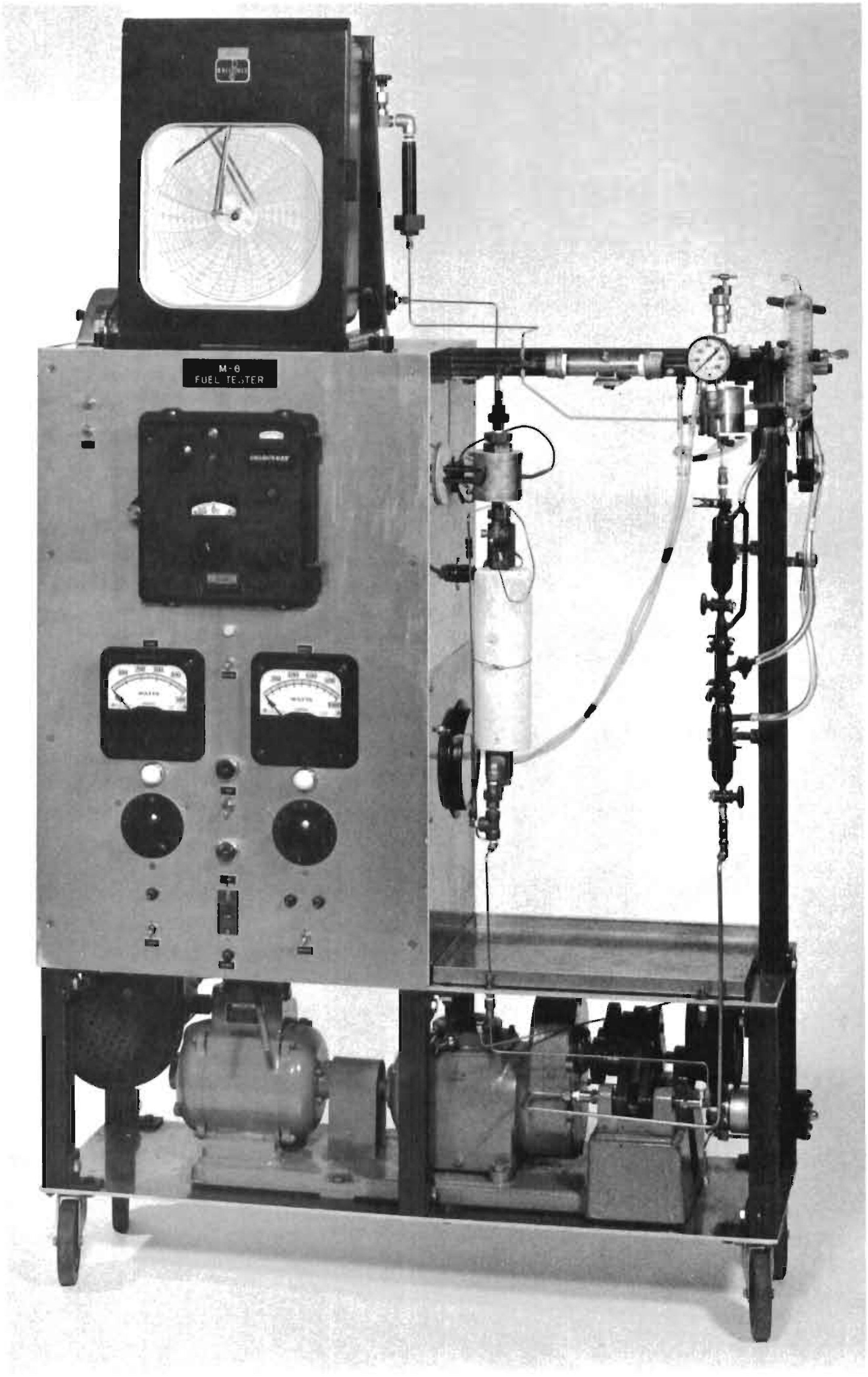

Figure 21. THE SD/M-6 HIGH TEMPERATURE FUEL COKER

for our coker equipment and also as possible feed stocks for our laboratory reaction studies.

c) Thermal stability evaluation of candidate fuels of high heat sink potential. These fuels will include those which will be or have already been subjected to endothermic reaction studies.

d) Investigations into methods for increasing the thermal stability of candidate endothermic jet fuels. For example, thermal stability of fuels will be assessed both with and without the presence of inhibitors and other additives. Also, special pretreatments and removal of troublesome components and contaminants will be looked into.

e) Additional fuels having potentially desirable thermal stability properties will also be tested. These will be mainly pure hydrocarbons whose structures appear promising based on our own thermal stability work and that available in the literature. Not all of these fuels will undergo endothermic catalytic reaction studies, but coker data should help in the prediction of fuels possessing both high thermal stability as well as high heat sink capacity.

Comparison of M-6 and Erdco Results

Comparative results between the Erdco and M-6 cokers are not yet conclusive, but do indicate trends. The majority of tests to date have been with the M-6 coker because of its simplicity and small sample requirements. An insufficient amount of matching Erdco data has been accumulated. However, results shown in Tables 20 and 21 are of interest. Possibly, there will be no consistent relationship between the two coker ratings for all fuels. For example, RAF-163-60a) (Table 20) jet fuel fails the M-6 coker test at 160 minutes (pressure drop across the test filter has reached 25-inches Hg) at temperatures of 450/500°Fb) and 150 psig; while at the same conditions, the filter pressure drop in the Erdco has reached only 0.55-inch Hg in 300 minutes. Clearly, in this instance the M-6 coker has rated the identical fuel more severely than the Erdco relative to filter plugging. The discharge zone of the Erdco preheater tube showed evidence of boiling and subsequent runs were made at 250 psig total pressure to ensure liquid phase at all times. Here the filter pressure drop was about the same (0.07-inch Hg) and repeated runs by both cokers confirmed that M-6 filter ratings were more severe than the Erdco ratings.

By contrast, the M-6 filter rating (2.6-inches Hg) of n-dodecane (Table 21) was not significantly different than that of the Erdco coker (0.95-inch Hg) when each coker was operated for 300 minutes at temperatures of 450/500°F and 150 psig pressure.

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a) RAF-163-60 consisted of 10% paraffins and 90% naphthenes.
b) 450/500°F refers to 450°F temperature of fuel at the discharge end of the preheater and 500°F in the filter.

TABLE 20
M-6/SD AND ERDCO COKER RATINGS OF RAF-163-60a) JET FUEL

10% paraffins;
90% naphthenes

Coker Rating Method	Total Time of Test, minb)	Temp, °Fc)	Total Press., psig	Preheater Tube Ratingd)	Highest Filter Pressure Drop, in. Hgb)	Physical State of Fuel in Test Sections	
						Preheater	Filter
SD/M-6e)	36	450/500	150	3.5/21	25	Liquid	Boiling(?)
SD/M-6e)	72	450/500	150	3.5/20	25	Liquid	Boiling(?)
SD/M-6e)	80	450/500	150	3.5/21	25	Liquid	Boiling(?)
SD/M-6e)	105	450/500	150	3.5/25.5	25	Liquid	Boiling(?)
SD/M-6e)	106	450/500	150	3.5/25.5	25	Liquid	Boiling(?)
Erdcof)	300	350/400	150	1/1	0.00	Liquid	Liquid
	300	375/500	250	2/2	0.33	Liquid	Liquid
	300	400/500	250	3.5/11.5	0.01	Liquid	Liquid
	300	450/500	250	4.5/21	0.07	Liquid	Liquid
	300	450/500	150	6/37.5	0.55	Boiling(?)	Vapor(?)

a) Complete properties and description of RAF-163-60 will be found in Table 39, Appendix.

b) Coker tests are normally run for 300 minutes or until a filter pressure drop of 25-inches Hg is reached, at which time the test is terminated. These pressure drops are for flows of 6 pounds of fuel per hour.

c) Test temperatures are expressed as preheater temperature/filter temperature in degrees Fahrenheit.

d) Preheater tube ratings are expressed as maximum code deposit rating/total tube deposit rating. Higher numbers correspond to larger amounts of deposits.

e) Using a steel preheater inner tube with aluminum overlay.

f) Using a stainless steel inner preheater tube.

TABLE 21
M-6/SD AND ERDCO COKER RATINGS OF n-DODECANE[a)]

Coker Rating Method	Total Time of Test, min[b)]	Temp, °F[c)]	Total Press., psig	Preheater Tube Rating[d)]	Highest Filter Pressure Drop, in. Hg[b)]	Physical State of Fuel in Test Sections	
						Preheater	Filter
SD/M-6[f)]	300	400/487	150	1.5/4.5	7.8	Liquid	Liquid
SD/M-6[f)]	300	450/500	150	2/8[f)]	2.6[e)]	Liquid	Liquid
SD/M-6[f)]	300	550/600	150	3/15	0.1	Liquid	Liquid
SD/M-6[f)]	300	650/700	250	5.5/18	0.4	Liquid	Liquid and Cracking
SD/M-6[f)]	300	750/800	250	6/24	0.1	Boiling and Cracking	Vapor and Cracking
SD/M-6[f)]	300	765/932	250	2/5	0	Boiling and Cracking	Vapor and Cracking
SD/M-6[f)]	300	650/700	400	5.5/24	14.2	Super Critical Fluid	Super Critical Fluid; Cracking
Erdco[g)]	300	450/500	150	3/8	0.95	Liquid	Liquid

a) n-Dodecane was obtained from kerosene by molecular sieve separation. Approximate analysis (%w): nC_{12}.

b) Coker tests are normally run for 300 minutes or until a filter pressure drop of 25-inches Hg is reached, at which time the test is terminated. These pressure drops are for flows of 6 pounds of fuel per hour.

c) Test temperatures are expressed as preheater temperature/filter temperature in degrees Fahrenheit.

d) Preheater tube ratings are expressed as maximum code deposit rating/ total tube deposit rating. Higher numbers correspond to larger amounts of deposits.

e) Average of 3 determinations.

f) Using a steel inner preheater tube with aluminum overlay.

g) Using standard ASTM-CRC aluminum preheater assembly.

TABLE 22
THERMAL STABILITY RATINGS OF THREE SELECTED CRC FUELS[a]

By SD/M-6, Research,[b] Eppi modified ASTM-CRC,[b][c] modified high temperature Erdco,[d] and ASTM-CRC cokers

Fuel Designation[e]	Coker	Test Time, min	Temp, °F[f]	Total Press., psig	Tube Deposit Ratings	Filter, ΔP, in. Hg	Test Evaluation[g]
RAF-159-60	M-6	300	425/500	250	1.5/11.5	1.85	Pass
RAF-159X	Eppi Modified CRC	300	500/600	250	2/21	0	Pass
RAF-159X	Research	300	500/600	250	1/9	0	Pass
RAF-163-60	M-6	106	450/500	150	3.5/25.5	25	Fail
RAF-163-60	Erdco	300	450/500	150	6/37.5	0.55	Fail
RAF-163-60	Erdco	300	400/500	250	3.5/11.5	0.01	Fail
RAF-163-60	Erdco	300	450/500	250	4.5/21	0.07	Fail
RAF-169-61	ASTM-CRC	300	475/500	250	0.3/1.4	0.1	Pass
RAF-169-61	Eppi Modified CRC	300	450/500	250	2/15	0.0	Pass
RAF-169	Eppi Modified CRC	300	550/600	250	3/28	0.0	Fail
RAF-169	Research	300	450/500	250	3/36	1.0	Fail
RAF-169	Research	300	550/600	250	3/31	0.5	Fail

a) Properties and description of these fuels are given in Tables 38, 39, and 40 of the Appendix.

b) Research and modified ASTM coker ratings were selected from reported values in Eppi Precision Products Report No. 63-253, February 28, 1963, "Final Report on Extended CRC Thermal Stability Program".

c) Rate of fuel flow in the modified coker was 2.5 lb/hr, compared to a rate of 6 lb/hr in all other cokers listed.

d) The modified Erdco coker is substantially the same as the Research coker except as modified to minimize contamination tendencies.

e) RAF fuels rated here and those rated at the Eppi Laboratories were shipped from the same CRC fuel bank at Wood River, Illinois, but at different times. RAF-159X is possibly a different batch than RAF-159-60.

f) Discharge fuel temperature from preheater/fuel temperature in the filter cavity.

g) Using ASTM criteria.

TABLE 23
SD/M-6 COKER RATINGS OF METHYLCYCLOHEXANE[a]

Phillips Pure Grade, 99.0%m minimum purity

Total Time of Test, min[b]	Temp, °F[c]	Total Press., psig	Preheater Tube Rating[d]	Highest Filter Pressure Drop, in. Hg[b]	Filter Deposit Weight, % of Total	Pre-Test Treatment[e]	Physical State of Fuel in Test Sections	
							Preheater	Filter
300	200/400	150	1.5/14.5	2.7	0.089	None	Liquid	Boiling
241	275/400	150	1.5/18.5	25	0.133	None	Liquid	Boiling
104	350/400	150	1.5/14.5	25	0.167	None	Liquid	Boiling
41	400/500	400	1.5/15	25	0.279	None	Liquid	Liquid
300	250/400	150	2.5/29	3.2	0.059	Silica Gel	Liquid	Boiling
300	275/400	150	1.5/14	6.7	0.089	Silica Gel	Liquid	Boiling
232	325/400	150	1.5/11.5	25	0.13	Silica Gel	Liquid	Boiling
198	300/400	150	1/9.5	25	0.114	Silica Gel	Liquid	Boiling

a) Methylcyclohexane used was 99.8%m pure by GLC and contained about 0.1%m toluene, 0.1%m normal heptane, together with traces of two unknown components. All but the last run shown were from the same bottled sample. The 300/400°F run was from a 5-gallon can which had never been opened but was several years old.

b) Coker tests are normally run for 300 minutes or until a filter pressure drop of 25-inches Hg is reached, at which time the test is terminated. These pressure drops are for flows of 6 pounds of fuel per hour.

c) Test temperatures are expressed as preheater temperature/filter temperature in degrees Fahrenheit.

d) Preheater tube ratings are expressed as maximum code deposit rating/total tube deposit rating. Higher numbers correspond to larger amounts of deposits.

e) MCH was tested either directly from the Phillips bottle, or after silica gel chromatography. No further prefiltering was performed.

At these same conditions, preheater tube ratings of n-dodecane were nearly the same by the two methods: 2/8[a] by the M-6, and 3/8 by the CRC Erdco (A standard ASTM-CRC aluminum preheater assembly was used in this test.) However, actual failure of n-dodecane by the M-6 method did not occur until temperatures of 550/600°F were reached, indicating a slightly more severe tube rating by the standard ASTM equipment. Similar tube ratings of RAF-163-60 could not be fairly compared between the two cokers since Erdco tests of this fuel always ran a full 300 minutes, whereas M-6 tests were terminated early due to severe filter plugging. Also, the M-6 test utilized an aluminum surfaced preheater inner tube, while stainless steel was used in the Erdco.

Tentatively, then, it appears that the M-6 coker will rate some fuels more severely by filter plugging than will the Erdco, whereas with other fuels there may be no significant difference. Preheater tube ratings in the M-6 coker will probably be slightly less severe than in the standard CRC coker. However, further comparative data are needed to reach final conclusions, and no direct comparison of tube ratings of the high temperature version Erdco and the M-6 cokers is yet available.

Standardization of Coker Ratings

Three standardization fuels have been rated: RAF-163-60, a naphthenic jet fuel (see Table 20); and two highly paraffinic fuels, RAF-159-60 and RAF-169-61. Properties for these fuels are detailed in Tables 38, 39, and 40 of the Appendix. An additional standardization fuel, RAF-156-60, is now being tested (properties are shown in Table 40, Appendix). All of these are CRC fuels and represent high quality state of the art materials.

Thermal stability data selected from coker runs on these fuels in these laboratories, together with selected data on different batches of the same fuels, from the Eppi Laboratories, are presented in Table 22. While the conditions at which these results were obtained were not identical in all cases, there is sufficient similarity to permit some tentative comparisons.

In the previous discussion of coker characteristics it was explained that M-6 filter plugging would have a tendency to be severe. This tendency illustrates itself to different extents with the CRC fuels: first, with RAF-159 where M-6 filter plugging was not excessive, but significantly higher at slightly lower temperatures than in either the Research or Eppi modified cokers; second, with RAF-163-60 where M-6 filter plugging reached 25-inches Hg in 106 minutes versus negligible amounts of filter plugging at 300 minutes in the high temperature Erdco coker.

Comparing tube ratings, the M-6 appears to be consistent in its rating of RAF-159 with that of the Eppi modified coker. However, the Eppi modified coker, which was designed to duplicate Research coker ratings, rated RAF-159 more severely than did the Research coker at identical temperatures.

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a) A preheater rating expressed as 2/8 means a maximum localized deposit rating of code 2 and a sum of code ratings for the tube of 8. Code ratings are from a standard ASTM comparator, and preheater tubes are rated for each of 13 one-inch increments. High ratings mean heavy deposits.

On RAF-163-60, early termination of the M-6 test prevented direct comparison with Erdco results, but it appears that tube ratings would be in agreement at equivalent times.

Of interest with RAF-163-60 is the effect of pressure on the Erdco ratings. At 150 psig and 450/500°F, the inner tube showed definite markings attributable to boiling near the discharge port of the preheater. By increasing pressure to 250 psig without changing temperatures, these "boiling deposits" were eliminated and tube ratings were reduced from 6/37.5 at 150 psig to 4.5/21 at 250 psig. In tests at similar conditions and the lower pressure, no evidence of boiling occurred on the M-6 inner tube. This difference is attributed to either a lower tube surface temperature (because of outside insulation) in the M-6 coker, or to heat transfer from the filter furnace which is more likely in the Erdco set up. Regardless of the cause, the increased amount of deposits when boiling does occur is of significant interest when vaporizing and endothermic fuels are considered.

With a standard coker preheater installed, our Erdco coker is essentially an ASTM-CRC coker. In this form, the Erdco was used to rate RAF-169 and found to give far milder test results than either the modified or Research coker results reported by Eppi. Although the fuel was from the same source, different drum samples were of course tested, and the differences in tube ratings observed could have been due to contamination or could be attributed to the greater age of the fuel.

Viewing the over-all picture of relative thermal stabilities in Table 22, there is a clearly decreasing order: RAF-159 > RAF-169 > RAF-163, the two paraffinic fuels being more stable than the highly naphthenic one. Where fuel to fuel comparisons are possible, no contradictions appear in the relative order in which the various cokers would rate the thermal stability, except for the ASTM-CRC preheater/Erdco coker rating of RAF-169 which makes this fuel look superior to the other two. Perhaps our sample of RAF-169 is the most stable. The three fuels are presumably most comparable by following the Research and high temperature Erdco coker results, since the preheater in each are identical and the inner tube surface is stainless steel. The preconditioning tank of the Research coker was not heated in the runs cited.

Thermal Stability of Endothermic Fuels

Two prototype endothermic heat sink fuels have been examined by the M-6 coker method, and one of these by the Erdco coker using a standard ASTM-CRC aluminum preheater tube. These include n-dodecane, mentioned above, and methylcyclohexane (MCH), a hydrocarbon of particularly promising heat sink potential via catalytic dehydrogenation reaction. In this connection, the dehydrogenation product from MCH reaction, toluene, has also been tested by the M-6 method.

Of the three fuels mentioned, n-dodecane was found to be the most stable. In the liquid state, n-dodecane did not fail the M-6 coker test until 550/600°F at 150 psig pressure (Table 21). Filter pressure drop in this test was only 0.1-inch Hg when the preheater tube rating reached a rating of 3/15.

In fact, all M-6 failures of n-dodecane were by tube deposits rather than filter plugging. Failure by the Erdco coker with standard ASTM-CRC preheater occurred at lower temperatures (450/500) and a tube rating of 3/8. In the Erdco also, the maximum filter pressure drop was low (0.95-inch Hg).

M-6 coker tests were also run at temperatures where boiling and cracking of n-dodecane were occurring, and in most instances preheater tube deposits were unacceptably heavy, although filter plugging was usually slight. At supercritical fluid conditions (650/700°F and 400 psig) tube ratings (5.5/24) were in substantial agreement with those at the same temperatures but subcritical pressure (250 psig; tube ratings, 5.5/18). In both situations a small amount of thermal cracking (as shown by gas evolution and mass spectrometric analysis) was occurring in the filter. Filter plugging was slight (0.4-inch Hg) at low but excessive (14.2-inches Hg) at high pressure.

Since tentative specifications (ASTM D1655-62T) for aviation turbine fuels require less than code 3 maximum on preheater tube deposits and less than 12-inches Hg filter pressure drop for 300/400°F operation, n-dodecane easily meets these requirements. However, thermal stability decreased under conditions of boiling and thermal cracking where maximum code ratings of 5.5 to 6 were observed. Further work will be necessary to improve the thermal stability of n-dodecane to a satisfactory level.

The thermal stability of MCH has been tested only in the M-6 coker (see <u>Table 23</u>). Test failure occurs by filter plugging at 300/400°F and 150 psig. Under these conditions, MCH exists in the liquid state in the preheater, but boils in the filter. It might be suspected that boiling in the filter is responsible for the large amount of filter plugging. However, with higher temperatures (400/500°F) and sufficient pressure (400 psig) to maintain liquid state in both preheater and filter, filter plugging became catastrophic (test failure in 77 minutes). Therefore, the temperature level rather than just the occurrence of boiling appears to be responsible for filter plugging. Moreover, the filter plugging tendency of MCH at constant filter temperature was found to bear a nearly linear relationship with preheater temperature (see <u>Figure 24</u>) indicating formation of particulate matter or its precursors in the preheater zone.

Toluene would first exist in the high temperature MCH catalytic reaction zone, and from there would be subject to high temperature until burning occurred. The thermal stability of such reaction products could therefore easily be as important as their original fuel precursors.

The thermal stability of toluene measured by the M-6 coker was found to be surprisingly low considering its high resistance to thermal cracking. When run at 450/500°F and 400 psig (liquid), a preheater tube rating of 3/32 (failure) and filter pressure drop of 6-inches Hg (acceptable) were obtained. Thus, the thermal stability of toluene, while lower than expected, was still considerably better than that of MCH. Purity of the Baker "CP" toluene used was 99.9%m, with a trace of benzene, about 0.1 ppm peroxide, and less than 0.01 ppm copper. Silica gel treatment reduced peroxide to less than 0.01 ppm, but made no thermal stability improvement nor change in GLC analysis.

Methods for Increasing Thermal Stability

While the primary objective of the current contract is to discover a fuel or fuels and concomittant endothermic reactions adequate to provide heat sink capacity for hypersonic flight, it is not unlikely that thermal stability of the original fuel, its vapor, or its reaction products will in the end be a major limiting factor in specifying suitable fuels. Therefore, an important corallary objective is to determine means of improving the thermal stability of fuels having desirable heat sink properties. Such means as have already been used or contemplated in this contract are as follows:

Removal of Impurities and Minor Fuel Components

Economics normally restrict purification of fuels to a minimum within specification limits. While not all minor or trace components are responsible for poor thermal stability properties, it is desirable to know whether selective removal of such materials will improve stability and to what extent. Moreover, the stringent requirements of multi-Mach number jet fuels will tend to favor the use of pure hydrocarbon compounds, singly or in precise and simple blends. Candidate endothermic fuels must therefore be considered at varying levels of purity, and thermal and storage stabilities are likely to be more sensitive to impurities than will any other fuel specification determinant.

Some tentative conclusions regarding causative factors in thermal stability failure may be deduced from comparison of M-6 and Erdco coker tests. For instance, where poor thermal stability ratings arise from trace impurities, these substances may be quickly reacted and used up in the small sample recycle M-6 test, whereas in the 5-gallon once-through Erdco test such impurities are continually replenished. With such a fuel the Erdco coker would be expected to rate more severely than the M-6. Opposed to this situation is that in which a major fuel component is the culprit.

Here, the ratings, particularly of the preheater tube, would be expected to be similar, granting similar operating conditions and tube metal surfaces. The filter plugging tendency of the M-6 may be, even for this case, more severe because of the conditions favorable toward particle growth (and the formation of less stable oxidation products) as the fuel is repeatedly heated and cooled on recycle.

The n-dodecane (99.0%m) used in the work reported here is probably an example of a fuel in which the limiting component is n-dodecane itself. Evidence for this lies in the fact that filter plugging was essentially the same in both coker tests, and Erdco tube deposition was only slightly greater than in the M-6 (see Table 21).

Pure grade (99.7%) MCH from Phillips Petroleum Company used in the present M-6 coker tests provided an opportunity to demonstrate the influence of trace impurities. About 0.3 percent total minor components were present in the MCH "as received", including 0.15% toluene and small amounts of n-heptane with probably other C_7 isomers making up the difference. Silica gel chromatography of the MCH produced no observable change in the number or size of component peaks, but did increase the thermal stability rating by as much as 75°F relative to filter plugging tendency. Therefore, a trace material, something present at a concentration of less than about 0.02%, is probably responsible for the change in filter plugging found. Analysis also showed no copper present (< 0.01 ppm), but peroxide content was reduced from 5 ppm to less than 0.01 ppm by the silica gel treatment, to which the improvement in thermal stability may be traceable.

Deaeration

Coker test fuels are conventionally aerated to the saturation point at ambient temperature prior to the start of the test. Thus, the ASTM thermal stability test method specifies bubbling air into the entire 5-gallon fuel sample at a rate of one to two liters per minute for 3 minutes prior to test if the fuel has been stored under air, or for 20 minutes if it has been stored under nitrogen. This standard procedure is followed with both Erdco and M-6 cokers. However, the fuel charge to the M-6 coker being continuously recycled, the initial dissolved air would soon be consumed. Therefore, air is continuously bubbled through the fuel in the M-6 fuel reservoir for the entire period of the test. The air is vented through a water-cooled condenser to return condensable liquids to the fuel reservoir.

Since dissolved oxygen may play an important role in thermal stability, at least for some fuels, deaeration and nitrogen blanketing of endothermic jet fuels both during storage and in flight may be required. Comparative testing of candidate fuels with and without dissolved oxygen and at known concentrations will be utilized to determine the amount of upgrading which may be obtained in this manner. No runs have yet been made on deaerated fuels.

Additives

Further efforts to improve fuel thermal stability will be made via oxidation inhibitors and metal deactivators. These will be examined for both their direct affect on coker ratings and for their long range effect through improved storage stability. Additives such as surfactants and biocides will receive little attention since they are outside the scope of this contract; but the effect of such additives likely to be found as contaminants may be briefly inspected in final selection candidate fuels. Additives in general will usually only be tested in candidate fuels.

Other additives deserving at least a brief look here are compounds such as surfactants and dispersants which might modify the particulate matter to prevent growth and filter plugging.

Solvents and Dispersants

Also deserving some attention are materials which may act to increase the solvency of the fuel toward the resinous decomposition products it forms. Thus, filter plugging tendency or deposition might be reduced even though oxidation and polymerization reactions have not decreased.

Tube Rating Problems

The usual method of rating preheater tubes utilizes an ASTM color comparator and a tuberator (a standardized lighting arrangement). Five color codes, 0 through 4, ranging from bright shiny metal to a straw yellow in stepwise gradations, are provided. An Eppi scale has extended this to 8 by a set of comparator codes ranging in four steps from dark tan to black. Standardized lighting conditions are extremely important to this rating method, and even the tuberator ratings can be influenced by room or window light. Use of the tuberator should be in a dark room or under a photographer's shroud to avoid influence of outside light sources.

At best, color ratings do not necessarily relate to actual amounts of deposits laid down, and deposit colors often appear which simply do not come within the range of color codes provided. An example of the difficulty was encountered in the 5.5 to 6 maximum ratings of n-dodecane (Table 21). In these instances, thermal cracking was occurring and tube deposits were dark; actual amounts of deposits could have differed by far more than the color ratings indicate. In other instances, deposits are pink rather than yellow or tan.

Fuel thermal stability in Mach 3+ flight will be critically important not only because of potential catastrophic failure due to fuel filter and burner nozzle plugging, but because heat transfer coefficients of heat exchanger walls must remain high if the heat sink capacity of endothermic fuels is to be realized. It is therefore of utmost urgency that thermal stability measurements be as quantitative as possible. Ideally, thermal stability measurements should be translatable into loss in heat transfer rates.

To keep coker tests meaningful therefore, methods of quantitative measurement of preheater tube deposits will be sought. Among methods which will be explored or considered will be the following:

a) Measurement of deposits in situ by β-radiation. This might be accomplished either by first coating the tube surface with a β-emitter, or by irradiation of the deposit coated tube and measurement of back scattering. S^{35} would probably serve for the former technique and Pm^{147} for the latter.

b) Quantitative removal of deposits from the tube and subsequent gravimetric determination. Removal methods might include mechanical, solvent, or chemical reaction techniques (i.e., reaction with hydrogen peroxide).

c) Gravimetric determination by weighing preheater tubes before and after runs. This method suffers from errors due to metal transfer to or from the tube or its Swagelock ferrule fittings.

d) A highly desirable technique would be the direct measurement of heat transfer rate in a calorimeter, if this can be done with sufficient accuracy. This has the advantage of the direct determination of changes in heat transfer coefficient, a variable of primary concern in endothermic fuel stability studies. This approach will be attempted.

In addition, photographic techniques are being explored to aid in visual rating. By this means, precise records of deposit patterns may be preserved, and with the use of color film, deposit colors may also be captured. Examples of photographs of tubes are shown in Figure 22; the entire tube surface is displayed as a planar surface. Carefully standardized lighting is important to this method also. The same procedure as that used in photographically "unrolling" the tube surface so as to see its complete circumference can be applied to β-radiation scanning as well.

Test filter ratings are normally either by (1) the maximum pressure drop in 300 minutes testing or (2) the number of minutes required to reach 25-inches Hg pressure drop, whichever occurs first. An obviously undesirable feature of this approach is the use of two scales, each discontinuous and unrelated to the other. To bridge this gap a "Goodness Number" was devised which assigns a filter test rating number between 0 and 900; numbers from 450 to 900 relate to the logarithm of the maximum filter pressure drops of 0 to 25-inches Hg at 300 minutes test completing time (900 corresponds to zero pressure rise), while numbers from 0 to 450 bear a linear relationship with time to the point at which pressure drop reached 25-inches Hg. While this approach is arbitrary it has the advantage of ready visualization.

It is of interest, also, to gravimetrically determine deposits on the test filter. Obviously, the different character of particulate matter formed in different fuels will prevent correlation of deposit weights with filter plugging tendency.19) Moreover, errors sometimes may occur from metal exchange or deposit loss. But within runs made on a single fuel, we have found good correlations between filter deposit weights and pressure drop, Goodness Number, and certain operating parameters (cf Figures 23 and 24).

Fuel System Simulation Test Apparatus

This apparatus, which will be the source of much of the data to be obtained on endothermic fuels, has been designed and is currently under construction. Figure 25 is a simplified schematic diagram of this equipment. The fuel storage tank is large enough to provide for about three hours of operation at the maximum anticipated flow rate, 25 gal/hr. It can be heated to about 450°F, by circulating heating oil through coils on the outside of the vessel, in order to simulate exposure of the fuel to aerodynamic heating during supersonic flight. The feed pump will provide up to 1000 psi discharge pressure at the maximum design flow rate, and this has been used as the design pressure for the preheater, test section, and other equipment downstream from the pump. Two 16-kw electric furnaces in series make up the fuel preheater. This capacity is adequate to heat the maximum flow of fuel from a liquid at ambient temperature up to a vapor near the thermal decomposition temperature.

The test section, in which all of the data on fuel behavior will be generated, is being fabricated from Hastelloy C. Three ten-foot lengths of 5/16-inch OD 25 ga (0.2725-inch ID) tubing will be used for system check-out and initial testing. One of these lengths will subsequently be replaced by an interchangeable 3/4-inch OD packed tube reactor for studies of catalytic reaction.

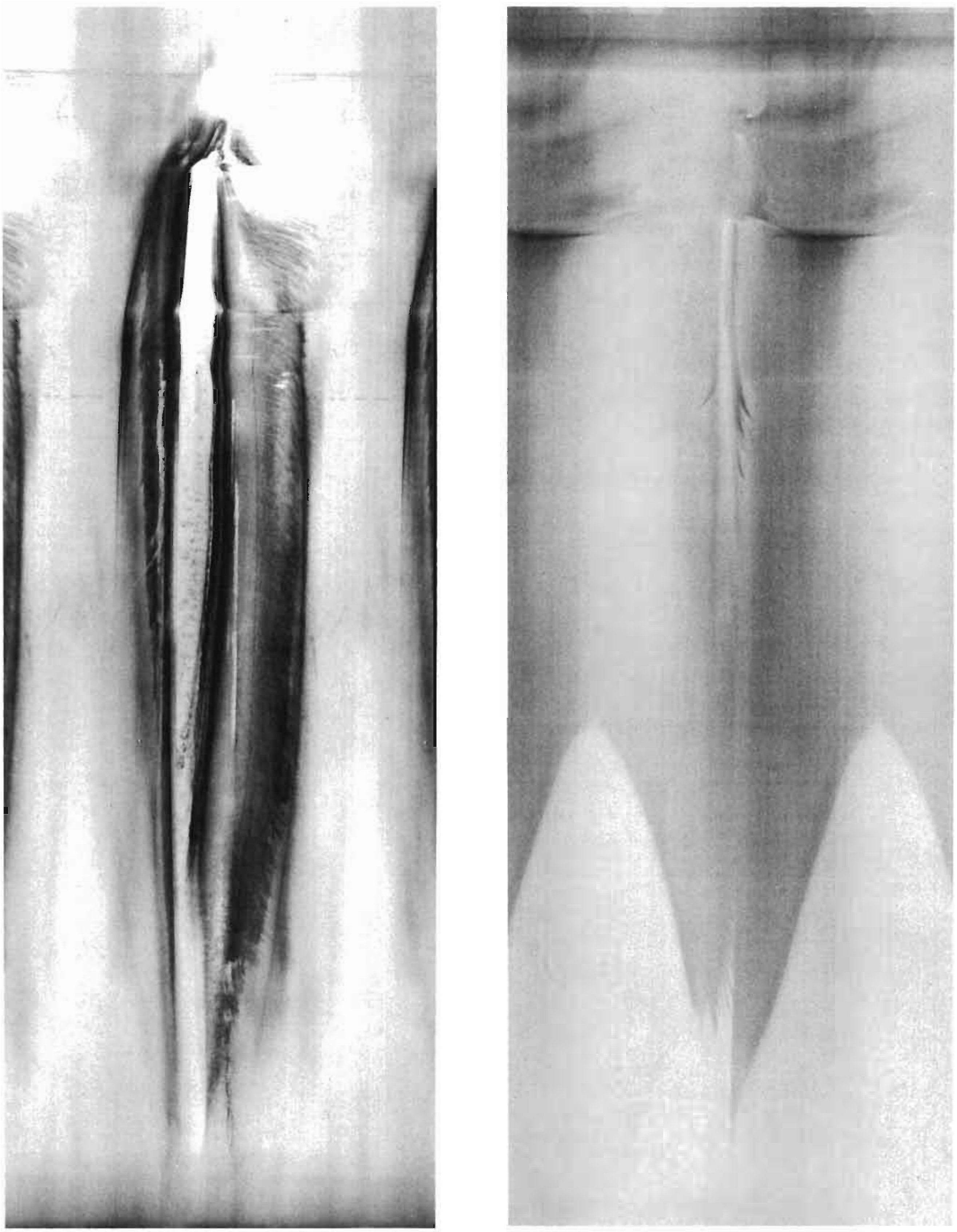


Figure 22. COKER TUBES FROM M-6 THERMAL STABILITY DETERMINATIONS

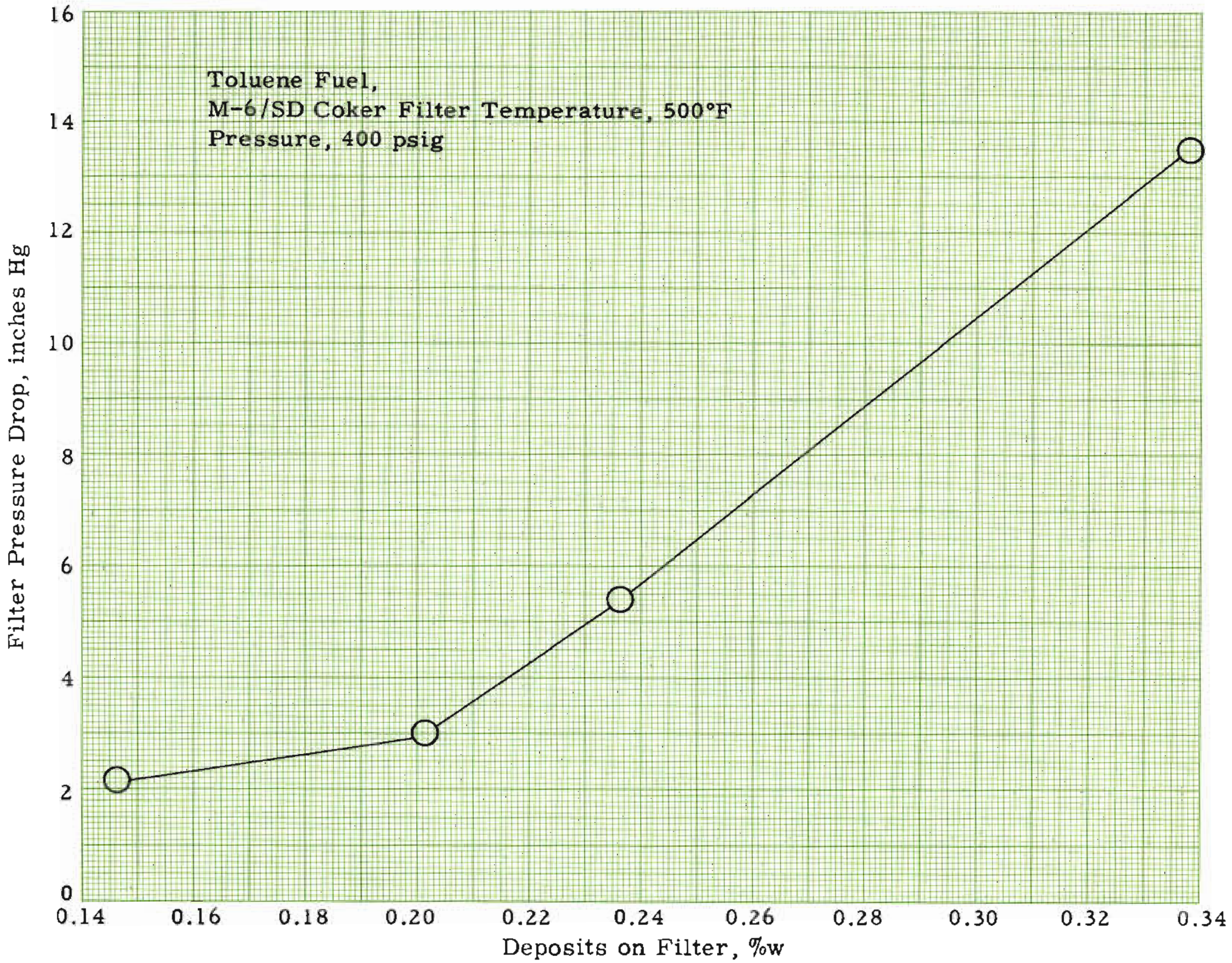


Figure 23. EFFECT OF DEPOSIT WEIGHT ON FILTER PRESSURE DROP

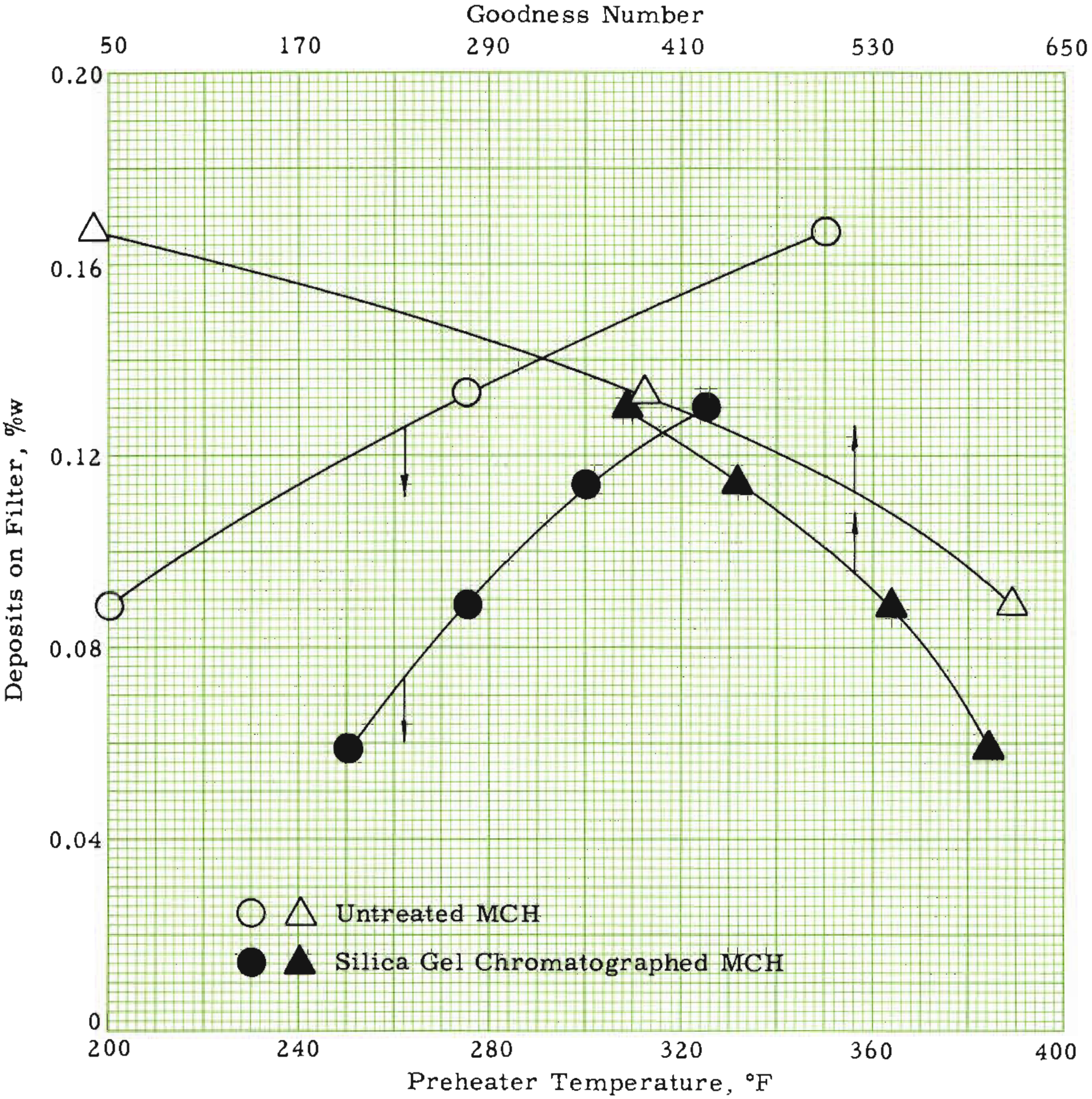


Figure 24. CORRELATION OF M-6/SD COKER FILTER DEPOSIT WEIGHTS WITH PREHEATER TEMPERATURE AND GOODNESS NUMBER: METHYLCYCLOHEXANE FUEL

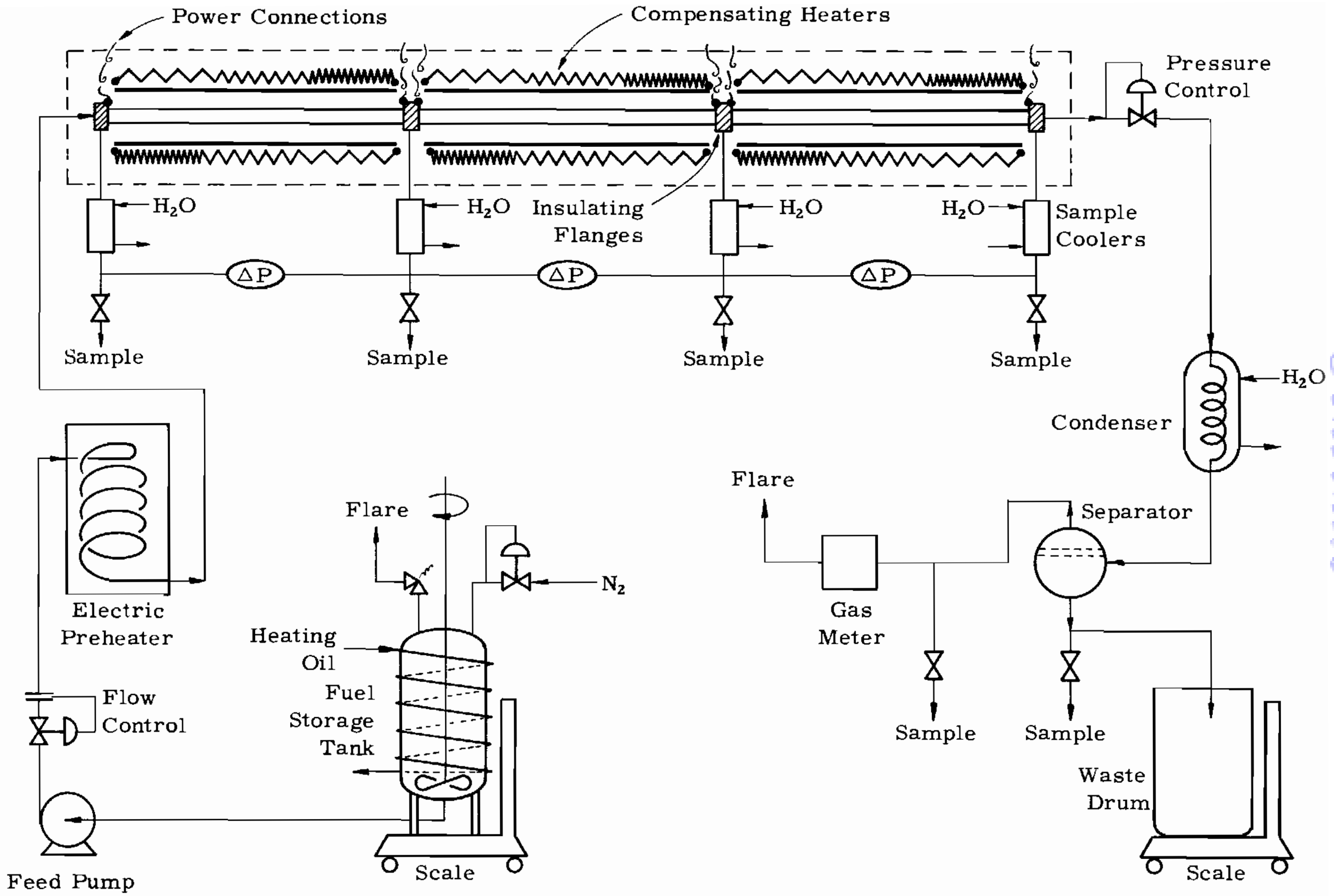


Figure 25. FUEL SYSTEM SIMULATION TEST EQUIPMENT

The three separate lengths of Hastelloy C tubing which make up the test section will be electrically heated by passing AC current through the tube wall itself. This will eliminate the thermal resistance which would exist between external heaters and the tube wall, and thus decrease the maximum temperature which the materials must withstand, and the amount of heat loss to the surroundings. These are important considerations since fuel outlet temperatures up to 1400°F are to be investigated. The three lengths of tubing will be electrically insulated from one another by means of composite metal-ceramic connectors as shown on Figure 26 so that there will be no interaction between the three commercial welding machines which are being used as power supplies, and so that the power input to each ten-foot long zone can be independently controlled.

The heating requirement in the test section was set by the consideration that no decomposition of the fuel should take place in the preheater. The test section heaters must, therefore, be able to provide the heat absorbed by the fuel during endothermic reaction and subsequent heating of the reaction products to the fuel outlet temperature. For the fuel flow rate being considered and the anticipated heats of reaction, the heating requirement is about 30 kw. This amount of heating capacity in the test section will allow examination of the behavior of a fuel over the entire range of interest in two tests. First, without preheating, the vaporization and heating of the fuel up to its decomposition temperature can be investigated. Second, with preheating up to the decomposition temperature, endothermic reaction and further heating to 1400°F can be studied.

In order to eliminate heat loss from the hot fuel-flow tube to the external environment it is insulated and surrounded by compensating heaters. These tubular electric heaters are being specially wound to provide a linearly varying power density along their length. Eight of these heaters will be mounted around a steel shell enclosing each length of the test section, and by installing adjacent heaters with their power density gradients in opposite directions, and controlling the two sets of heaters separately, the steel shell can be maintained at any desired linear temperature profile to approximate the test section temperature profile. In case a nonlinear profile is required to match the test section temperature (as would result from phase change or reaction of the fuel), then electric heating tape or cooling coils wrapped outside the insulation can produce a concave down or concave up profile.

Instrumentation of the test section will include fluid temperature measurement and fuel sample withdrawal at the inlet, the outlet, and the two internal points separating the three heater zones. These facilities are being incorporated into the composite metal-ceramic connectors shown on Figure 26. The pressure drop across each ten-foot length of the test section will be measured by differential pressure gages connected to the sampling lines. In order to minimize the possibility of plugging the small-diameter sample lines, a small bleed of fuel will be maintained through them at all times except for very brief periods while the pressure drop measurements are being made. Measurement of fuel flow rate and heater power input, along with the temperature and pressure data will allow calculation of the heat sink capacity of the fuel

Service Conditions:
Temperature: 1400°F
Pressure: 1000 psi
Fluid: Jet Fuel

Note: All Materials Used
Must be Completely
Free of Copper

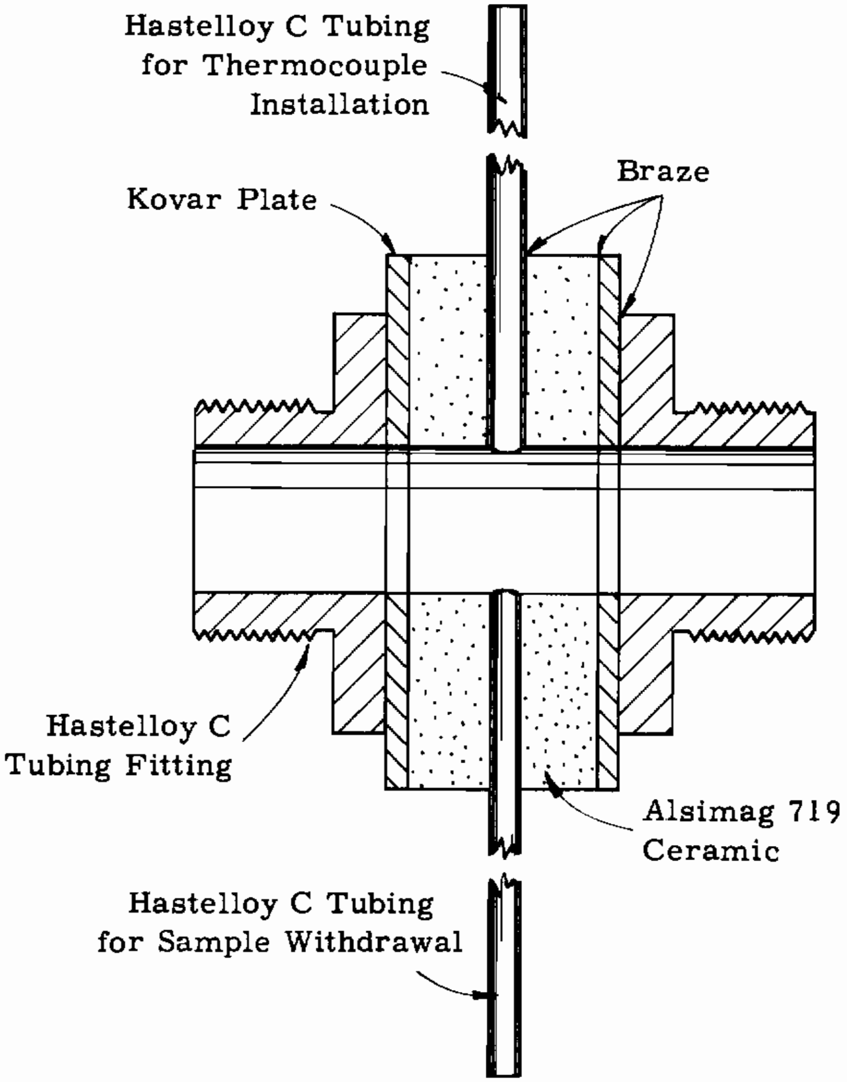


Figure 26. INSULATING TUBING CONNECTOR

over the temperature interval of the test and the frictional pressure losses through the tube. Sample analysis will provide information on decomposition rates and the composition of the products of endothermic reaction.

Additional instrumentation includes thermocouples for fluid and tube wall temperature measurement at the quarter-points of each ten-foot length of the hot-fuel flow tube. These data, along with the measured heater power input, will allow evaluation of the local heat transfer coefficient under the various conditions of temperature rise, change of phase, and endothermic reaction which will be taking place along the length of the test section.

Downstream from the test section a water cooled condenser and a vapor-liquid separator are installed. Flow measurement and sampling facilities are provided in both the vapor and liquid streams so that a material balance can be obtained. These streams of used test fuel will subsequently be discarded - the gas burned in the plant flare system and the liquid stored in drums for outside disposal.

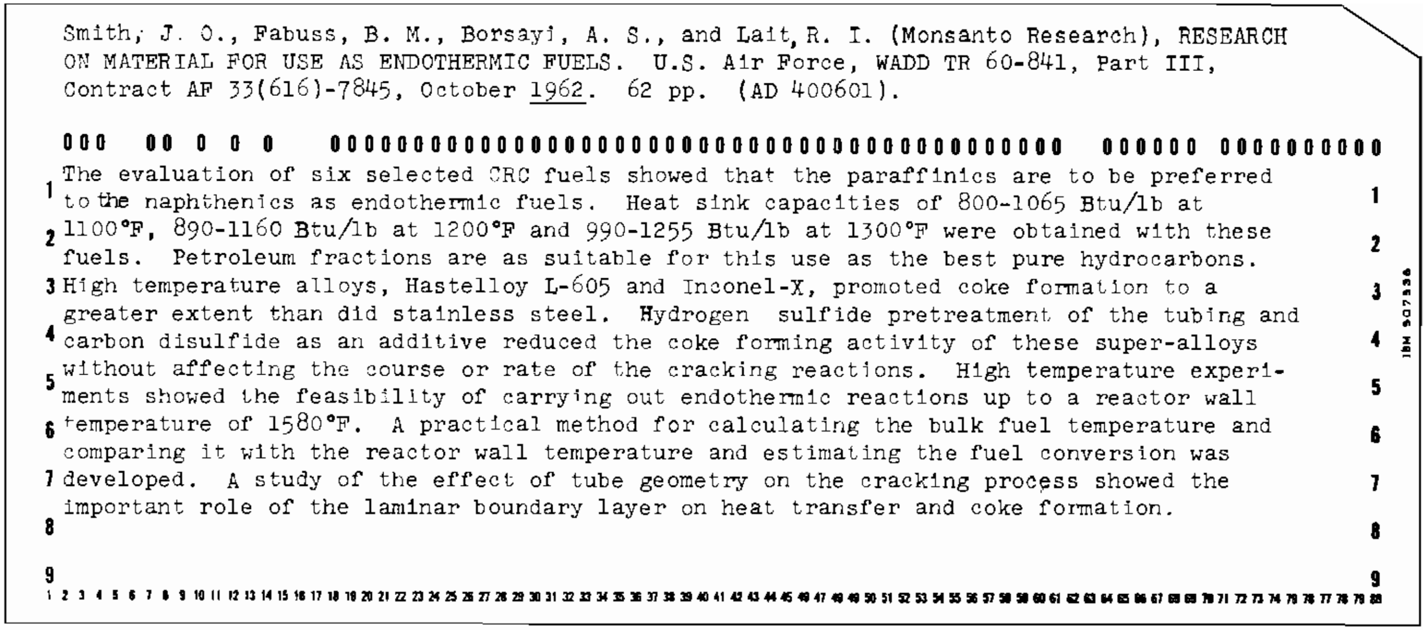
In the interst of safety, various alarm and automatic shut-down systems are included in the test installation. These include hydrocarbon leak detectors and alarm, pressure relief vents to the flare system, over-temperature alarm and shut-down devices at several points in the apparatus, shut-down on loss of pressure or flow in the test section, and a CO_2 fire extinguishing system capable of completely blanketing the test area.

While it is anticipated that some modification and "debugging" of the equipment will be required at start-up, every effort has been made to keep the apparatus and operation as simple as possible so as to minimize the sources of difficulty.

Literature Survey

A comprehensive literature search on the subject of endothermic fuels for supersonic aircraft has been undertaken as part of the contract performance. This survey includes references to government reports and to papers in the open literature, both domestic and foreign. It has been compiled from searches by DDC (ASTIA), examination of the extensive files of the Foreign Technology Division, and systematic search under pertinent headings in Chemical Abstracts, Applied Mechanics Reviews, Engineering Index, and International Aerospace Abstracts. The completed survey will be published as a separate report in the near future, and the same information will be made available on cards so that machine sorting according to the content of the documents will be possible. Supplementary cards added to the deck will also provide a convenient way to keep the survey up to date.

A typical reference card is shown on Figure 27. The cards contain the same bibliographic information and abstract as are being presented in the report, and in addition a set of punches for sorting. The subject catagories under which the references are classified and may subsequently be machine retrieved are listed below. These same headings are being used for indexing the literature survey report.



Smith, J. O., Fabuss, B. M., Borsayi, A. S., and Lait, R. I. (Monsanto Research), RESEARCH ON MATERIAL FOR USE AS ENDOTHERMIC FUELS. U.S. Air Force, WADD TR 60-841, Part III, Contract AF 33(616)-7845, October 1962. 62 pp. (AD 400601).

The evaluation of six selected CRC fuels showed that the paraffinics are to be preferred to the naphthenics as endothermic fuels. Heat sink capacities of 800-1065 Btu/lb at 1100°F, 890-1160 Btu/lb at 1200°F and 990-1255 Btu/lb at 1300°F were obtained with these fuels. Petroleum fractions are as suitable for this use as the best pure hydrocarbons. High temperature alloys, Hastelloy L-605 and Inconel-X, promoted coke formation to a greater extent than did stainless steel. Hydrogen sulfide pretreatment of the tubing and carbon disulfide as an additive reduced the coke forming activity of these super-alloys without affecting the course or rate of the cracking reactions. High temperature experiments showed the feasibility of carrying out endothermic reactions up to a reactor wall temperature of 1580°F. A practical method for calculating the bulk fuel temperature and comparing it with the reactor wall temperature and estimating the fuel conversion was developed. A study of the effect of tube geometry on the cracking process showed the important role of the laminar boundary layer on heat transfer and coke formation.

Figure 27. TYPICAL LITERATURE REFERENCE CARD

Subject Headings for Classification and Retrieval of Literature References

Supersonic Aircraft

- Military research programs
- Commercial SST program
- Cooling requirements, insulation, and aerodynamic heating
- General works on supersonic flight problems

Vaporizing and Endothermic Fuels

- Heat sink capacity
- Specific heat
- Heat of vaporization
- Heat of endothermic reaction
- Manufacturing processes

Thermal Reactions

- Reaction mechanisms
- Reaction rate
- Heat of reaction
- Conversion
- Product distribution
- Effect of reactor materials

Catalysis and Catalytic Reactions

- Heterogeneous catalysis
- Homogeneous catalysis
- Reaction mechanisms
- Reaction rate
- Heat of reaction
- Conversion
- Product distribution
- Properties and manufacture of catalysts

High Temperature Stability

- Effect of storage
- Effect of contaminants
- Effect of additives
- Environmental influences (including radiation)
- Large-scale tests
- Coker tests
- Small-scale tests
- Data for various fuels
- Processes for improvement

Fuel Contaminants

- Water
- Oxygen, nitrogen, and sulfur-containing compounds
- Metals
- Surfactants
- Microorganisms
- Sources
- Effects
- Allowable concentrations
- Removal

Fuel Additives

- Anti-icing additives
- Anti-static additives
- Corrosion inhibitors
- Oxidation inhibitors
- Metal deactivators
- Stability improvers
- Biocides

Combustion Characteristics

- Combustion efficiency
- Flame luminosity and smoking tendency
- Deposit formation
- Ignition properties

Physical-Chemical Properties

- Thermodynamic properties
- Transport properties

Heat Transfer and Flow Behavior

- Single-phase heat transfer and flow
- Heat transfer to supercritical fluids
- Two-phase heat transfer and flow
- Calculation methods
- Design and manufacture of equipment

Type of Reference

- Survey or compilation of data or references
- Theoretical prediction
- Experimental study
- Description of test methods or apparatus

Advanced Engines

- Turbine
- Ramjet
- Materials

The reference shown on Figure 27, for example, is punched to indicate a reference related to:

Supersonic Aircraft

- Military research programs

Endothermic Fuels

- Heat sink capacity
- Heat of endothermic reaction

Thermal Reactions

- Reaction rate
- Heat of reaction
- Conversion
- Product distribution
- Effect of reactor materials

Heat Transfer and Flow Behavior

- Single-phase heat transfer and flow

Type of Reference

- Experimental Study

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APPENDIX
SUPPLEMENTARY MATERIAL

APPENDIX (Contd)

Endothermic Reactions

Selection of a Standard Chromia on Alumina Catalyst

Chromia on alumina and molybdena on alumina catalysts are well known to be active for dehydrogenation reactions in the absence of hydrogen. While the purpose of this study was to examine various endothermic reactions rather than catalysts, nevertheless two commercial potassium promoted chromia on alumina catalysts and one molybdena on alumina catalyst were examined for relative activity. The activity of the catalysts proved quite varied and the results of the tests are tabulated in Table 25. The tests were carried out at 1112°F, 1 atm pressure and LHSV of 20 with and without added hydrogen in the feed.

The most active of the three catalysts tested was the potassium promoted chromia on alumina catalyst No. 8219-63-1 that contained 2% K_2O and 8% Cr_2O_3. With this catalyst at 1022°F and an LHSV of 10, propane conversion of 22.5% was observed (Table 25). The reaction was quite selective with selectivities for propylene of 94% and higher being obtained. Typical product analyses are shown in Table 26. The catalyst was reasonably stable during the test with only about a 6% decline in activity (i.e., conversion) being observed during the 90 minute test period. Presumably the activity decline was due to coke formation on the catalyst surface. At 1022°F (furnace temperature) the catalyst bed temperature was initially 94°F below the furnace temperature. During the test period, the bed temperature increased only a few degrees. This resulted in an "effective" reaction temperature somewhat below the furnace temperature. As equilibrium propane conversion at 1022°F is 29% (Figure 28) and is 18% at 932°F; it is probable that initially the reactor was running at or near equilibrium conversion. The data are summarized in Table 25.

At higher temperatures and space velocity (LHSV = 20) comparable conversions and selectivities were obtained at 1112°F with higher conversions and lower selectivities at 1200°F (Table 25). At these higher temperatures the catalyst was less stable than at 1022°F. Indeed, considerable coke was formed at 1200°F, not only on the catalyst surface but also on the reactor walls, the thermocouple well and on the metal sleeves below the catalyst bed in quantity great enough to plug the reactor. The coked catalyst was readily regenerable with a 5-10% oxygen in argon gas stream at 1030°F, but this treatment did not remove the coke deposited elsewhere in the reactor.

When hydrogen was added to the propane feed ($H_2/C_3H_8 = 1$) lower conversions, higher selectivities and enhanced catalyst stability were observed (Tables 25 and 26). Coke deposition was quite rapid at 1200°F, however, and the reactor plugged after 60 minutes reaction time (LHSV = 20). As in the case of no hydrogen added to the feed, the reactor plugging appeared to occur below the catalyst bed on the metal sleeves. The enhanced catalyst stability with the hydrogen-propane feed together with the copious coke deposition outside of the catalyst bed suggests that hydrogen is beneficial in removing coke from the catalyst (or suppressing its formation) but does not remove coke deposited on the metal surface within the reactor.

With another potassium promoted chromia on alumina catalyst (8219-63-3) lower conversions with high selectivities for propylene were observed

(Tables 25 and 26). This catalyst was less stable than the previously described catalyst although the coke deposition rate appeared to be lower. Possibly the loss in activity was due to poisoning other than coke. This catalyst was readily regenerable at 1022°F with a 5-10% oxygen in argon gas stream.

The molybdena on alumina catalyst gave very poor performance with only 1.5-7.4% conversion and 77.5-53.5% selectivity for propylene in the temperature region of 1022-1274°F (Tables 25 and 26). This catalyst was also regenerable at 1030°F with 5-10% oxygen in argon gas.

From the results of these preliminary experiments the 2% K_2O, 8% chromia catalyst No. 8219-63-1, was chosen as the standard chroma-alumina catalyst for our work.

Procedure for Carrying Out the Experiments

Chromia on Alumina Catalyst

To carry out a test the catalyst was loaded into the reactor tube, the reactor assembled and pressure tested (~400 psig) and the reactor brought to temperature with argon flowing through the reactor. The argon was then shut off and the propane (or propane and then hydrogen) flow started and maintained for the 90 minute test period. The propane flow was then stopped, the reactor flushed with argon for at least 15 minutes and the reactor brought to 1022°F for catalyst regeneration. The catalyst was regenerated by passing a mixture of 5-10% oxygen in argon through the reactor at 1022°F until the catalyst bed temperature was the same as was observed with pure argon flowing through the reactor. After regeneration was complete the reactor was flushed with argon for 15 minutes, the reactor brought to reaction temperature, and another test conducted in the manner just described.

Platinum on Alumina Catalyst

The platinum catalyst was stored in the unreduced form. Tests with this catalyst were carried out in the same manner as for the chromia catalyst except that the catalyst was reduced with hydrogen just before starting the experiment. The reduction was carried out as follows. After loading and pressure testing the reactor was brought to 572°F in argon and then hydrogen flow started. The catalyst was held at this temperature in hydrogen for 30 minutes and then brought to reaction temperature. The flow was maintained and the catalyst held at the reaction temperature for one hour after which the hydrogen was shut off and the feed flow started. After catalyst reduction the catalyst was always cooled to below 572°F or brought up to reaction temperature in an atmosphere of hydrogen.

Calculation of Conversions, Selectivities and Coke Formed

The conversions and selectivities were calculated on the basis of gas phase (at reaction temperature) product material only; any coke or polymer formed did not enter into the calculations. Thus, conversions are minimum and selectivities are maximum values. The coke formed during reaction was not measured directly. This was because some coke was deposited on the walls of the reactor tube, the thermocouple well and on the spaces below the catalyst bed that did not burn off when the catalyst was regenerated.

An estimate of the coke formed was made from the product analyses for the dehydrogenation of propane reaction. Analysis of the coke gave an empirical composition of $C_nH_{0.49n}$. Assuming no hydrogen transfer reactions (i.e., hydrocracking) then the percent propane converted to coke is given by 0.31 m, where $m = \%\ H_2$ formed $- \%\ C_3H_6$ formed. The values for the coke calculated by this method are recorded in Table 25.

Calculation of Heat Sinks and Heats of Reaction

Endothermic heats of reaction were calculated from the conversion, selectivity for a given product and the thermodynamic heat of reaction at 100% conversion. Thus, the contribution to the total heat of reaction by any given reaction is given by $H_R = C_P x S_P x H_P$ where

C_P = Conversion to product P

S_P = Selectivity for product P

H_P = Thermodynamic heat of reaction to form product P.

Thermodynamic heats of reaction H_R, for the various hydrocarbons are tabulated in Table 27.

Composition and Physical Properties of Catalysts

Platinum Catalysts

No. 7947-60:	1% Pt on Harshaw 0104 alumina, surface area = 91 m^2/g.
UOP-R8:	0.76% Pt, 0.35% chloride, 0.34% fluoride on alumina support, surface area = 180 m^2/g.

Chromia on Alumina Catalysts

No. 8219-63-1:	(standard catalyst), Catalysts and Chemicals, Inc. CCI-C94, 2% K_2O, 8% Cr_2O_3 on alumina support, surface area = 179 m^2/g.
No. 8219-63-3:	1.5% K_2O, 9% Cr_2O_3 on alumina support, surface area = 76 m^2/g.

Molybdena on Alumina Catalyst

No. 8219-63-5:	10% MoO_3 on alumina support, surface area = 84 m^2/g.

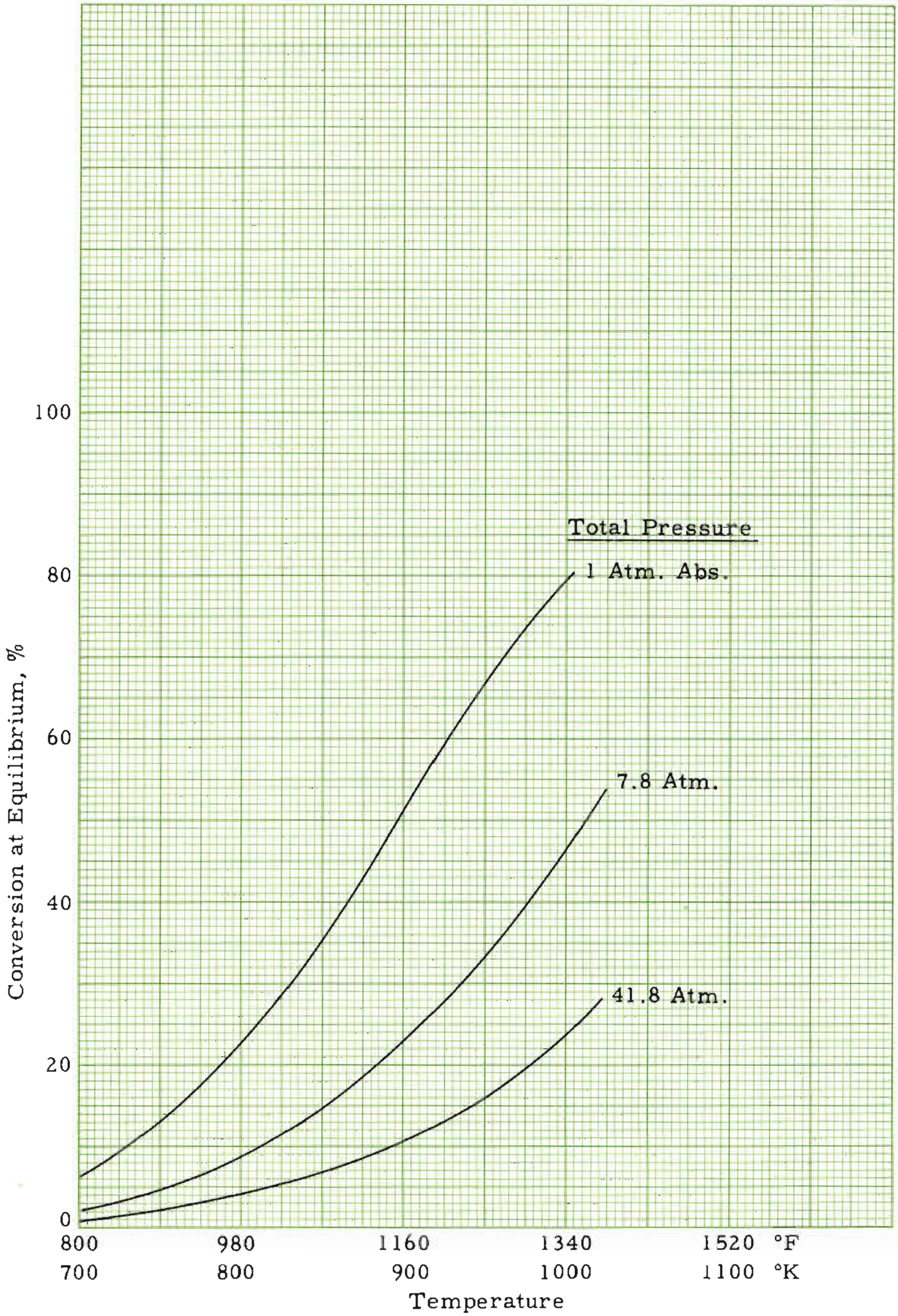

Figure 28. EQUILIBRIUM CONVERSIONS OF PROPANE TO PROPYLENE AND HYDROGEN WITH PURE PROPANE FEED

TABLE 24
CALCULATED CONTACT TIME AND SPACE VELOCITY FOR THERMAL CRACKING OF CETANE (AT 60% CONVERSION)

Rate data from WADD TR-60-841, Fig. 1 (J. O. Smith et al, Monsanto).

Based on:

$$t_{0.6} = \frac{2.303}{k} \log \frac{1}{.4} = \frac{0.92}{k} = \text{ACT}$$

and

$$\text{LHSV} = \frac{44 \cdot \text{Mol Wt} \cdot P(\text{ats})}{d_{68°F} \cdot T(°K) \cdot \text{ACT}} = \frac{44 \times 226}{0.78 \times 0.92} \cdot \frac{kP}{T} = 13857 \frac{kP}{T}$$

Temperature		Pressure		Specific Rate Constant, k, sec^{-1}	Apparent Contact Time Required for 60% Conv., seconds	Liquid Hourly Space Velocity, (LHSV)
°F	°K	psia	atms			
1000	811	20	1.4	0.009	102	0.21
"	"	100	6.8	"	"	1.05
"	"	200	13.6	"	"	2.1
"	"	500	34	"	"	5.2
"	"	1000	68	"	"	10.4
1100	866	20	1.4	0.058	15.3	1.3
"	"	100	6.8	"	"	6.3
"	"	200	13.6	"	"	12.6
"	"	500	34	"	"	31.6
"	"	1000	68	"	"	63.2
1200	922	20	1.4	0.23	4.0	4.7
"	"	100	6.8	"	"	23.5
"	"	200	13.6	"	"	47
"	"	500	34	"	"	118
"	"	1000	68	"	"	236
1350	1005	20	1.4	0.7	1.32	13.1
"	"	100	6.8	"	"	65.5
"	"	200	13.6	"	"	131
"	"	500	34	"	"	328
"	"	1000	68	"	"	656

TABLE 25
DEHYDROGENATION OF PROPANE

Pressure: 1 atm

Catalyst	Catalyst Weight, g	LHSV	Feed	Block Temp, °F	Catalyst Bed Temperature, °F			Conversion of Propane, %			Selectivity for Propylene, %			Propane Converted to Coke, %
					30 min Reaction Time	60 min Reaction Time	90 min Reaction Time	30 min Reaction Time	60 min Reaction Time	90 min Reaction Time	30 min Reaction Time	60 min Reaction Time	90 min Reaction Time	
8219-63-1	12.87	10	Pure C_3H_8	1022	928	932	938	22.5	21.5	21.0	94.5	94.4	94.1	1.9
2% K_2O; 8% Cr_2O_3;		20		1112	977	982	988	19.0	17.5	17.0	98.7	98.7	96.5	0.7
		20		1200	1034	1052	(a)	27.0	25.5	(a)	89.5		(a)	3.1
	12.91	10	50% C_3H_8 50% H_2	1022	995	990	988	10.2	8.6	9.9	97.9	98.0	97.9	-
		20		1112	1031	1040	1040	13.5	12.8	11.8	98.8	98.5	98.5	-
		20		1200	1103	1107	(a)	19.5	18.6	(a)	94.9	83.9	(a)	-
8219-63-3	18.97	10		1022	948	961	-	21.0	17.8	-	97.7	98.0	-	0.00
1.5% K_2O; 9% Cr_2O_3;		20		1112	1018	1051	1060	15.9	11.0	6.8	98.5	99+	98.4	0.06
		20		1200	1148	1168	1171	10.5	4.2	3.5	94.8	92.7	91.1	0.17
		20		1274	1236	1245	(a)	12.6	12.3	(a)	74.3	66.0	(a)	0.63
	18.44	10	50% C_3H_8 50% H_2	1022	975c)	991	989	8.5c)	10.6	10.5	99+c)	99+	99+	-
		20		1112	1040	1045	1051	15.9	13.4	14.0	96.5	98.6	96.0	-
		20		1200	1121	1114b)	-	20.0	19.5b)	-	91.4	88.2b)	-	-
8219-63-5	20.64	10		1022	1000	1011	1006	5.6	3.5	2.5	82.5	82.0	87.6	2.8
10% MoO_3		20		1112	1074	1081	1083	3.4	2.0	1.5	77.5	78.0	73.4	1.2
		20		1200	1168	1170	1175	3.8	3.2	3.4	67.6	71.0	66.6	0.9
		20		1274	1236	1243	1242	7.3	7.1	7.4	53.5	61.1	58.0	0.9

a) Reactor plugged due to coke after 60 minutes reaction time.
b) Reactor plugged due to coke after 44 minutes reaction time.
c) LHSV = 20.

TABLE 26
DEHYDROGENATION OF PROPANE PRODUCT DISTRIBUTION

Pressure: 1 atm
Compositions in mol %
LHSV = 10
Temperature: 1030°F

Run No. Catalyst	1 8219-63-1	2 8219-63-2	3 8219-63-3
Hydrogen	17.1	12.0	7.8
Argon	8.0	10.6	8.4
Methane	0.4	0.3	0.5
Ethane	0.3	0.1	-
Propylene	15.2	11.8	3.8
Propane	58.9	62.9	77.9
N_2 + CO	-	1.7	0.8
Ethylene	-	-	0.5

TABLE 27
THERMODYNAMIC HEATS OF REACTION

Hydrocarbon	Reaction Products	H_R, Btu/lb
Methylcyclohexane	toluene, H_2	940
	benzene, H_2, CH_4	710
	cyclohexene, CH_4	286
	cracked products	-60[a)]
Ethylcyclohexane	ethylbenzene, H_2	810
	styrene, H_2	1285
	toluene, H_2, CH_4	565
	benzene, H_2, C_2H_6	650
	benzene, H_2, C_2H_4	1200
	xylene, H_2	ca 810
	cracked products	-585[a)]
Propane	propylene, H_2	1260
	cracked products	850
n-Heptane	olefin, H_2	560
	diolefin, H_2	1000
	benzene, H_2, CH_4	875
	toluene, H_2	1090
	cracked products	271
n-Octane	octene, H_2	491
	octadiene, H_2	ca 900
	styrene, H_2	1425
	ethylbenzene, H_2	957
	xylene, H_2	915
	toluene, H_2, CH_4	718
	benzene, H_2, C_2H_6	804
	cracked products	258
i-Octane (2,2,4-trimethylpentane)	octene, H_2	473
	octadiene, H_2	907
	toluene, H_2, CH_4	762
	mixed aromatics	ca 950
	cracked products	-138[a)]
Dimethylhexanes (2,4- and 2,5-isomers)	octene, H_2	458
	octadiene, H_2	907
	toluene, H_2, CH_4	ca 760
	xylene	948
	cracked products	-240[a)]

a) Exothermic.

(Continued)

TABLE 27 (CONTD)
THERMODYNAMIC HEATS OF REACTION

Hydrocarbon	Reaction Products	H_R, Btu/lb
2,2,5-Trimethylhexane	nonene, H_2	408
	nonadiene, H_2	809
	xylene, H_2, CH_4	605
	cracked products	-480a)
n-Dodecane	dodecene, H_2	330
	dodecadiene, H_2	595
	aromatics, H_2	ca 640
	cracked products	-110a)
n-Hexadecane (cetane)	cracked products	131

a) Exothermic.

TABLE 28
SENSIBLE ENDOTHERMIC HEATS FOR VARIOUS HYDROCARBONS

Hydrocarbon	Sensible Heat, Btu/lb, at °F$^{a)}$					
	846	934	1022	1112	1202	1283
Methylcyclohexane	715	780	850	920	990	1065
Ethylcyclohexane	-	-	-	807	889	-
Propane	-	-	1000	1060	1117	1170
n-Heptane	-	-	763	838	917	-
n-Octane	-	-	820	890	980	1055
i-Octane (2,2,4-trimethylpentane)	-	-	-	830	910	-
Dimethylhexanes	-	-	-	835	910	-
2,2,5-Trimethylhexane	-	-	-	835	910	-
n-Dodecane	-	-	615	685	755	-
n-Hexadecane (Cetane)	-	-	-	825	900	-

a) Includes heat of vaporization. Starting temperature taken as 70°F for all hydrocarbons except for propane methylcyclohexane and n-octane for which starting temperature was the freezing point.

TABLE 29
HYDROCARBON FEEDSTOCKS

Hydrocarbon	Manufacturer	Grade	Manufacturer's Specifications, % Minimum	Laboratory Analysis
Methylcyclohexane	Phillips	Pure	99	99.8% MCH
Methylcyclohexane	Phillips	Technical	95	1.1% lighter than MCH, 98.9% MCH
Methylcyclohexane	Phillips	Commerical	-	75% MCH, 7.6% toluene, 17.4% lighter than MCH
Ethylcyclohexane	Mathieson	Practical	-	2.3% methylcyclohexane, 97.7% ethylcyclohexane
Propane	Mathieson	Pure	99	0.6% propylene, 99.4% propane
n-Heptane	Phillips	Pure	99	-
n-Octane	Phillips	Pure	99	-
i-Octane (2,2,4-trimethylpentene)	Phillips	Pure	99	-
Mixed Dimethylhexenes	Phillips	Pure	99	-
2,2,5-Trimethylhexane	Phillips	Pure	99	-
n-Dodecane	Humphry-Wilkinson	-	-	98.5% n-dodecane, 1.5% lighter than C_{12}
n-Hexadecane (cetane)	Humphry-Wilkinson	-	-	97% hexadecane, 3% lighter than C_{16}

TABLE 30
DEHYDROGENATION OF n-HEPTANE

Run No. 8277-	197			199		200		8546-6		Thermal Reaction (Metal Reactor)		
Catalyst	Cr_2O_3/Al_2O_3 a)			Cr_2O_3/Al_2O_3 a)		Cr_2O_3/Al_2O_3 a)		Pt on Al_2O_3 b)				
Pressure, atm	1			10		10		10		10		
LHSV	7.4			26		26		20		20		
Block Temp, °F	1112	1112	1112	1112	1112	1202	1202	1112	1112	1022	1112	1202
Catalyst Temp, °F	1047	1052	1058	973	979	1065	1080	1027	1027	981	1053	1121
Reaction Time, min	30	60	90	30	60	30	60	30	60	20	20	20
Product Analysis, %												
n-Heptane	52.7	60.5	66.0	69.0	68.5	52.1	59.0	72.6	76.0	98.7	85.4	66.0
Heptenes	7.1	6.9	6.7	10.9	8.8	5.5	4.0	3.8	2.5	-	-	-
Heptadienes	2.0	1.7	1.9	1.4	1.4	1.6	0.9	0.6	0.3	-	-	-
Benzene	1.2	0.9	0.9	0.4	0.3	1.0	0.3	0.3	0.1	-	-	-
Toluene	14.6	10.5	8.6	5.6	3.4	5.3	1.3	1.8	0.9	-	-	-
Other Aromatics	0.2	0.1	0.2	-	-	-	-	0.5	0.4	-	-	-
Cracked Products	22.3	19.7	15.9	12.0	17.9	34.1	34.4	20.1	19.7	1.3	14.6	34.0
Heptane Conv., %	47.3	39.5	34.0	31.0	31.5	47.9	41.0	27.4	24.0	1.3	14.6	34.0
Heat Sink, Btu/lb												
Reaction	464	559	537	553	481	413	331	369	357	ca 1	40	92
Total	1302	1397	1375	1391	1319	1330	1248	1207	1195	ca 764	878	1009

a) 2% K_2O, 8% Cr_2O_3 on Al_2O_3.

b) UOP-R8: 0.76% Pt, 0.35% Cl, 0.34% F on Al_2O_3.

TABLE 31
DEHYDROGENATION OF n-OCTANE OVER CHROMIA ON ALUMINA CATALYST

Catalyst: 2% K_2O, 8% Cr_2O_3 on Al_2O_3

Run No. 8219-	177		179		181		184	
Pressure, atm	1		1		1		10	
LHSV	0.9		6.5		6.5		21.8	
Block Temp, °F	1022	1022	1112	1112	1202	1202	1202	1202
Catalyst Temp, °F	986	988	1065	1085	1146	1157	1049	1065
Reaction Time, min	30	90	30	90	30	90	33	90
<u>Product Analysis, %</u>								
n-Octane	85.8	88.0	48.7	64.2	28.1	36.1	40.5	50.3
Octene	7.6	6.3	6.4	6.4	3.2	5.0	3.3	1.9
Octadiene	1.1	1.0	1.7	1.1	0.6	0.8	0.2	0.2
Benzene	0.3	0.3	2.9	0.8	2.5	0.9	0.7	0.3
Toluene	0.3	0.3	2.1	0.8	2.4	1.0	0.6	0.1
Ethylbenzene[a)]	1.0	0.7	5.8	2.2	4.2	1.8	0.7	0.1
o-Xylene	1.1	0.7	5.9	2.3	4.6	1.7	0.6	0.1
Styrene	0.1	-	1.3	0.4	2.0	0.4	0.1	T
Cracked Products	2.6	2.7	26.1	21.6	52.4	52.3	53.3	47.0
Octane Conv., %	84.2	12.0	51.1	35.8	71.9	63.9	59.5	49.7
<u>Heat Sink, Btu/lb</u>								
Reaction	64	55	317	198	420	320	236	206
Total	825	816	1154	1035	1335	1235	1151	1121

a) Ethylbenzene and m,p-xylene were not separable on the GLC

TABLE 32
DEHYDROGENATION OF ISOOCTANE

Run No. 8546-	20		21		18			31		
Catalyst	Cr_2O_3/Al_2O_3 a)		Cr_2O_3/Al_2O_3 a)		Thermal Reaction (Vycor Reactor)			Thermal Reaction (Metal Reactor)		
Pressure, atm	1		10		1			10		
LHSV	5		20		5			20		
Block Temp, °F	1112	1112	1202	1202	1030	1119	1208	1022	1112	1202
Catalyst Temp, °F	1076	1089	1096	1105	1030	1119	1208	977	1058	1130
Reaction Time, min	30	90	30	90	20	20	20	20	20	20
Product Analysis, %										
Isooctane	73.1	88.0	52.2	57.9	98.4	95.6	69.2	97.7	94.3	71.4
Octenes	7.6	2.6	1.5	1.6	-	0.6	1.8	0.8	0.7	1.7
Octadienes	0.9	0.5	1.0	0.7	-	0.2	1.1	-	-	0.7
Benzenes	0.2	-	-	-	-	-	0.1	-	-	-
Toluene	1.4	0.5	0.7	0.4	-	-	0.2	-	-	0.2
Xylene	9.8	2.5	1.3	0.6	-	-	-	-	-	-
Cracked Products	6.8	5.6	43.1	38.7	1.6	3.5	27.4	1.6	4.8	25.7
i-Octane Conv., %	26.9	12.0	47.8	42.1	1.6	4.4	30.8	2.3	5.7	28.6
Heat Sink, Btu/lb										
Reaction	111	38	-29	-30	-	0	1	-	-	-
Total	941	868	881	880	ca 750	830	911	ca 750	ca 830	991

a) 2% K_2O, 8% Cr_2O_3 on Al_2O_3.

TABLE 33
DEHYDROGENATION OF MIXED DIMETHYLHEXANES

Run No. 8546-	25		27		
Catalyst	Cr_2O_3/Al_2O_3 b)		Thermal Reaction (Metal Reactor)		
Pressure, atm	10		10		
LHSV	20		20		
Block Temp, °F	1112	1112	1022	1112	1202
Catalyst Temp, °F	972	975	974	1053	1123
Reaction Time, min	30	90	20	20	20
Product Analysis, %					
Dimethylhexane (DMH)	57.8	62.8	97.6	85.6	68.0
Dimethylhexene	9.4	8.1	0.1	0.6	1.0
Dimethylhexadienes	1.3	1.3	-	-	0.6
Toluene	1.0	0.9	-	-	-
Xylene a)	9.5	6.4	-	-	0.1
Cracked Products	20.7	21.1	2.3	14.1	30.6
DMH Conv., %	42.2	37.2	2.4	14.4	32.0
Heat Sink, Btu/lb					
Reaction	261	162	-	-35	-74
Total	1096	997	ca 760	800	836

a) Xylene fraction contained no ortho-xylene.
b) 2% K_2O, 8% Cr_2O_3 on Al_2O_3.

TABLE 34
DEHYDROGENATION OF 2,2,5-TRIMETHYLHEXANE

Run No. 8546-	23		29		
Catalyst	Cr_2O_3/Al_2O_3 [c]		Thermal Reaction (Metal Reactor)		
Pressure, atm	10		10		
LHSV	20		20		
Block Temp, °F	1112	1112	1022	1112	1202
Catalyst Temp, °F	997	1000	968	1049	1119
Reaction Time, min	30	90			
<u>Product Analysis, %</u>					
Trimethylhexane (TMH)	66.4	72.3	97.3	92.8	76.6
Olefins	5.0	3.5	0.3	0.7	2.1
Diolefins	0.8	0.6	-	-	0.7
Benzene	0.2	0.1	-	-	0.2
Toluene	0.2	0.2	-	-	0.1
Xylene [a]	2.3	1.1	-	-	0.1
Styrene [b]	0.6	0.3	-	-	-
Cracked Products	24.6	22.1	2.4	6.5	20.0
TMH Conv., %	33.6	27.7	2.7	7.2	23.4
<u>Heat Sink, Btu/lb</u>					
Reaction	-66	-74	ca -1	ca -3	-92
Total	769	761	ca 759	ca 832	818

a) Xylene fraction contained no ortho-xylene.
b) Styrene indentified by GLC emergence time.
c) 2% K_2O, 8% Cr_2O_3 on Al_2O_3.

TABLE 35
DEHYDROGENATION OF n-DODECANE

Run No. 8219-	188		190		193	
Catalyst	Cr_2O_3/Al_2O_3 b)		Cr_2O_3/Al_2O_3 b)		Cr_2O_3/Al_2O_3 b)	
Pressure, atm	1		1		10	
LHSV	5		5		20	
Block Temp, °F	1022	1022	1202	1202	1112	1112
Catalyst Temp, °F	966	980	1143	1155	957	959
Reaction Time, min	30	90	30	90	30	90
<u>Product Analysis, %</u>						
Dodecane	58.6	70.4	14.1	14.3	38.8	50.6
Dodecenes	10.3	8.8	3.9	3.3	5.8	3.8
Dodecadienes	4.1	3.1	3.9	2.4	2.4	0.3
Aromatics a)	15.1	7.4	6.7	3.3	3.6	0.4
Cracked Products	11.8	10.7	71.1	76.8	49.6	44.9
Dodecane Conv., %	41.4	29.6	85.9	85.7	61.2	49.4
Heat Sink, Btu/lb						
Reaction	137	86	-3	-36	+2	-31
Total	750	699	753	720	685	652

a) Aromatics were mostly hexylbenzenes.
b) 2% K_2O, 8% Cr_2O_3 on Al_2O_3.

TABLE 36
DEHYDROGENATION OF n-HEXADECANE (CETANE)

Run No. 8546-	8		11			40		
Catalyst	Cr_2O_3/Al_2O_3 a)		Thermal Reaction (Vycor Reactor)			Thermal Reaction (Metal Reactor)		
Pressure, atm	10		1			10		
LHSV	8.7		5			8.7		
Block Temp, °F	1112	1112	1022	1122	1209	1024	1116	1206
Catalyst Temp, °F	1065	1065	1033	1119	1209	995	1062	1128
Reaction Time, min	30	60	20	20	20	20	20	20
Product Analysis, %								
n-Hexadecane	8.0	16.1	79.2	51.7	18.7	46.1	23.3	6.0
Hexadecenes	1.4	1.0	0.3	0.5	0.2	1.3	1.1	0.2
Diolefins	-	-	-	-	-	-	-	-
Aromatics	-	-	-	-	-	-	-	-
Cracked Products	90.6	82.9	20.5	47.4	81.1	52.5	76.1	93.5
Hexadecane Conv., %	92.0	85.9	20.8	48.3	81.3	53.9	76.7	94.0
Heat Sink, Btu/lb								
Reaction	120	108	27	63	106	70	100	122
Total	945	933	777	888	1006	820	925	1022

a) 2% K_2O, 8% Cr_2O_3 on Al_2O_3.

TABLE 37
DEHYDROGENATION OF METHYLCYCLOHEXANE OVER PLATINUM ON ALUMINA CATALYSTS

Pressure: 10 atm
Feed: Pure Methylcyclohexane
Catalyst Size: 10-20 mesh

Run No. 8277-	Catalyst	Catalyst Volume, ml	Feed	Total Reaction Time, min	LHSV	Reaction Temp, °F		Liquid Product Analysis, %				MCH Conv., %	Selectivity for, %			Heat Sink, Btu/lb	
						Block	Catalyst Bed	MCH	Toluene	Cracked Product	Others[a]		Toluene	Cracked Product	Others	Reaction	Total at Block Temp
68	1% Pt; Lab Catalyst No. 7947-60	20	Pure Grade	30 60 90	20 20 20	1022 1022 1022	640 653 659	8.9 8.6 8.5	90.4 90.7 90.8	0.5 0.5 0.5	0.2 0.2 0.2	91.1 91.4 91.5	99.2 99.2 99.2	0.6 0.6 0.6	0.2 0.2 0.2	856 859 860	1706 1709 1700
69	1% Pt; Lab Catalyst No. 7947-60	20	Pure Grade	30 60	53 53	1112 1112	649 686	39.6 39.3	60.0 60.3	0.4 0.4	T T	60.4 60.7	99.4 99.2	0.6 0.7	- -	565 571	1485 1491
73	1% Pt; Lab Catalyst No. 7947-60	20	Pure Grade	30 60	53 53	1202 1202	718 729	35.0 33.9	64.4 65.2	0.4 0.5	0.2 0.4	65.0 66.1	99.1 98.6	0.6 0.8	0.3 0.6	607 618	1597 1608
76	1% Pt; Lab Catalyst No. 7947-60	20	Pure Grade	30 150	20 20	1022 1022	684 700	16.2 21.6	83.2 77.9	0.5 0.5	0.1 T	83.8 78.4	99.2 99.4	0.6 0.6	0.2 -	788 735	1638 1585
79	1% Pt; Lab Catalyst No. 7947-60	20	Pure Grade	30	20	1022 1202 1202 1202	622 684 684 750	11.1 31.8 16.9 14.3	88.2 67.6 82.3 84.3	0.5 0.4 0.5 0.6	0.2 0.2 0.3 0.8	88.9 68.2 83.1 85.7	99.3 99.1 98.9 98.3	0.6 0.6 0.6 0.7	0.2 0.3 0.4 0.9	837 637 780 806	1687 1627 1770 1796
88	1% Pt; Lab Catalyst No. 7124-117	20	Pure Grade	30 60	20 20	1022 1022	626 631	10.6 12.2	88.9 87.2	0.5 0.5	0.1 0.1	89.4 87.8	99.3 99.2	0.6 0.6	0.1 0.1	840 825	1690 1675
95	0.7% Pt-Platforming Catalyst UOP-R8	20	Pure Grade	30 60	20 20	1022 1022	626 633	8.2 9.0	90.8 90.0	0.7 0.8	0.3 0.2	91.8 91.0	98.8 98.9	0.8 0.9	0.3 0.2	862 855	1712 1705
97	0.7% Pt-Platforming Catalyst UOP-R8	20	Tech. Grade[b]	30 60	20 20	1022 1022	626 624	12.1 13.0	85.2 84.2	2.4 2.4	0.2 0.2	87.9 87.0	96.8 96.7	2.7 2.8	0.2 0.2	800 791	1650 1641
98	0.7% Pt-Platforming Catalyst UOP-R8	20	Comm. Grade[c][d]	30 60	20 20	1022 1022	682 686	12.7 14.5	85.2 82.4	2.8 2.8	0.3 0.3	87.3 85.5	97.6 96.3	3.2 3.3	0.3 0.3	617 596	1467 1446
Diluted Catalyst Bed																	
100	1% Pt; Lab Catalyst No. 7947-60	7	Pure Grade	30 60	20 20	842 842	646 640	3.0 2.0	96.4 97.2	0.5 0.7	0.1 0.1	97.0 98.0	99.4 99.2	0.5 0.7	0.1 0.1	912 921	1692 1701
101	1% Pt; Lab Catalyst No. 7947-60	7	Pure Grade	30 60	50 50	1112 1112	838 835	2.8 3.0	95.2 96.1	0.8 0.6	0.4 0.3	97.2 97.0	98.0 99.1	0.8 0.6	0.4 0.3	896 903	1816 1823
103	1% Pt; Lab Catalyst No. 7947-60	7	Pure Grade	30	100	1202	918	36.1	62.5	0.6	0.8	63.9	97.8	1.3	0.9	588	1578
Thin Catalyst Bed																	
92	1% Pt; Lab Catalyst No. 7947-60	7	Pure Grade	30 30	20 50	842 1022	690 684	4.0 30.5	95.2 69.0	0.6 0.5	0.2 -	96.0 69.5	99.2 99.3	0.6 0.7	0.2 -	900 654	1680 1504

a) "Others" = methylcyclohexene plus benzene.
b) Feed analyzed to be 99.0% MCH, 1.0% lighter than MCH.
c) Feed analyzed to be 75.0% MCH, 7.4% toluene and 17.6% lighter than MCH.
d) Analyses based on MCH reacted and do not include amounts present in feed.

Thermal and Storage Stability

Background and Evaluation

The jet fuel thermal instability problem has been with us now a decade. Early experience with the problem was recently summarized as follows:(51)

"The problem of jet fuel thermal instability was first brought to industry's attention in 1953. Serious performance problems encountered in engines installed in high-performance aircraft are described in reference 1.[1]) Lack of thermal stability in jet fuels, resulting in deposits which plugged critical strainers and orifices, were determined to be the cause of difficulty in many cases. This led to extensive work by the engine manufacturer and numerous petroleum companies to develop tests which would permit evaluation and control of thermal stability characteristics of jet fuel. The paper quoted above is but one of many which have been presented on this subject. Unfortunately, despite considerable effort by many groups, none of the various bomb, glassware, or other simple laboratory devices studied have been developed to a completely satisfactory level.

"Despite the obvious desirability of a small, simple laboratory test, it soon became obvious that this objective was not to be easily achieved. Accordingly, a major aircraft company, with the cooperation of a number of major petroleum companies, developed a dynamic test referred to as 'fuel coker'. A prototype unit of the coker provided early test results which lined up closely with the full-scale rig used by the engine manufacturer for evaluating the basic problem. At this point, it was recognized that a considerably greater developmental effort would be required before a 'fuel coker' could be considered a useful and acceptable tool for evaluating and controlling fuel thermal stability. Accordingly, the problem was presented to the Coordinating Research Council for assistance in 1954.

"Despite the existence of a number of 'fuel cokers' at that time, the CRC program undertaken was extensive. Although the problems involved in studying test repeatability and reproducibility were straightforward, it was already known that a test of this type would involve some wide variations. An even greater problem was that of establishing the significance of the test, i.e., would the fuel coker predict fuel performance in the same manner as the full-scale engine under flight conditions. There were also many mechanical problems to be expected in a device which required the circulation of fuel under high-temperature and high-pressure conditions. The CRC group to cope with these problems was organized March 1, 1955, and was known as the CFR-AFD Fuel Thermal Stability Group. This group pursued its studies of the fuel coker and also directed its efforts to develop other small-scale laboratory tests. The results of this work are described in detail in a CRC released report.[53]) Reference 54 provides a convenient summary of this activity.

"The ASTM-CRC Fuel Coker had definite limitations on the temperatures and pressure which could be used for evaluation of thermal stability. In view of the interest by both the Military and industry in thermal stability evaluation at higher temperatures, studies were made by the Equipment Panel of the

CRC Fuel Thermal Stability Group to develop means of achieving high-temperature fuel evaluation either through modification of existing equipment or development of new equipment. Since equipment was desired for evaluation of fuel thermal stability under conditions of supersonic flight, it was recognized that fuel in the tanks would be heated by the high stagnation temperatures surrounding the airframe under supersonic flight conditions. Preliminary studies led to the development of the CRC High-Temperature Research Fuel Coker. This equipment provides for long residence time fuel heating comparable to that which may be expected in aircraft fuel tanks under supersonic conditions, as well as short residence time heating which may be expected in critical engine components. Temperatures up to 750°F or higher may be achieved in the short residence time components."

The earlier work on the effect of composition, contaminants, storage, treatment and additives on thermal stability has been reviewed in a recent book.[55)] Excerpts from this publication are included by permission of the author.

"Fuels are rated both on their tendency to cause deposits on the preheater and the rate at which they increase the pressure drop across the filter. The problem with respect to thermal stability is essentially one of oxidation stability since rigorous exclusion of oxygen greatly reduces the tendency of the fuel to form heat exchanger or filter deposits (109). Also, as is shown in Table XIX, the deposits contain a substantial amount of oxygen. This is true whether the deposits were formed in the laboratory apparatus, in a bomb or in an actual jet engine.

TABLE XIX

Composition of High Temperature Deposits

	Cumulative heat exchanger deposits[a)]		Oxygen bomb[b)]	Jet (44) engine nozzle
	Tube	Filter	Deposit	deposit
Oxygen, %w.	14.7	29.5	22.5	14.8
Sulfur, %w.	1.4	-	3.6	5.3
Nitrogen, %w.	3.3	-	2.1	4.6
Carbon, %w.	70.6	40.8	60.6	31.6
Hydrogen, %w.	4.7	5.3	5.2	4.0
C:H atomic ratio	1:0.8	1:1.6	1:1	1:1.5
Acidity, eq./100 g.	0.02	0.25	1.38	-
Ash and unacc.	5.3	20	6.0	34.4

a) At 450°F.

b) 5 hr. at 320°F + 100 psig O_2.

"The nature of the oxygen present in the deposits is difficult to ascertain owing to the great insolubility of the deposits and their very dark color. However, it is possible to detect the presence of carbonyl and aldehyde functional groupings. Also, the material behaves like a strong acid when titrated with caustic (being somewhat similar in nature to a base exchange resin), but the nature of the configuration responsible for this behavior is not known (109). Generally speaking, increasing the temperature in the preheat section increases the deposition rate on the preheater heat exchange surface and decreases the filter plugging time. However, there is some evidence that with some fuels these rules may not be followed (81). Decreasing the contact time by increasing the flow rate may have a variable effect depending upon the nature of the fuel (36, 44). The efficiency of the deposits in plugging the filter varies widely. Minor, Nixon, and Thorpe (116) show differences in the amount of deposit required to increase the pressure drop across the 5 micron stainless steel filter from 0 to 30 psi, of from 1 milligram to more than 30 milligrams with different fuels in the absence of additives. In the presence of a dispersant type additive the amount of material to plug the filter rose to more than 55 milligrams; this behavior is undoubtedly related to the different character of the insolubles as referred to the above. A hard crystalline material has little tendency to plug the filter, whereas a soft diaphanous type is very effective. In the presence of a dispersant, the deposit penetrates into the filter thus allowing accumulation of a great deal more deposit before the filter plugs.

"B. Effect of fuel composition. In general, there is no overall correlation between jet fuel composition and thermal stability. Barringer (12) found for 34 JP-4 fuels in the CFR coker that there was no apparent correlation between fuel source, sulfur content, olefin and aromatic content and performance. All of the fuels were well within specification limits in these respects as well as in regard to existent and accelerated gum. Some of the poorest fuels in the CFR coker tests were the lowest in gum and sulfur. Barringer's results confirm those obtained by Nixon, et al (104, 116, 117) who found similar results with their different type of apparatus. They also investigated the effect of adding small quantities of fractions of hydrocarbons and compounds separated from a catalytically cracked gas oil by a chromatographic procedure. The results in terms of increase in pressure drop across a 5-micron filter are shown in Figures 11 and 12. All the fractions with the exception of the olefins and saturates decreased the thermal stability of the fuel. The phenols, resins, nitrogen bases and diolefins were particularly deleterious. It should be noted, however, from the deposition rate on the filter and the time required for the run that the greatest effect was on the filter plugging efficiency of the insolubles formed as measured by the weight of insolubles caught on the filter rather than a very great effect on the rate of production of insolubles.

"As far as the thermal stability of the bulk hydrocarbons is concerned there is scarcely enough data under enough conditions to warrant general statements. Heath, et al (73) examined alpha-methylnaphthalene, cetane, triisobutylene and tetralin in the CFR coker at 400°F. preheater temperature, 500°F. filter temperature and decided that all of these compounds when freed from contaminants were essentially stable, triisobutylene being the least stable. Nixon and co-workers (116), on the other hand, found that dodecanes, dodecene-1, cetene and cis-decalin were very stable followed by tetralin and cetane, with alpha-methylnaphthalene being least stable in their 'heat exchanger' test at 450°F. Again there was a very great variation in the rate at which filter deposits were formed and the efficiency of the deposits in plugging filters. In all cases there is some increase in soluble gum as measured by steam evaporation of the hydrocarbon after it is passed through the apparatus, but there is no relation between the magnitude of the increase in gum value and the efficiency of the material in plugging the filter. This is particularly true with the olefins, where the gum content rose by 600 and 1000 mg./dl. The analysis of the residue left after steam evaporation in the case of dodecene-1 was as follows: molecular weight, 1089; acidity, equiv./100 g. 0.006; ester value, equiv./100 g., 0.009; carbon, %wt., 84.6; hydrogen, %wt., 14.0; oxygen, %wt., 1.47. It appears that the residue consists largely of a polymer of dodecene. It is remarkable that there is such a small amount of oxygen in this material compared to the usual gum formed in jet fuels that consists of 15 to 20% oxygen. Here, there is only about 1 atom of oxygen per molecule of polymer. It suggests that the polymer is formed by a chain reaction with an average length of 6 units that is probably initiated or terminated by a RO· radical. From the contact time, it appears that this material was formed at the rate of about 30 millimoles per minute per liter. It is apparent that considerable work remains to be done before an adequate body of knowledge is built up on the effect of hydrocarbon structure on thermal stability.

"C. <u>Effect of contaminants</u>. The most probable contaminants to be found in jet fuels are soluble metals and of these, copper and iron are probably the most abundant. <u>Nixon et al</u> (104) report finding 0.5 to 0.24 p.p.m. soluble copper in 15 different jet fuels from various sources. Activation analyses also showed nickel to be present in two fuels at about 0.1 p.p.m. and also a smaller trace of vanadium. In tests to determine the effect of added copper and iron in the CFR coker, copper had quite a deleterious effect on the preheater rating but no significant effect on the filter plugging tendency. Iron, on the other hand, degraded both properties. In neither case was the commercial metal deactivator particularly effective (see Fig. 13). In the recycle heat exchanger type test the effect on the filter plugging tendency of the fuel was more pronounced; and again, the metal deactivator was not adequate to overcome the effect of the metal. With both copper and iron, it is apparent that the metal is acting as an oxidation catalyst and that the diimine type of deactivator is not able, at the temperature of the test, to prevent this action.

"D. <u>Effect of storage</u>. It would be generally expected that the degradation that goes on during storage of fuel would decrease its thermal stability, and indeed, this seems to be the general experience. However, this is by no means universally true nor is it readily predicted from the behavior of fuels in accelerated aging tests. <u>Nixon and co-workers</u> (104, 117) tested the thermal stability of two groups of fuels before and after approximately one year of storage at 43°C. in the presence of air. In the first group of five fuels, in the absence of additives, all of the fuels decreased in thermal stability by as much as 20 to 70% of the original value. Three of these fuels were straight run materials; one, an olefin-containing referee fuel, and the other, a special fuel containing 80% of catalytically cracked material. There was no correlation between the percentage decrease of thermal stability and the type of fuel or the amount of gum formed during the aging period. The results of the second study are shown in Table XX. With the group of six fuels it is seen that one showed no change in thermal stability, two increased in thermal stability by 100 and 200%, and three fuels decreased in thermal stability by 35-60%. There is no obvious explanation for this behavior. The fuel that improved most in thermal stability actually built up the most peroxide and gum during the aging period, whereas the fuels that were most degraded, regarding thermal stability, showed very little evidence from the standpoint of gum and peroxide that they had suffered any degradation. It should be noted also that the two fuels which improved in thermal stability did not contain oxidation inhibitors whereas those that suffered the most did contain oxidation inhibitors as did those that were unaffected by aging. There was no correlation between the composition of the fuels in terms of hydrocarbons or sulfur and nitrogen compounds and their behavior on aging. Barringer (12) reported that the results of studies with a group of fuels aging at 110°F. for 12 weeks showed a distinct decrease of thermal stability in the CFR coker apparatus.

"E. In-flight oxidation. When jet fuels are used in supersonic aircraft, fuel temperatures in the tanks may rise to several hundred degrees F. Some oxidation will take place in the fuel tanks under these conditions; this would be expected to have some effect on the subsequent thermal stability of the fuel. This effect was investigated (104) with seven different fuels by heating them to 100°C for 48 hours in the presence of air followed by a thermal stability test at 450°F It was found that three of the fuels were substantially unaffected with respect to filter plugging time, one was upgraded by about 50%, one was only slightly affected, another was degraded by about 20% and another by a factor of 2. Generally speaking, the deposition rates of insolubles on the filter were only slightly affected. Again there was no correlation between the tendency to form gum in the prior aging and high temperature performance. Very little peroxide was formed during the aging period except for one fuel, a paraffinic kerosene, which formed little gum but considerable peroxide. However, this did not affect the thermal stability of the fuel adversely.

"F. Effect of treatment. Generally speaking, the thermal stability of a jet fuel can be improved by any treatment that removes minor components of greater than average reactivity. But because of the variable nature of the substrate, similar treatments on different base stocks are often not equivalent in effectiveness. Crampton et al (44) found heavy sulfuric acid treatment gave an acceptable jet fuel from the thermal stability standpoint. Extraction of a kerosene with SO_2 did not yield satisfactory products. Hydrotreating appeared to be more effective but no details were given of the method employed. Heath, et al (73) conducted a more complete study of the effect of various treatments. They reported that clay percolation of alpha-methylnaphthalene greatly improved its stability but that hydrotreating was even more effective. Thus, a commercial product produced a pressure drop of 20-inches Hg across the filter in 90 minutes, the clay percolated, the same pressure drop in about 300 minutes and the hydrotreated, a pressure drop of less than 1 inch in 600 minutes. On the other hand, hydrotreating of a East Coast JP-4 straight run fuel was not as successful; the 25-inch ΔP time was increased only from 28 to 155 minutes. The treatment of a West Coast JP-5 type fuel showed the following effects in terms of the 25-inch Hg ΔP time: the original gave 57 minutes; sulfur dioxide extraction increased this to 119 minutes, acid treating of the extracted product improved it to 148 minutes, and further processing by hydrotreating increased the time to 515 minutes. No information, unfortunately, is given in this paper on the conditions of treating or their effect on the other properties of the products. The authors also state that hydrocracking, a process of catalytic cracking carried out in the presence of hydrogen, can produce stable JP-4 and JP-5 fuels, citing examples in which the 25-inch Hg ΔP time was about 300 minutes. Both of the fuels produced had low olefin and aromatic contents and low sulfur contents.

"Removal of polar materials by silica gel treatment also usually has a beneficial effect on the thermal stability of jet fuels. The opposite effect was found with sodium treatment which was effective in reducing nitrogen and sulfur contents but actually made very little improvement in the filter plugging time because the plugging efficiency of the deposits was increased (117).

"G. Effect of additives. Since the reactions that bring about poor thermal stability involve oxidative reactions it would be expected that antioxidant type additives would be beneficial, and since metals are known to accelerate the oxidative reaction in this system, it would be expected that chelating compounds would improve thermal stability. In a general sense, these expectations are realized. However, because of the great diversity of crude stocks and the concentration and type of minor constituents present, instances are found in which all three types of additives fail to render any improvement.

"1. Antioxidants. A great deal of work is being done investigating the possibility of improving the performance of jet fuels by means of antioxidants, but much of it is of a proprietary nature and quite often the additive is not even identified as to type. Nixon and co-workers (104, 117) reported results of tests on a number of different antioxidant type materials. Some of these are shown in Figs. 14 and 15. These include alkylated phenols, alkylated bis-phenols, durene diamine and phenyl β-naphthylamine (PBN). They also show the effect of aging on the performance of the fuel. Generally, all of the antioxidants improved the performance of the fuels somewhat, the bis-phenol, 2B4M6F,a) being particularly outstanding. All were adversely affected by aging (except 26B4Fa) and PBN), in some cases considerably more than the base fuel. The bis-phenol, 2M6B4X,a) has been offered commercially as a jet

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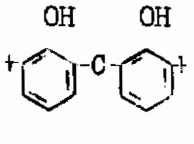
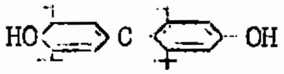
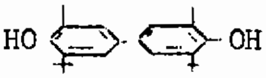
a) Note structure of these phenols



2B4M6F



26B4F



2M6B4X

fuel thermal stabilizer (4). The suggested dosages range from 0.0035%w to 0.028%w. Substantial improvement is reported with two fuels; from 25 inches in 62 minutes to 0.2 in 300 minutes and from 25 inches in 86 minutes to 0.5 in 300 minutes. In both cases the tube deposits were very greatly improved. However, no information is available regarding the effect of aging on this additive.

"2. Dispersants. The thermal stability of jet fuels as measured by a test which involves filter plugging, can be improved by means of dispersants that prevent the clogging of the filter by the insoluble material formed at the high temperature of the test. Nixon and Minor (131) reported the effect of three dispersants on the thermal stability of a composite JP-4 fuel and showed that the filter plugging time was increased by factors of 5, 10 and 20 fold over that of the base fuel. However, as is pointed out above, the dispersant functions mainly to increase the amount of deposit that the filter can tolerate before it becomes plugged. It is still a matter of concern as to whether the material will function as satisfactorily under practical conditions. Similar data are shown in Figs. 16 and 17, which show the effectiveness of several dispersants in both the Shell test and the CFR coker. In this particular fuel the effectiveness of the dispersants do not appear to be as great probably because the base fuel is more stable than the previous one. However, the plugging time is increased by factors of 2 to 3 in the Shell test, while in the CFR coker test the filter merit rating was increased by 20 to 100%.

"Figure 16 also shows the effect of aging the fuels for one year at 110°F. in the presence of one atmosphere of air. It will be noted that the thermal stability is degraded with all the fuels and the samples containing the dispersants suffered relatively more severely than did the undoped fuel. It will be noted that in all cases the rate of filter deposition has been increased as the result of the oxidation occurring in storage. Whether this could be overcome by the introduction of antioxidants is a matter that requires investigation; however, the data shown in the lower two bars of Fig. 17 suggest that complications might exist. In the penultimate bar is shown the effect of adding to the best dispersant in the figure the best antioxidant found in Fig. 16. This indeed improved the filter plugging properties of the fuel but also seriously increased its tendency to deposit on the preheater. An attempt to improve the situation by the addition of metal deactivator actually somewhat decreased the filter merit rating and also made the preheater deposits worse. Heath (73) also cites an instance in which what is believed to be a dispersant type additive improved filterability characteristics but also increased the preheater deposit tendency. Barringer (12) reports improvement in the filter plugging tendency brought about by the addition of a dispersant additive, but does not mention the effect on the preheater tube. He also mentions that storage of the fuel for 12 weeks at 110°F reduces the filter plugging time by about 25 to 60% of the initial value. A large number of petroleum chemical suppliers are now offering antioxidants, dispersants or combination types of additives for improving the thermal stability of jet fuel as measured by the CFR coker. This introduction of additives of this type is not without danger since co-mingling of fuels from different sources could introduce incompatibility if they contain different minor components and different additives.

"3. Metal Deactivator. The body of data available on the effect of metal deactivator on thermal stability is quite inadequate to give a final opinion as to whether this type of agent has a beneficial or deleterious effect on thermal stability. In the discussion above it appears that the effect of adding the metal deactivator was deleterious. Other data from the same source (104) indicate that, in the recycle type of test, although the deactivator did not extend the plugging time it greatly reduced the amount of deposit on the filter without increasing the deposit on the preheater. Other information on the effect of the metal deactivator on the presence of soluble copper and iron are given in Fig. 13 in which the filter merit rating in the CFR coker test is indicated for different samples. Here the indications are that in the presence of copper the deactivator can have a slightly beneficial effect on preheater deposits, and it may have a slightly deleterious effect on filter plugging at low copper contents. In the presence of iron the deactivator had no effect on either filter plugging rate or preheater rating. In the Shell recycle type of test the metal deactivator had a definitely deleterious effect both by itself and in the presence of copper and iron. The effect wss more pronounced in the presence of copper. The addition of 0.3 ppm. of MDA reducing the plugging time from 7.7 to 3.0 hours whereas the addition of 0.03 ppm. of copper (as the naphthenate) reduced the plugging time from 7.7 to 4.2 hours. The addition of 0.3 ppm. of MDA to the latter fuel reduced the plugging time to 0.8 hours. In each case the effect on the rate of deposition on the filter was approximately proportional to the effect on the plugging time. The addition of 0.25 ppm. of iron (as iron naphthenate) reduced the plugging time to 2.6 hours and adding MDA decreased it still further to 2.0. The rate of deposit on the filters in these last two cases were 5.9 and 4.5 mg. per hour, respectively. Other data (ibid. p. 101), suggests that the metal deactivator can reduce the amount of deposits formed but that it is possible for such deposits to be quite efficient in causing filter plugging."

More recent work was summarized at the joint CRC meeting at Dayton[43]) by Dr. George Kittredge[47]) as follows:

"(1) Four out of five JP-6 grade jet fuels stored through 78 weeks at ambient temperatures have shown significant deterioration in thermal stability performance. To date storage sealed-under-nitrogen as opposed to vented containers has not proved effective in retarding deterioration.

"(2) The single test fuel showing no storage instability at any time is very low in aromatic compounds, sulfur and trace copper content.

"(3) Phenol type antioxidants were moderately effective both in upgrading a single base fuel to a passing level of thermal stability performance when fresh and in maintaining this improved performance throughout storage. However, relatively massive additive concentrations were required.

"(4) Most test fuels rating poor in Fuel Coker performance after storage also showed reduced ability to transmit ultraviolet light of 340 through 425 millimicrons wavelengths. Such an effect could be accounted for by limited oxidation of aromatic nucleus hydrocarbons.

"(5) Fuel copper contamination using copper naphthenate and copper cyclohexane butyrate showed pronounced adverse effects on thermal stability performance at concentrations above 300 parts per billion. However, at concentrations below 40 parts per billion no adverse effects on storage deterioration could be shown in terms of the Coker test, though light transmission losses were apparent.

"(6) Pure aromatic compounds showing measurable adverse effects on 400°F plus thermal stability performance when added in small concentrations to a paraffinic base fuel include polymethylbenzenes, aromatic olefins, and methylnaphthalene.

"(7) Aromatic compounds showing measurable adverse effects on storage stability in terms of the Fuel Coker test include indene, cumene, secondary butyl benzene, and 2-methylnaphthalene, though the changes in some of these cases were rather slight."

The view of ASD on the effect of storage on thermal stabilities succinctly stated recently by H. R. Lander[43] as follows:

"The inability of high temperature petroleum jet fuels to maintain their thermal stability during storage prior to their consumption is a problem which, although it has not been uncommon in the past, is occurring with increased regularity as the thermal stability requirements are increased. Fuel deterioration with respect to deposit and gum formation is one of the consequences of fuel storage. Storage effects of this nature are not surprising, since they have been witnessed for years in products of this nature. They are not a problem of fuels alone. Many other petroleum products make use of preservatives, additives, etc. to retain their original characteristics during storage. However, with the advent of a high thermal stability fuel, the storage stability problem has taken on new dimensions and prospectives. The high thermal stability requirements of the fuels desired in some aircraft of today and most certainly needed in those of tomorrow has given us fuels which are highly sensitive.

"Fuel storage could be broken down into a number of aspects, these would include treatment, handling, transportation and physical storage. Any one or all of these aspects could effect the thermal stability of a fuel, especially when these stability requirements are in the region of 400°F and above. The storage stability problem, at this point, becomes very complex. It involves a great many variables. The first of these variables begin to appear the moment a fuel is processed at refinery, while the last are present at the use point. They include all of the handling, transportation and environmental conditions encountered by the fuel on its journey to the actual physical storage facilities. The physical storage of a fuel is very important and consists of many variables also, such as container characteristics, geographic location, cleanliness of transporting, transferring and storage facilities and many others which might arise in individual instances. In other words, once a fuel finally reaches its point of use it has run the gamut; it has passed over or through many types of materials, it has been stored for varying lengths of time in a variety of equipment, it has in some cases been exposed to varying climatic conditions. This list could go on for a considerable length of time, with individual fuels adding certain irregularities which might arise in their particular path from refinery to use point. These variables, be what they are, combined with actual thermal deterioration of the fuel caused by the reaction of components of the fuel within themselves or caused by contaminants introduced in the past history of the fuel are principles which must be considered when attempting to solve the problem of storage stability. A great many of the contamination and cleanliness variables can be eliminated, to some extent, by good housekeeping practices and careful consideration in handling of the delicate nature of the product. If this could be done, then the problem becomes one of thermal degradation during storage and can be approached in a more scientific manner."

Thermal Stability Test Methods

The previous section dealt with the importance of thermal stability as a criterion of jet fuel performance acceptability. The present section is an attempt to present a comprehensive review of the various methods that have been (or are being) used for determining this important jet fuel property. Thermal stability tests are intended to predict, by means of a relatively short time exposure of a fuel to some stressing condition, what will happen in an aircraft fuel system over a long period of use. They are, and must be, accelerated tests and so are subject to all the problems inherent in any predictive method. These are particularly troublesome in thermal stability tests because the reactions which occur are oxidative free radical reactions which are notoriously prone to acceleration by catalysts such as heavy metal ions and to deceleration by chain termination such as inhibitors.

Coker Tests

While many tests have been developed, the so-called coker tests are the only ones in general use at the present time for predicting thermal stability of jet fuels.2) A description of the historic development of fuel cokers and the ultimate ASTM-CRC Coker has been given by Stone.4)

Coker fuel testing has served a useful purpose for specification control and is claimed to give results which correlate with jet engine performance factors.5) Partly, however, the coker test has succeeded by the default of other candidate thermal stability test methods; and the standard coker test method, in its present form, leaves much to be desired in terms of repeatability and reproducibility, quantity of fuel required per test, and application to the broad temperature range encompassed by both subsonic and supersonic jet aircraft application.6)

The standard ASTM-CRC fuel coker equipment is limited to a maximum temperature of about 500°F,[7] which is considerably below the level of interest for supersonic flight. Thus, modifications to the standard coker have been made to extend its application to 750°F (CRC High-Temperature Research Fuel Coker[11][12][4]) and even to 900°F[8] (SD Coker[9]). The SD Coker also has the advantage that it can be operated on as little as 125 ml of fuel, utilizing cooling and recycle of effluent fuel. (This compared to a fuel requirement of six gallons for the standard CRC coker test.[10]) Kittredge, Streets, and Ratchford developed a similar recycling system utilizing a one-liter sample.[6]

A micro coker, operating on only 50 ml of fuel, has recently been devised.[38][44] The original design consisted of helical channel on a tapered plug which fitted into a hole of similar contour. Fuel was passed through the channel at operating conditions up to 500 psig and 1000°F. Difficulties with maintaining reliable seals led to the abandonment of this design and the adoption of a simpler one in which a flat test plate is bolted onto a flat plate in which the fuel carrying grooves have been cut. Operating conditions are about as before and fuel flow is 3 ml/hour. Preliminary results on comparative runs with the CRC fuels were claimed to show consistent correspondence with the modified micro coker.[45]

While serving the purpose of a test method for thermal stability specification control, the ASTM-CRC Coker has also been used, as such and with modification, as an empirical means of investigating comparative stability of experimental fuels. For example, the Texaco Research Coker[13][14] utilizes the essential CFR Research Coker equipment substituting for the "milk can" an autoclave for preheating the test fuel to 200 to 500°F A means is thus provided for studying directly the effect of preheat on the thermal stability of the test fuel. However, the use of the fuel coker to study the effect of preheat on fuel stability has been reported earlier by several investigations.[11][12][15][16]

A need has been felt to improve the repeatability of and to simplify the coker test.[18] The two main causes of fuel coker errors are probably variations in fuel cleanliness and temperature deviations from standard values due to calibration errors.[19] The use of a millipore fuel line filter at the preheater inlet has been suggested as a replacement for the present standard micronic filter, as a means of insuring clean fuel.[19] Results of a large CRC exchange program suggested the need for a standardized coker fluid for coker calibration,[17] but efforts along this line have been unable to reduce calibration test temperature uncertainty to less than 25°F.[19]

Still another modification of the CRC coker is the CFR Fuel Coker Step Temperature Test.[16][18][20] After warm up to initial test conditions by the same procedure as that of the standard method, temperatures are increased 25°F every 30 minutes (in contrast to the constant temperatures held in the CRC coker method). Further difference relative to the CRC standard method lies in the use of a pyrex outer preheater tube (instead of stainless steel) which permits determining tube deposit ratings while running, in addition to the normal ratings after tear down.[2] Ratings during runs checked closely those obtained after disassembly, showing no difficulty in rating deposits through the glass and fuel film. The test time requirement is 240 minutes, resulting in a direct saving in time and fuel sample of at least 20 percent over the standard method. The step-test procedure has the advantage that it determines limiting fuel temperatures in a single test, whereas the standard coker may require several tests to accomplish this goal. Moreover, correlation with standard fuel coker ratings has been described as fairly good.16)

Whatever the method, the first criterion of acceptance must be the ability of the test to predict full-scale performance.2) Efforts to correlate coker results with full-scale flight tests have resulted in limited general success,5)17) particularly for those fuels of clear-cut "fail" or "pass" coker ratings. However, coker tests themselves have been subject to poor reproducibility, and the insensitivity of the test leaves open doubts as to the performance of "borderline" fuels. Thus, there is justified concern that total reliance on thermal stability predictions of cokers might impose unrealistically severe refining conditions in some instances, or that fuels of poor flight performance might be passed in other instances.2) Actual comparison of flight experience with coker tests is the only - and highly expensive - insurance of predictive reliability.

Woffshagen, et al, have used an aircraft fuel system-engine thermal simulator32) test method to compare thermal stabilities of five JP-6 type and five higher temperature fuels with coker results.22) This equipment is intended to simulate the high temperatures which will be experienced by the aircraft fuel system in Mach 3 and Mach 4 engines; it consists of a preheat tank, a single tube heat exchanger, and an inline filter. Good correlation was found between the simulator and CFR coker. But the Erdco Research Coker, which presumably should have given better correlation at the simulated Mach 3 to Mach 4 environmental conditions of the fuel system test, was actually more severe than the simulator.

A further important difficulty with coker tests has been the interpretation of results. Confusion has arisen from the dual nature of the test, i.e., rating according to filter plugging and rating according to the color of the preheater test tube. It is common experience that a fuel may pass one rating and fail the other; hence the relationship between filter plugging and heater coating tendency received early consideration.21) Moreover, the practice of rating deposition tendency by color rather than by deposit quantity is probably fallaceous, since deposit color has been shown to be more related to fuel type than to amount of deposit.22) The problem of developing a suitable rating scale for expressing CFR Fuel Coker results was formalized in a recommendation by a CRC Planning panel in 1958;17) more recently, Shamblin and Johnston have considered some of the suggested interpretations of coker data and rating systems such as "goodness number" and "filter merit rating".12) More developmental work is needed on the coker test to make it a more acceptable method.

Non-Coker Thermal Stability Tests

While military usage of fuel coker testing as an acceptance test has popularized coker tests, other thermal stability tests have received attention over the period of time from the pre-coker period to the present. Following the logical lead of experience with gum problems in gasolines, the effects of high gum content fuels on jet engine fuels systems was explored at an early date using stainless steel bombs heated in a constant temperature oil bath. Even good fuels as judged by JP-4 quality specifications gave serious deposition at temperatures above 250°F.23) This test resembles the ASTM D 873-57 T-oxidation stability test,10) but was only qualitative.

Among the early efforts at thermal stability testing of jet fuels was that of Strauss24) who used a heated coil and small orifice for measuring accumulation of insoluble deposits. The rate of decline in fuel flow under a constant pressure head was the measure of gum forming tendency of the fuel.

McLean and Goodrich25) studied the thermal stability of JP-4-type fuels using a hot plate test and a small-scale burner heat exchanger test. In the hot plate test, deposits were collected in a heated test cell, through which jet fuel was recirculated. The second method, a small-scale heat exchanger test, involved a coil of stainless steel tubing immersed in a hot oil bath. Fuel passing through the tubing at test conditions was subsequently passed through a screen filter and the change in pressure drop observed at constant flow rate. These workers also observed UV and IR spectra of polar fractions of the fuels tested and ran hot plate and heat exchanger tests on these fractions for comparison. A similar test utilizing a glass coil immersed in a 400°F bath was devised by Barringer, Corzilius and Rogers.26) Correlations were obtained between the glass coil test results and results from a full-scale rig. Other similar tests are described in the literature.33)

A realistic approach to the thermal stability testing problems was taken by Miller.27) In this test the fuel is burned in a small-scale combustor. Basis of the rating was the fuel pressure required on the nozzle to maintain a constant 1150°F exhaust temperature. Fuels giving strongly "fail" or "pass" ratings on the CFR coker gave good correlation with the small-scale combustor, but poor correlation was found for borderline fuels, as might be expected since coker tests themselves are poorly reproducible for borderline fuels.

Minor, Nixon and Thorpe developed a laboratory heat exchanger test apparatus,15)28) in which they studied the effect on the thermal stability of adding pure hydrocarbons to jet fuels. The pre-filtered test fuel was placed in a reservoir from which the exit fuel was preheated to 450°F by heat exchange and passed through a sintered metal test filter. Test measurements included time required for 5-lb differential pressure increases across the filter and increases in weight of both the filter and heat exchange coil. This test resembles that of McLean and Goodrich, described above, and the hot tube fuel tester of Shamblin and Johnston.18) These tests are all similar in principle to the fuel coker test. It is not surprising therefore that the CFR coker and the hot tube fuel tester, for example, give fairly good correlation of results.16)

Several bomb tests have been used,[34] including the Esso Bomb Test,[18] the Southwest Research Institute Bomb Tests,[18] and the CRC Fuel Bomb.[8][16] These tests all involve exposure of a fuel sample to a heating cycle, followed by filtering out and measuring solids formed from the fuel. They differ mainly as to the details of bomb design and size, tests conditions, method of heating, and types of filters. Except for the CRC bomb, no means is available for predicting preheater deposits. Although poor reproducibility has been reported for bomb test procedures,[26] Shamblin and Johnston described the Southwest Research Institute Bomb 2 test as being a very useful screening device to predict thermal stability of fuels.[18]

Bombs have also been used for oxidation testing of fuels by Sablina and Gureev,[29] in the U.S S R. In the latter test the fuel is placed in a bomb which is air pressure to seven atmospheres and then placed in a constant temperature bath at temperature up to 250°F. This latter method is somewhat similar to ASTM test method D 873-57 T, Oxidation Stability of Aviation Fuels.[10] A second, low pressure, oxidation test is described in the Soviet literature.[30] In this test prefiltered fuel is simply heated at atmospheric pressure and 200°K for 20 minutes, cooled, and filtered to determine the weights of deposits formed.

The electron microscope has been applied successfully to the evaluation of insolubles formed by heat stressing fuels.[12][49] For example, Shamblin and Johnston employed a small-scale heating test consisting of a closed loop tube sample holder which was immersed in a hot oil bath. Fuel pretreated in this apparatus was then observed using an RCA Model EMU-3C electron microscope. Sizes, types, frequency of particle occurrence were noted. Ratings were based on estimates of particle frequency by scanning and were found to provide the same general alignment of fuels as given by fuel coker ratings.[50]

The Panel Coker Test, described by Shamblin and Johnston,[18] involves a temperature controlled hot plate on which fuel is splashed in a controlled manner in the open atmosphere. Vaporization occurs on the hot plate and so has not been meaningful in thermal stability prediction of jet fuels in subsonic aircraft. However, a similar test might well have significance relative to vaporizing fuels for Mach 3+ flight if it were performed in an enclosure where vapor composition is controlled.

A promising test, because of its simplicity, is the Laboratory Light Scattering Method described by Sheeler, Krynitaky and Carhart.[31] The test fuel is subjected to whatever treatment desired, constant temperature soak, oxygen exposure, etc. Light scattering measurements are made, before and after treatment, at three angles, 45, 90, and 135°, and at a wavelength of 436 microns using a Phoenix Brice photometer. The extent of light scattering gives a relative measure of the formation of insolubles. Light transmission in the 340 to 45 millimicron ultraviolet range has also been used to detect fuel storage deterioration,[46][47] and these tests have shown some correlation with coker tests,[34] except for fuels containing certain antioxidants.[48]

In recognition of a need for a small-scale test which would require a quart of fuel or less and would align the thermal stabilities of jet fuels in the same order as full-scale test equipment for subsonic and supersonic aircraft, Kittredge, et al[6] have explored several small-scale tests. In addition to the CRC bomb, mentioned above, two miniature thermal stability testers have been investigated. In these tests a one-eighth inch stainless steel tube served the dual purpose of a heat source and a deposit surface. From tests with the first static units designs it was decided that a flowing environment was essential to obtain meaningful results. Accordingly, the test was modified to use a constant fuel flow rate, constant pressure and fuel and tube temperatures, and constant heat input. Deposit accumulation was followed by measuring changes in heat transfer coefficient. Still another apparatus tested by Kittredge was the hot wire stability tester.[34] The principle involed in this test was to measure the resistance of a wire immersed in the test fuel, which resistance changes because deposits build up on the wire and its temperature increases. Heat input to the wire was held constant. The method was abandoned, however, because of its poor correlation with coker ratings.

Looking to the higher temperature fuel thermal stability problems of multi-Mach number aircraft, Bachman, Matthews and Zudkevitch[35] describe both a static and a dynamic test for evaluating vaporizing fuels. The static thermal cracking test utilizes simply a heated bomb in which gross thermal degradation is detected by sudden pressure rise due to cracking. The second, Esso High-Temperature Heat exchanger test, is much more elaborate and comprises a stainless steel fuel tank, a preheater coil, and several electrically heated test sections in series which can be made from different metals to evaluate the catalytic effect of surface on fuel stability. Arrangements are provided to obtain interstage fuel samples and to observe deposit formation by heat transfer measurements. Initial indications are that this apparatus is less severe than the ASTM Coker.[56]

A method used to determine the temperature of the beginning of appreciable fuel decomposition involves the use of the isoteniscope, but does not concern itself with the formation of insolubles.[36][37] A static test apparatus has been used by Fabuss, et al, wherein the fuel is pyrolyzed in a sealed glass tube at a constant temperature.[38][42] Products of cracking are then analyzed by suitable techniques.

In addition to the foregoing tests which are mostly concerned with deposit formation in the fuel distribution system, several small-scale combustors have been developed for rating deposit forming tendencies and other properties of fuels during combustion.[39][40][41]

Despite the number of tests which have been developed, none has been generally accepted nor officially adopted except for the ASTM-CRC Coker test, and even this test leaves much to be desired. A test is still needed which will possess the characteristics of good reproducibility, short test and clean-up time, small sample requirement, and which has meaning in terms of full-scale tests.

Characteristics of High Temperature Cokers

Temperature

The standard ASTM-CRC Fuel Coker equipment is limited to a maximum temperature of about 500°F, which is less than the maximum level of interest for supersonic flight. To partially bridge this need, the Erdco 02FC-381 Coker, a modification of the ASTM Coker, was designed for testing up to 750°F. The M-6 coker extends this range to 950°F, and with minor further modifications can be increased to 1300°F.

Fuel Charge

Standard ASTM-CFR Cokers require approximately five gallons of fuel per test, on a once-through basis. The M-6 coker may also be run on the same regime, but is normally operated on continuous recycle requiring only about 125-150 ml per test.

This can have a considerable bearing on the results given by the test. Lusebrink52) has remarked:

"One difference between results run on a once-through basis and the recycle coker which could have a major effect on results is the disparity in the amounts of fuel used. The once-through tests pass approximately 5 gallons (18,900 ml) once through the system. The recycle test uses 125 ml cycling it approximately 150 times through the system. If the heat exchanger and filter deposits are due primarily to reactive compounds present in minor concentrations, then the once-through test would be expected to give the lower rating because of the greater quantity of deposit percursor passing through the system. If, on the other hand, deposits are derived primarily from a slightly unstable major fuel constituent, then the recycle test would be expected to be the more severe. Of course, very stable or very unstable fuels would be expected to give similar extreme results in both tests. Comparison of test results from once-through and recycle tests for a number of fuels tend to confirm these expectations. If this hypothesis is correct then recycle test results with pure hydrocarbon fuels should give meaningful relative ratings of stability."

This expectation is being borne out by experience. In fact, we found the recycle method to provide an extremely sensitive test for filter plugging tendencies of jet fuels. We believe it will give a sharper distinction between fuels on this basis than will the ASTM or Erdco cokers.

Preheater

Both the M-6 and Erdco cokers are fitted with 11/16-inch ID stainless steel preheater outer shells, and both use 5/8-inch OD inner tubes. This contracts to the standard 1/2-inch OD aluminum inner tube and 9/16-inch ID aluminum outer tube of the ASTM-CRC coker. The inner tube of the Erdco coker, as provided, is stainless steel. Eventually, stainless steel, titanium, and possibly other metal surfaces will be used for the M-6 inner tube, but until now a Duplex steel tube with aluminum overlay has been used. It will be noted that the annular clearance is the same in all preheaters, but the cross-sectional area in the M-6 and Erdco preheaters (0.0644 sq in.) is 23.5% greater than in the ASTM-CRC preheater (0.0522 sq in.). Therefore, at constant mass flow rate the residence time in the ASTM-CRC coker is only 79% that in the M-6 and Erdco cokers.

The heat transfer pattern within the coker is rather complex and once the inner and outer tube diameters are changed an interesting problem of mathematical analysis must be solved to define the precise net effects. Changes which can influence thermal stability ratings are residence time and inner tube surface temperature. Most of the heat transferred is required to supply sensible heat to the fuel, which enters the preheater annulus at essentially ambient temperature at one end and leaves at the specified control temperature at the other. However, some heat is conducted from the calrod, through both inner and outer tubes and the fuel, and lost by convection. Convection heat losses are greater from the high temperature Erdco than from the ASTM-CRC preheater because of the larger outside surface of the Erdco. Convection losses from the M-6 preheater are less than from that of either Erdco or CRC cokers because the M-6 preheater is insulated with one-inch thick Caltemp pipe covering whereas the other two are bare. This insulation should result in a slight further lowering of the temperature of the M-6 compared to the Erdco preheater since the outer surface areas of the two are about identical.

When the inner tube diameter is increased and the annular spacing held constant, the hot heat transfer area of the inner tube is increased and the volume of the annulus is also increased. The result is greater residence time of the fuel and greater heating surface. In the present case, the surface area of the Erdco and M-6 inner tubes is 25% greater and the residence time is 23.5% greater than in the standard CRC preheater. Therefore, to obtain the same liquid temperature the surface temperature need not be as high in the Erdco and M-6 inner tubes. Consequently, with once-through operation and at the same mass fuel flow and preheater temperature, both M-6 and Erdco tube ratings should be somewhat less severe than those obtained with the ASTM-CRC preheater. (With recycle operation the M-6 coker could give more severe ratings where major fuel components are at fault, and less severe ratings where trace components are to blame.)

Further differences exist in physical arrangement of the preheaters: both the Erdco and CRC cokers' preheaters are situated in a horizontal plane, while the M-6 preheater stands vertically. The choice of the M-6 position arose from earlier experience in that tests run in the vertical position gave greater ease and reproducibility of rating, particularly when boiling was occurring in the preheater. Moreover, the horizontal arrangement in the Erdco and CRC cokers results in the portion of the inner tube at the exit opening of the preheater "looking" up into the commonly higher temperature zone of the filters. In borderline cases, radiation from the filter has apparently caused boiling near the preheater exit, since no evidence of boiling occurred at identical conditions when the preheater was in the vertical position, in which case the inner tube cannot "see" into the filter as it is presently arranged in the M-6 coker.

Finally, the heating element is inserted from the opposite end of the M-6 preheater from that in the Erdco and CRC preheaters. So long as the heater is positioned the same in each preheater, this difference should be unimportant.

Pump and Flow Control

Both CRC and Erdco cokers normally equipped use an Eastern gear-type pump, driven at 1725 rpm, and therefore delivering a constant flow. Flow control is normally by needle valve, the undesired excess flow splitting off ahead of the flow rotameter and recycling to the fuel supply pump via a pressure control-relief valve. We have replaced this sytem in our Erdco coker with one similar to that used in the M-6 coker, as follows. A Zenith No. 1 or 2 precision metering-type stainless steel pump is used; flow control is achieved through a variable speed Graham transmission. The arrangement eliminates potential and unnecessary contamination buildup inherent in the recycle control system of the original Erdco. But gradual buildup in pump born contamination may likewise occur in the M-6 recycle coker test; the extent of this contamination buildup is being investigated and will be reported in the future.

The Zenith pump has proven successful in a wide range of liquids, from very viscous liquids such as cellulose acetate solutions for which it was originally designed, to kerosene and even methylcyclohexane and toluene in our own applications. At the latter viscosity level, a new Zenith pump failed by seizure while pumping methylcyclohexane (MCH) at 400 psig, although numerous successful MCH runs have since been made using a Zenith pump previously broken in on more viscous fuels. Using a previously broken in pump, n-heptane was successfully pumped at 150 psig, but pump damage was incurred at 400 psig. Evidently, the Zenith pump requires more viscosity or lubricity than that supplied by MCH or n-heptane to avoid borderline failure tendencies.

A Northern Ordinance nitralloy gear-type pump has also been tried because of reports that it gave exceptionally low fuel contamination. However, our brief experience indicated that the pump was not suitable for our desired application. First, it could only be used as a direct replacement for the Eastern pump in the original by-pass flow control system. "Slippage" was so great that satisfactory flow control could not be obtained through speed regulation. Second, rather large amounts of pump-born contaminants were in evidence when a non-viscous fuel such as MCH was used. Other liquid drive methods will likely be investigated in the future, especially for application to very low viscosity, high vapor pressure fuels. Of interest here is the use of a Greer accumulator with flexible diaphragm and secondary driving fluid. Such a system would be advantageous for contamination control.

Controls and Recorders

The M-6 coker utilizes a dome loaded Grove Regulator for pressure control, and a duplicate device has been installed in the Erdco coker, replacing the original pressure relief valve. This arrangement is essential to the speed-flow control system in use and described above.

Pressure, both total and differential, are presently recorded continuously and automatically by a Bristol recorder in the M-6 coker. In the Erdco coker, pressure and differential pressure are indicated by a pressure gauge and a mercury manometer, respectively, as in the original semi-automatic CRC coker equipment.

Neither of these systems is regarded as being satisfactory from a contamination standpoint due to danger of carryover contamination from previous runs. In the Erdco coker, both the high side of the manometer and the over-pressure and underpressure switches are connected by a pressure connection between the preheater and the filter. It is unlikely that normal flushing procedures can prevent residual quantities of fuel from previous runs contaminating subsequent runs. Moreover, the flushing process itself leaves trisolvent and stoddard solvent in these lines. At least some improvement would be made if the manometer were connected ahead of the preheater to avoid degradation products.

Similar problems to the above exist with the M-6 Bristol pressure recorder d/P cell, and it is believed that these must be solved to avoid chance false test results. An attempt had been made to isolate the Bristol d/P cell using Greer Accumulators, but the equipment size required would increase the fuel inventory from 150 ml to 350 ml, thus depreciating the small sample feature. Therefore, investigation into the use of pressure transducers is planned, where pressure detection can be made directly in the fuel line.

Temperature control is automatic in both M-6 and Erdco cokers. The Erdco operates up to 800°F, while the M-6 controls to temperatures of about 950°F.

Micronic In-Line Filtering

Two Purolator micronic filters (5 micron) are used in the model O2FC CFR coker, and also in the high temperature Erdco. One of these is located ahead of the fuel rotameter, upstream of the preheater, while the other protects the needle flow control valve on the spent fuel discharge line. (For contamination control purposes, the rotameter has been moved to the position normally occupied by the needle valve.)

A single identical Purolator filter was at first installed ahead of the M-6 preheater, but was later removed when it was demonstrated that the Purolator filter itself could act as a contamination source and cause accelerated plugging of the test filter. Further investigation showed that a new micronic filter element allowed to stand for a short time in trisolvent caused yellow discoloration of the liquid.

The micronic filter element consists of a pleated fibrous paper impregnated with a dark material (probably phenolic resin), and it is this material which dissolves into the trisolvent. Moreover, used filter elements appeared to have less visible resin at the ends of the pleated paper than new ones, indicating some material could have been dissolved into the test fuel. Finally, duplicate tests with and without the micronic in-line filter showed less tendency toward test filter plugging with the micronic filter removed, provided the test fuel had been millipore filtered prior to the test. The micronic filter appeared to be acting as a coalescer of small particles, and microscopic viewing of test filters also showed fibers from the micronic filter element.

Although no specifications are given in the ASTM-CRC coker test method, it is evident from the fact that trisolvent partially dissolves resin from the micronic filter that (1) these filters should be removed or bypassed during flushing operations in the Erdco and CRC cokers and (2) the filter upstream of the preheater should be renewed for each test. While it is believed that these are probably adequate precautions for operation of once through flow systems, the 5-micron pleated paper filter appears to aid particle growth which is a continuous cyclic process in the M-6 recycle test. In some cases a similar particle growth appears to occur on the downstream side of the test filter. If these particles are dislodged they will subsequently be recycled and deposited on the front side of the test filter, unless there is an effective in-line filter in advance of the preheater. Further efforts will be made to find such a filter which will not have the disadvantages of the pleated paper type. A 2-micron sintered metal in-line filter will be tried in the near future.

Contamination

Every effort is being made to reduce extraneous contaminants whether they arise from the residues from previous tests, from the pump construction materials, or from outside sources due to poor fuel handling and cleanliness practices. Early experience showed the M-6 coker to be extremely sensitive to contaminants, thus lending further emphasis to our war against contamination sources. Besides those items discussed above, special design considerations and subsequent modifications which have been made to combat contamination are as follows:

a) All flow lines (except the pump supply line from fuel reservoir) in the M-6 coker were constructed of 1/8-inch stainless steel tubing and made as short as possible consistent with other design considerations. This not only helps to minimize the sample size requirement and surfaces where contaminants may accumulate, but also increases the effectiveness of solvent flushing. Although the original 1/4-inch lines in the Erdco coker have been retained, these have been shortened wherever possible, and the flow rotameter has been removed.

b) Attempts have been made to eliminate stagnation points, particularly in the high temperature zones of the M-6 coker. Such regions could result in excessive heat exposures of portions of fuel causing misleading test results.

Fuel Preconditioning

The CRC Research coker is equiped with a heated fuel reservoir for thermally prestressing the test fuel, while the Eppi high temperature conversion kit for converting the standard ASTM-CRC coker provides a similar preconditioning unit with automatic temperature control. Fuels are commonly heated to as high as 300°F in these heated reservoirs prior to test. In the Research coker test the run is started as soon as the fuel reservoir reaches the predetermined temperature, by starting the pump and turning on the coker heaters. Normally, in the modified coker test, the fuel is held in the preconditioning unit at the prescribed temperature for four hours from the time the heater was first turned on. A rapid quench follows, and the fuel is then used in the coker test.

The foregoing heated fuel reservoirs are obviously vapor pressure limited, and it has been anticipated that fuels in supersonic flight above Mach 2 speed might be exposed to temperatures above 300°F. To extend the temperature range of fuel preconditioning above 300°F, Texaco13) have designed and built a well instrumented autoclave capable of operation from 90° to 500°F and up to 100 psig. This autoclave is the fuel reservoir of the Texaco Research coker.

A stirred, heated, stainless steel autoclave similar to that used with the Texaco coker has been built for use with our high temperature Erdco coker. This unit has a capacity of 8 gallons of fuel and is hot oil jacket heated. The large reservoir may on occasion also be used for once-through operation of the M-6 coker.

Finally, a similar small autoclave has been obtained for preconditioning of M-6 coker fuel. This autoclave can be used on recycle operation by inserting it between the pump and the preheater, in which case operation would be similar to that of the CRC Research coker except for the fuel recycle feature.

Despite the provision of these preconditioning vessels, they will only be used for occasional coker tests. In fact, the necessity for such preheat-soaking of test fuels is an unsettled question. While the approach is based upon the assumption that supersonic jet fuels may be exposed to high temperatures for several hours in the fuel tanks, it is equally possible, that in order to avoid thermal stability problems, airframe design will have to provide for adequate fuel tank insulation to prevent such overheating. Furthermore, it is an open question as to whether the type of thermal stressing being advocated for the high temperature cokers, does, in fact, provide any significant parallel to the effects that might occur in a high speed aircraft. Therefore, tentatively, coker tests involving pre-thermal stressing will be made only upon the more promising of endothermic fuel candidates.

Effect of Vapor Pressure on Coker Ratings

It is apparent that the thermal stability of jet fuels when used for heat sink purposes may be different for each physical state and transition. Therefore, the deposition tendency of candidate fuels is of concern in the liquid, vapor, and (possibly) the supercritical states. Moreover, the occurrence of boiling in either the coker preheater or the test filter may lay down heavier deposits. For these reasons, particular care is being taken to regulate test pressure to give predictable physical states or transitions in the coker test zones, based on available vapor pressure data (cf Figure 29) and measured test section temperatures.

Coker Operating Procedure

M-6 Coker (on Fuel Recycle Basis)

The procedure outlined here is followed at present and embraces the best techniques of which we are presently aware. However, the details of the procedure have been modified several times in the past and will probably be further modified in the future, and is therefore not considered finally standardized.

Apparatus

The M-6 coker was largely designed and built at Shell Development Company. The basic design has been described in a previous report.[52] Most of the recent modifications have been described elsewhere in this report, and as pointed out, further modifications and improvements are anticipated.

As used in the thermal stability tests reported herein, the inner tube of the preheater was an aluminum-clad steel Duplex tube. Stainless steel, titanium, and other metals will also be used in future work.

In the M-6 coker, shown schematically in Figure 20, the test fuel comes into contact with only stainless steel and glass (full reservoir). The glass fuel reservoir has been painted on the outside with black paint to exclude light. Fuel flow measurements are made by stopwatch measurement of the time required for a metering bulb in the system to fill to a calibration mark. From this time, a knowledge of the fuel density and the calibrated volume, the weight flow rate is easily determined.

Fuel Preparation

Test fuel is filtered through a 1.2-micron Millipore membrane prior to testing. A 25-mm diameter filtration unit is used for this purpose since only a few hundred milliliters are filtered at a time. Where single hydrocarbon components are being tested, the fuel is first passed through silica gel to remove peroxides or other polar impurities. Finally, before use the fuel is aerated for 20 minutes to ensure saturation.

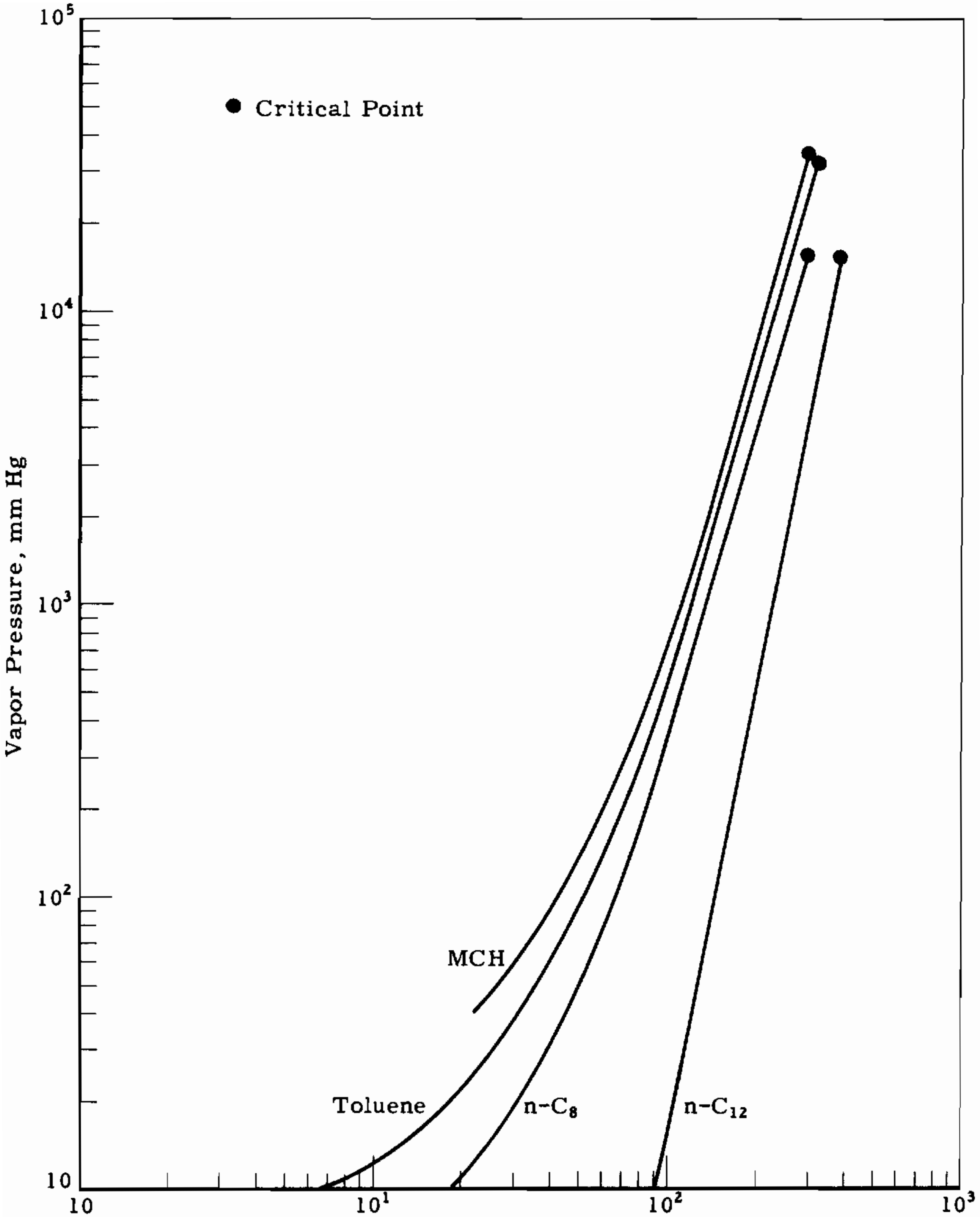


Figure 29. VAPOR PRESSURE OF SELECTED HYDROCARBONS

Test Procedure

1. Fill fuel reservoir with 150 ml of prefiltered and aerated fuel.

2. Turn on cooling water to heat exchanger.

3. Turn on and adjust air flow to the fuel reservoir aerator.

4. Turn on main coker power supply switch and start fuel pump.

5. Establish operating pressure by adjusting the nitrogen pressure to the dome of the Grove Regulator.

6. Adjust the Graham transmission speed until fuel flow is 6.0 pph.

7. Turn on temperature controllers and set initial temperature and heat loads by the schedule shown in Table 38.

8. Start timer immediately following step 7.

9. When initial temperatures are reached, adjust temperature controllers and powerstats to their final settings, using the schedule of Table 38. Initial heating rates are such that preheater warm-up time is about 7-11 minutes, and filter warm-up time is about 11-15 minutes.

10. Zero the Bristol ΔP recorder.

11. Make occasional flow rate and temperature control checks.

12. If the filter pressure drop reaches 25-inches Hg, then the test is either terminated or the filter is by-passed and the filter heater turned off, as desired. Record is made of time when filter ΔP reaches 25-inches Hg.

13. When timer reaches 300 minutes, turn off both heaters, but allow pump to run to cool system.

14. During cooling, observe test section connections for leaks. Reduce pump speed or open by-pass if filter ΔP becomes excessive.

15. When filter temperature reaches 150°F, turn off pump and reduce pressure.

16. Collect used fuel sample from fuel reservoir in clean amber bottle. Nitrogen blanket sample and place in cold storage.

17. Shut off water and air supplies.

18. Remove preheater and filter assemblies from coker.

19. Carefully remove preheater tube, rinse with normal heptane, dry, and rate in Tuberator.

20. Carefully remove test filter element, rinse in normal heptane, and dry in vacuum oven at 90°C. Allow element to cool, then weight to four decimal places. Determine deposit weight by different from original "new" weighing.

Equipment Cleaning and Reassembly

Triple solvent, consisting of 1/3 toluene, 1/3 ethyl acetate, and 1/3 isopropyl alcohol, is used in all cleaning and flushing operations. Normal heptane is used for final rinsing. The following steps are followed:

1. Clean interior of preheater and filter furnace using triple solvent and cleaning brushes supplied by Erdco.

2. Rinse preheater and filter furnace with n-heptane and dry with nitrogen stream.

3. Clean and polish inner tube as follows:

    a. If there are adherent deposits, clean with triple solvent and soft cloth.

    b. Polish surface with A-1 metal polish.

    c. Wipe tube with soft cloth wet with n-heptane and repeat until no traces of black deposits are observed.

    d. Polish with clean, dry, lint-free cloth.

4. With preheater held in a vice or suitable jig, tube is picked up with lint-free rag and gently inserted into preheater.

5. Swagelock nut and preheater jam-nut with teflon seal are tightened.

6. With filter furnace held in a vice, a new weighed filter element is put in place with clean tongs, and the hex locking nut tightened down with a 1-1/2-inch open-end wrench.

7. Flush the fuel reservoir, pump and connecting lines with triple solvent.

8. Install temporary stainless steel by-pass line in place of test section and flush fuel reservoir, pump, and heat exchanger with triple solvent. Contaminated solvent is collected at discharge of the heat exchanger[a)]

[a)] Following runs in which heavy deposit formation or pronounced filter plugging occurred, the heat exchanger is replaced with a clean spare and the dirty one cleaned.

(Grove Regulator and fuel reservoir disconnected). All solvent flushing of the system is done at rates of 15 to 20 pounds per hour.

9. Same as step 8, but triple solvent is allowed to flow through from the heat exchanger and through the Grove Pressure Regulator. Again, contaminated solvent is not allowed to recycle to the fuel reservoir.

10. Repeat step 9 using normal heptane.

11. Dry the system with nitrogen.

12. Repeat step 9 using the test fuel for the next run.

13. Remove temporary by-pass and install preheater and filter furnace assemblies.

14. Clean filter by-pass line and valve with triple solvent and n-heptane. Dry and replace, making sure valve is open.

15. Connect and tighten all fuel line connections and fittings.

Modified High Temperature Erdco Coker

The operating procedure with the Erdco coker is basically similar to that of the SD/M-6 coker, except that operation is not normally by fuel recycle. Our Erdco operating procedure may most simply be described in terms of deviations from that of the SD/M-6.

Apparatus

The Erdco coker, as supplied, was a model 02FC-381, CRC Research moel, except that no heated fuel reservoir is being used as yet. Modifications effected in these laboratories have been discussed elsewhere in this report (cf p. 122f).

Two preheaters are available for the use in this coker:

a) The ASTM-CFR standard 1/2-inch diameter inner tube aluminum preheater.

b) The stainless steel, 5/8-inch diameter inner tube preheater. Other tubes available for use in this preheater are a Duplex aluminum over steel, and titanium.

Fuel Preparation

Fuel is filtered through a 142-mm millipore membrane 0.45-micron filter and pumped with a stainless steel vane pump. Fuel flow is recycled for the first half hour and then introduced into the fuel reservoir without stopping the pump to avoid filter unloading phenomena. A new filter membrane is installed for each 5-6-gallon batch filtered, unless the new sample is the same as the last.

TABLE 38
M-6 COKER WARM-UP SCHEDULE

Initial Temp, °F		Initial Watts		Final Temp, °F		Final Watts	
Preheater	Filter	Preheater	Filter	Preheater	Filter	Preheater	Filter
191	385	165	263	200	400	140	150
215	385	196	253	225	400	170	138
238	385	230	243	250	400	200	127
262	385	262	233	275	400	230	117
286	385	296	223	300	400	260	105
310	385	329	211	325	400	290	92
344	385	362	200	350	400	320	80
286	485	296	368	300	500	260	180
310	485	329	357	325	500	290	167
344	485	362	342	350	500	320	153
358	485	395	327	375	500	350	138
382	485	426	310	400	500	380	160
406	485	462	295	425	500	410	140
430	485	495	278	450	500	440	120
382	585	426	473	400	600	380	210
406	585	462	461	425	600	410	196
430	585	495	441	450	600	440	183
455	585	528	421	475	600	470	163
480	585	562	397	500	600	500	163
505	585	597	380	525	600	530	136
530	585	628	361	550	600	560	108
480	685	562	500	500	700	500	240
580	685	692	484	600	700	620	193
630	685	756	447	650	700	750	123
680	735	830	491	700	750	810	138
630	785	756	450	650	800	750	253
680	785	843	404	700	800	810	223
730	785	913	367	750	800	870	138
730	910	913	500	750	925	870	416

Aeration is the same as in the SD/M-6 coker fuel preparation.

Test Procedure

Five gallons or more of prefiltered and air saturated test fuel is introduced to the freshly cleaned, glass-lined fuel reservoir, immediately prior to the test.

Operating procedure is the same as with the SD/M-6 coker except that temperature controllers require that only initial heat load and final temperature settings be made (taken from Table 38). Further, filter pressure drop is read from a mercury manometer, which must be zeroed or read once the filter temperature is up. Preheater warm-up time is about 8-12 minutes, and filter, about 9-18 minutes when using the stainless steel preheater, and about 8-16 minutes in the preheater and about 11 minutes in the filter, when using the standard ASTM-CRC preheater.

Equipment Cleaning and Reassembly

Again, basic procedure for the SD/M-6 coker is followed. However, the ASTM procedure (D1660) for flushing the mercury manometer is followed.

TABLE 39
HISTORY AND DESCRIPTION OF JET FUEL RAF 163-60 FROM THE CRC FUEL BANK

Date Produced:	September 1960	Additives:	20 ppm 2,6B4M + 0.5 ppm mercaptobenzothiazole
Date Drummed:	September 1960		
Date Into Storage:	October 11, 1960		
Date Rec'd Emeryville:	January 1, 1964	Date Issued:	August 2, 1963
Crude Source:	RAF 162-60	Replaces Issue of:	Original
Processing Method:	SO_2 Extraction	No. of Drums in Storage:	56

PROPERTIES

Grav ASTM D287, °API	32.5	Water Tol, F-791, 3251, Interface Rating	1B
Distillation, ASTM D86, °F		Sulfur, D1266, %w	0.004
I.B.P.	396	Mercaptan Sulfur, D1323, %w	Nil
10%	421	Corrosion, Cu Strip, D130, 2 hr at 212°F	2c
20%	430	Aromatic Content, D1319, %v	Trace
30%	436	Bromine No. D1159	0.4
40%	444	Naphthalenes, F791, 3704T, %v	Nil
50%	450	Smoke Point, D1322, mm	18
60%	456	Luminometer No., D1740	41
70%	462	Existent Gum, D381, mg/dl	1
80%	470	16-Hr Potential Gum, D873, mg/dl	1
90%	480	Net Heat of Combustion, Btu/lb	
95%	490	ASTM D240 (Paar 2600 Modified)	18,461
E.P.	504	NBS 5917[a]	18,506[a]
Residue, %	1.0	Hydrogen, D1018, %w	13.5
Loss, %	1.0	Copper, mg/liter[b]	<0.02
Flash Point, TCC, D56, °F	164	Nitrogen, ppm	<5
Freezing Pt, D1477, °F	<-76	Basic Nitrogen, ppm	<0.3
Color Saybolt, D156	30+	Peroxide No., D1563	<0.04
Viscosity, D445, cs		Water Separometer Index, Severity 15	92
at 100°F	2.53	Light Transmission, % at 425 mμ	100
at 0°F	12.1	Sediment, mg/gal, 0.45 micron[c]	
at -30°F	28.0	Average	1.5
Aniline Point, D661, °F	145	Range, Five Determinations	1.0-1.8
Aniline-Gravity Constant	4712	Other	
		Paraffins, %v Mass Spec	10
		Naphthenes, %v Mass Spec	90

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a) Calculated by equation for kerosine boiling range materials containing less than 10% aromatics. $Q_p = 18110 + 0.0841 \times ACP \times °API$.

b) Copper extraction by hydrochloric acid (Petroleum Refiner 33, 158 (1954)). Copper content by neocupreine complex (ASTM E-39-56T).

c) Determined by filtering 1 gallon samples through 0.45 micron Millipore Filter paper. See ASTM Committee D-2 report for 1962, Appendix X.

TABLE 40
HISTORY AND DESCRIPTION OF JET FUEL RAF 159-60 FROM THE CRC FUEL BANK

Date Produced:	November 1961	Additives:	20 ppm 2, 6B4M
Date Drummed:	February 9, 1962	Date Issued:	August 2, 1963
Date Into Storage:	February 20, 1962	Replaces Issue of:	March 25, 1963
Date Rec'd. Emeryville:	January 1, 1964	No. of Drums in Storage:	5
Crude Source:	West Texas	Comments:	Highly paraffinic fuel, commercially available.
Processing Method:	Hydrotreatment and SO_2 Extraction		

PROPERTIES

Grav ASTM D287, °API	50.7	Water Tol, F-791, 3251, Interface Rating	1
Distillation, ASTM D86, °F		Sulfur, D1266, %w	0.0007
I.B.P	399	Mercaptan Sulfur, D1323, %w	Nil
5%	403	Corrosion, Cu Strip, D130, 2 hr at 212°F	1B
10%	407	Aromatic Content, D1319, %v	0.8
20%	410	Bromine No. D1159	0.7
30%	413	Naphthalenes, F791, 3704T, %v	Nil
40%	418	Smoke Point, D1322, mm	35
50%	423	Luminometer No., D1740	100
60%	428	Existent Gum, D381, mg/dl	1
70%	436	16-Hr Potential Gum, D873, mg/dl	2
80%	450	Net Heat of Combustion, Btu/lb	
90%	471	ASTM D240 (Paar 2600 Modified)	18,903
95%	496	NBS 5917a)	18,886a)
E.P.	533	Hydrogen, D1018, %w	14.9
Residue, %	1.5	Copper, mg/liter b)	<0.02
Loss, %	0.5	Nitrogen, ppm	<5
Flash Point, TCC, D56, °F	164	Basic Nitrogen, ppm	<0.3
Freezing Pt, D1477, °F	-32	Peroxide No., D-1563	<0.04
Color Saybolt, D156	30+	Water Separometer Index, Severity 15	99
Viscosity, D445, cs		Light Transmission, % at 425 mμ	100
at 100°F	1.81	Sediment, mg/gal, 0.45 micron c)	
at 0°F	6.75	Average	4.6
at -30°F	12.9	Range, Eight Determinations	1.8-9.8
Aniline Pt, D661, °F	182	Other	
Aniline-Gravity Constant	9227	Paraffins, %v Mass Spec	80
		Naphthenes, %v Mass Spec	19

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a) Calculated by equation for kerosine boiling range materials containing less than 10% aromatics. $Q_p = 18110 + 0.0841 \times ACP \times °API$.

b) Copper extraction by hydrochloric acid (Petroleum Refiner 33, 158 (1954)). Copper content by neocupreine complex (ASTM E-39-56T).

c) Determined by filtering 1 gallon samples through 0.45 micron Millipore Filter paper. See ASTM Committee D-2 report for 1962, Appendix X.

TABLE 41
HISTORY AND DESCRIPTION OF JET FUEL RAF 156-60 FROM THE CRC FUEL BANK

Date Produced:	March 1960	Additives:	20 ppm 2,6B4M
Date Drummed:	May 26, 1960	Date Issued:	August 2, 1963
Date Into Storage:	June 8, 1960	Replaces Issue of:	March 25, 1963
Date Rec'd. Emeryville:	January 1, 1964	No. of Drums in Storage:	37
Crude Source:	Selected West Texas	Comments:	Highly paraffinic fuel, commercially available.
Processing Method:	Hydrotreatment and Extraction		

PROPERTIES

Grav ASTM D287, °API	50.9
Distillation, ASTM D86, °F	
I.B.P.	384
5%	394
10%	397
20%	402
30%	407
40%	412
50%	418
60%	424
70%	431
80%	440
90%	456
95%	470
E.P.	487
Residue, %	1.4
Loss, %	0.6
Flash Point, TCC, D56, °F	160
Freezing Pt, D1477, °F	-26
Color Saybolt, D156	30+
Viscosity, D445, cs	
at 100°F	1.58
at 0°F	5.08
at -30°F	11.4[d]
Aniline Pt, D661, °F	175
Aniline-Gravity Constant	8908

Water Tol, F-791, 3251, Interface Rating	1
Sulfur, D1266, %w	0.005
Mercaptan Sulfur, D1323, %w	Nil
Corrosion, Cu Strip D130, 2 hr at 212°F	1B
Aromatic Content, D1319, %v	0.7
Bromine No. D1159	<0.01
Naphthalenes, F791, 3704T, %v	Nil
Smoke Point, D1322, mm	38
Luminometer No., D1740	103
Existent Gum, D381, mg/dl	4
16-Hr Potential Gum, D873, mg/dl	4
Net Heat of Combustion, Btu/lb	
ASTM D240 (Paar 2600 Modified)	18,876
NBS 5917[a]	18,859[a]
Hydrogen, D1018, %w	14.9
Copper, mg/liter[b]	<0.02
Nitrogen, ppm	<5
Basic Nitrogen, ppm	<0.3
Peroxide No., D-1563	<0.04
Water Separometer Index, Severity 15	85
Light Transmission, % at 425 mμ	100
Sediment, mg/gal, 0.45 micron[c]	
Average	2.1
Range, Five Determinations	1.4-3.1
Other	
Paraffins, %v Mass Spec	70
Naphthenes, %v Mass Spec	29

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a) Calculated by equation for kerosine boiling range materials containing less than 10% aromatics. $Q_p \approx 18110 + 0.0841 \times ACP \times °API$.

b) Copper extraction by hydrochloric acid (Petroleum Refiner <u>33</u>, 158 (1954)). Copper content by neocupreine complex (ASTM E-39-56T).

c) Determined by filtering 1 gallon samples through 0.45 micron Millipore Filter paper. See ASTM Committee D-2 report for 1962, Appendix X.

d) Estimated.

TABLE 42
HISTORY AND DESCRIPTION OF JET FUEL RAF 169-61 FROM THE CRC FUEL BANK

Date Produced:	July 1961	Processing Method:	SO_2 Extraction and Clay Treat
Date Drummed:	June 1962		
Date Into Storage:	December 24, 1962	Date Issued:	August 2, 1963
Date Rec'd Emeryville:	January 1, 1964	Replaces Issue of:	Original
		No. of Drums in Storage:	40

Additives: 5 lb/M bbl N,N-Di-secondary butyl p-phenylene diamine; 2 lb/M bbl N,N'-Disalicylidene-1,2-propanediamine

Comments on Availability: Highly paraffinic fuel, not commercially available.

PROPERTIES

Grav ASTM D287, °API	46.6	Water Tol, F-791, 3251, Interface Rating	0
Distillation, ASTM D86, °F		Sulfur, D1266, %w	0.004
I.B.P.	382	Mercaptan Sulfur, D1323, %w	0.001
5%	390	Corrosion, Cu Strip, D130, 2 hr at 212°F	1B
10%	394	Aromatic Content, D1319, %v	2
20%	399	Bromine No. D1159	-0.1
30%	401	Naphthalenes, F791, 3704T, %v	<0.2
40%	406	Smoke Point, D1322, mm	32
50%	412	Luminometer No., D1740	78
60%	418	Existent Gum, D381, mg/dl	1
70%	424	16-Hr Potential Gum, D873, mg/dl	1
80%	433	Net Heat of Combustion, Btu/lb	
90%	448	ASTM D240 (Paar 2600 Modified)	18,758
95%	462	NBS 5917[a]	18,763[a]
E.P.	476	Hydrogen, D1018, %w	14.6
Flash Point, TCC, D56, °F	154	Copper, mg/liter[b]	-0.008
Freezing Pt, D1477, °F	-48	Nitrogen, ppm	<5
Color Saybolt, D156	30+	Basic Nitrogen, ppm	0.6
Viscosity, D445, cs		Water Separometer Index, Severity 15	99.5
at 100°F	1.66	Light Transmission, % at 425 mμ	100
at 0°F	6.02	Sediment, mg/gal, 0.45 micron[c]	
at -30°F	11.10	Average	0.5
Aniline Point, D661, °F	166.5	Range, Five Determinations	Nil-1.5
Aniline-Gravity Constant	7759		

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a) Calculated by equation for kerosine boiling range materials containing less than 10% aromatics. $Q_p = 18110 + 0.0841 \times ACP \times °API$.

b) Copper extraction by hydrochloric acid (Petroleum Refiner 33 158 (1954)). Copper content by neocupreine complex (ASTM E-39-56T).

c) Determined by filtering 1 gallon samples through 0.45 micron Millipore Filter paper. See ASTM Committee report for 1962, Appendix X.

(Continued)

TABLE 42 (CONTD)
HISTORY AND DESCRIPTION OF JET FUEL RAF 169-61 FROM THE CRC FUEL BANK

INSPECTION PROPERTIES FROM FUEL SUPPLIER

Grav ASTM D287, °API	46.9	Water Tol, F-791, 3251, Interface Rating	1B
Distillation, ASTM D86, °F		Sulfur, D1266, %w	<0.002
I.B.P.	378	Mercaptan Sulfur, D1323, %w	0.000
5%	391	Corrosion, Cu Strip, D130, 2 hr at 212°F	1A
10%	398	Aromatic Content, D1319, %v	2
20%	403	Naphthalenes, F791, 3704T, %v	0.0
30%	409	Smoke Point, D1322, mm	35.5
40%	414	Luminometer No., D1740	83
50%	419	Existent Gum, D381, mg/dl	<1
60%	425	16-Hr Potential Gum, D873, mg/dl	1
70%	432	Net Heat of Combustion, Btu/lb	
80%	441	ASTM D240	18,686
90%	456	NBS 5917a)	18,765a)
95%	468	Hydrogen, D1018, %w	14.6
E.P.	485		
Residue, %	1.5		
Loss, %	0.5		
Flash Point, TCC, D56, °F	155		
Freezing Pt, D1477, °F	-48		
Color Saybolt, D156	30+		
Viscosity, D445, cs at -30°F	11.0		
Aniline Point, D661, °F	166		
Aniline-Gravity Constant	7785		

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a) Calculated by equation for kerosine boiling range materials containing less than 10% aromatics. $Q_p = 18110 + 0.0841 \times ACP \times$ °API.

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