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AFWAL-TR-87-2034

ADVANCED AIRCRAFT FUEL EVALUATION

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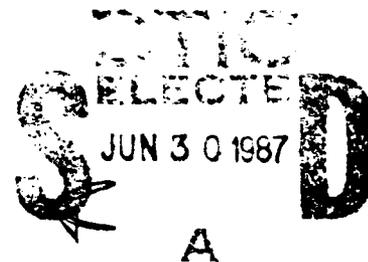
AD-A182 029

MARCH 1987

FINAL REPORT FOR THE PERIOD JUNE 1986 - JANUARY 1987

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

  
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SECURITY CLASSIFICATION OF THIS PAGE

ADA182029

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>			1b. RESTRICTIVE MARKINGS <b>N/A</b>			
2a. SECURITY CLASSIFICATION AUTHORITY <b>N/A</b>			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release, distribution unlimited.			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE <b>N/A</b>						
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) <b>AFWAL-TR-87-2034</b>			
6a. NAME OF PERFORMING ORGANIZATION <b>Partnerships Limited</b>		6b. OFFICE SYMBOL <i>(If applicable)</i>	7a. NAME OF MONITORING ORGANIZATION <b>Aero Propulsion Laboratory Fuels and Lubrication Div. (AFWAL/POSF)</b>			
6c. ADDRESS (City, State and ZIP Code)			7b. ADDRESS (City, State and ZIP Code) <b>AFWAL/POSF Wright-Patterson AFB OH 45433-6563</b>			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL <i>(If applicable)</i>	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER <b>F33615-86-C-2663</b>			
8c. ADDRESS (City, State and ZIP Code) <b>P.O. Box 6503 Lawrenceville NJ 08648</b>			10. SOURCE OF FUNDING NOS.			
11. TITLE (Include Security Classification)			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
			<b>65502F</b>	<b>3005</b>	<b>20</b>	<b>62</b>
12. PERSONAL AUTHOR(S)						
13a. TYPE OF REPORT <b>Phase I Final Report</b>		13b. TIME COVERED FROM <b>Jun 86</b> TO <b>Jan 87</b>		14. DATE OF REPORT (Yr., Mo., Day) <b>Mar 87</b>	15. PAGE COUNT <b>78</b>	
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) <b>Advanced Jet Fuels Hydrogenation of Methyl Naphthalenes Hydrodealkylation</b>			
FIELD	GROUP	SUB. GR.				
<b>21</b>	<b>04</b>	<b>-</b>				
<b>07</b>	<b>01</b>	<b>-</b>				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The objective of this program was to evaluate the potential of naphthenic hydrocarbon fuels for advanced hypersonic vehicles. The availability and potential of these fuels was evaluated from currently available or near term refining feedstocks or petrochemical products. Novel processing routes were assessed as to their potential for producing suitable fuels. Small test samples of candidate fuels were produced for analysis. The availability of these fuels was estimated through the year 2000.						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>			
22a. NAME OF RESPONSIBLE INDIVIDUAL <b>WILLIAM E. HARRISON III</b>			22b. TELEPHONE NUMBER <i>(Include Area Code)</i> <b>513-255-6601</b>	22c. OFFICE SYMBOL <b>AFWAL/POSF</b>		

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## PROJECT SUMMARY

The objective of this project was to provide estimates of the availability, cost and quality of naphthenic hydrocarbon fuels for advanced hypersonic vehicle propulsion as a function of time.

To accomplish this objective a proposed specification of the fuel was established. Potential sources of feedstocks were surveyed with particular attention to petroleum based refinery streams. Three promising feedstocks were identified in addition to purchased petroleum derived naphthalene, which served as the basis of comparison.

Processing routes to convert the identified feeds to specification fuel were identified. These are based on existing refining technology and require no process innovation or research for successful fuel production. *(of the proposed fuel)*

Samples of the proposed fuel were produced in the Air Force Aero Propulsion Laboratory Hydrogenation Reaction System. The samples substantially met the desired properties of the advanced fuel. In addition rate constants were derived for the hydrogenation of naphthalene and the cis-trans- isomerization of decalin. Other rate constants relevant to the production of advanced fuel from refinery feedstocks were also measured. The requirements for the design of the aircraft system to use these fuels were estimated.

Finally, the availability and cost of advanced fuels from the identified refinery streams were estimated and a possible scenario for supplying this fuel through the year 2000 was developed.

The advanced fuel in question is intended for application in hypersonic aircraft of the future, particularly those intended for high mach flight with extensive fuel cooling of the airframe and engine. The specification of the fuel is close enough to current military jet fuels, however, that it could be applied advantageously to next generation commercial and military aircraft and engines,



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Availability Codes	
Normal and/or	
Dist	Special
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## FOREWORD/ACKNOWLEDGEMENT

Partnerships Limited Inc. prepared this final technical report under contract F33615-86-C-2663 for the Fuels Branch of the Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. This report documents work carried out under a Small Business Innovation Research Phase I contract from June to December 1986. Timothy L. Dues was the Air Force Technical Monitor and Paul H. Kydd was the Principal Investigator.

The authors wish to acknowledge the assistance and advice of W. E. Harrison III of the Fuels Branch in the planning and execution of this Project.

The experimental work reported on in Task 4 was carried out on the AFWAL Fuel Hydrogenation Unit. The work of Robert Morris, Mike Schumacher, Paul Hagadorn, Steve Jackson and Don Jackson in making this part of the program a reality is gratefully acknowledged. The POSF analytical group under Mr. Dues performed all the analyses reported in Task 4 which constitute the actual results of the experiments.

A sample of light cycle oil feedstock was provided by John Paraskos and Russel Krug of Chevron Research Co. and Tom Geif of the Chevron El Segundo refinery. Samples of reformate were provided by Doug Rundo and J. Knapper of Amoco and Robert A. Sailor of Mobil. The helpful cooperation of these companies and individuals is gratefully acknowledged.

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## INTRODUCTION

The solicitation to which this project was a response read as follows:

AF86-183. TITLE: Advanced Fuel Evaluation

DESCRIPTION: The potential of liquid hydrocarbon fuels as energy sources for advanced hypersonic vehicles must be addressed. From laboratory tests, naphthenic hydrocarbons have been demonstrated to have the potential for cooling and supplying energy to high speed aircraft. The availability and potential of these fuels will be evaluated from currently available or near-term refining feedstocks or petrochemical products. In addition, novel processing routes will be assessed as to their potential for producing suitable fuels. Small (pint or less) samples of candidate fuels will be produced and appropriate analyses will be performed to determine the quality of the fuels and the cost of production. Estimates will be projected to determine the availability, cost, and quality of this family of fuels as a function of time. The feasibility of such fuels could provide the Air Force with higher energy liquid hydrocarbons that could cool advanced systems, increase heating value, and produce high energy gaseous fuels such as acetylene and hydrogen.

The proposal in response to this solicitation stated the overall objective to be:

"to provide estimates of the availability, cost and quality of naphthenic hydrocarbon fuels for advanced hypersonic vehicle propulsion as a function of time."

The program consisted of the following six tasks:

- Task 1. Review of Advanced Fuel Specification
- Task 2. Survey of potential feedstocks
- Task 3. Survey of processing options, existing and novel
- Task 4. Preparation of laboratory samples of fuels
- Task 5. Fuel availability scenarios through the year 2000
- Task 6. Final report

This report summarizes all of the work done on this project, the conclusions drawn and recommendations for the future.

## SUMMARY OF RESULTS

The fuel proposed for hypersonic aircraft as a result of this Phase I program is a mixture of decalin isomers and methyl decalins. These compounds have the potential for acting as a sink for approximately 1000 BTU/lb. of sensible heat and almost 1000 BTU/lb. of endothermic heat of dehydrogenation. In addition they have physical properties which can very nearly meet existing specifications for kerosene type military aircraft fuels. This makes them potentially convenient and safe to use in current as well as advanced systems. Combustion of the resulting hydrogen-naphthalene mixture is likely to result in a more luminous flame than that of conventional fuels. This may not matter in advanced systems with premixing combustors.

In addition to purchased petroleum derived naphthalene, three refinery streams were identified as potential feedstocks for advanced fuels. These are:

- Reformate stripper bottoms
- Aromatic extracts from kerosene products such as Jet A
- Light cycle oil from fluid catalytic crackers

We have found that reformate intended for gasoline blending contains a high boiling tail which may provide a very favorable feedstock for the production of advanced fuels. This material consists largely of naphthalene and alkyl naphthalenes and is substantially free of deleterious sulfur and nitrogen compounds. The total available supply could amount to thousands of barrels per day and require minimum processing to recover and convert to saturated compounds. These results should be investigated further and if confirmed would make available an advantageous source of feedstock at an affordable cost.

An advanced fuel feedstock can be prepared by solvent extraction of kerosene products. An aromatic extract has been prepared from commercial Jet-A and found to have a similar composition to the reformate stripper bottoms. Available quantities will be similar also, though the processing required may be greater.

Light cycle oil can be extracted to provide a mixed naphthalene-alkyl naphthalene feedstock. The quantities of LCO are in the hundreds of thousands of barrels per day and the price is likely to be lower than the above feeds. Most LCO is expected to be high in heteroatom content and definitely will require severe hydrotreatment to produce a suitable feed.

The basic process for production of advanced naphthenic fuels is aromatics saturation. Mild conditions of 500 PSI and 450 degrees<sup>o</sup>F over a platinum on alumina catalyst are sufficient. The process requires a very clean feedstock with a sulfur content in the low parts per million range.

Hydrodesulfurization can be achieved by treatment at pressures in the neighborhood of 1000 psi and temperatures of 650 to 750<sup>o</sup>F over sulfided cobalt molybdenum on alumina catalyst.

Extraction of aromatics can be accomplished with tetramethylene sulfone (Sulfolane) and with other polar compounds.

If it is desirable to remove methyl groups from alkyl naphthalenes in the feed, this can be done with either catalytic or non-catalytic hydro dealkylation processes operating at 600 psi and 1200 to 1400<sup>o</sup>F.

All of these processes are available as commercially proven technology and the required process units are found in a number of U.S. refineries. The production of reformer stripper bottoms may be a novel approach to producing feedstock, but the technology for implementing this approach is straightforward.

Laboratory samples of advanced aircraft fuel were prepared by hydrogenating purchased naphthalene. The samples closely reproduced the desired fuel properties for advanced systems including the Jet Fuel Thermal Stability Test.

Literature data suggested that it would be possible to simultaneously desulfurize and dealkylate feeds such as light cycle oil. Two series of runs using different catalysts were made to investigate this point. We found that little dealkylation takes place even under very severe hydrocracking conditions. This suggests that the presence of methyl groups on the fuel will have little effect on the endothermic heat sink potential of the fuel. This point also should be confirmed in further studies.

The processing costs of the various routes to advanced fuels were estimated. The results are dominated by the cost of feedstock. Hydrogenation of purchased petroleum naphthalene is the simplest route to advanced fuels but by far the most expensive. It is suitable for production of component test fuel in the 1980's.

Advanced fuels from reformat stripper bottoms and kerosene extracts are roughly comparable in cost, quantity and complexity of manufacture. These sources could serve for initial production in the 1990's.

Light cycle oil requires the most processing but features the lowest price and the largest quantity. Dedicated processing facilities could produce this fuel in the late 1990's and post 2000 time period.

Refineries with facilities applicable to production of advanced fuels have been identified.

## TASK 1. REVIEW OF ADVANCED FUEL SPECIFICATION

The objective of this task was to define the advanced aircraft fuel characteristics for which the rest of the study will attempt to provide:

Feedstocks (Task 2),  
Process routes (Task 3),  
Laboratory samples (Task 4), and  
Availability scenarios (Task 5).

The advanced fuels for hypersonic aircraft to be studied in this program are naphthenic (cycloparaffin) hydrocarbons. They offer the possibility of cooling engine and airframe components by virtue of both the sensible heat they can absorb and the endothermic heat of dehydrogenation at 450-500°C to the corresponding aromatic hydrocarbons. The aromatics in turn are extremely stable and can be heated to still higher temperatures of 650-750°C without decomposition, particularly in the presence of the hydrogen released in the endothermic dehydrogenation.

Having absorbed this heat from the airframe, the fuel now has an effective heating value approximately 10% greater than the chemical heat of combustion, which is available to provide thrust. In addition, the associated hydrogen can provide the rapid ignition and combustion required in supersonic combustion ramjet engines.

The higher molecular weight dicyclic naphthenes (decalins) have been of interest recently as fuels for conventional aircraft because they have a high density and thus a higher volumetric heating value than conventional fuels. High density fuels have the potential for providing a longer range in volume limited aircraft.

The original proposal for this Phase I program suggested a fuel composition consisting primarily of a mixture of cis- and trans-decalin with a small admixture of cyclohexane to reduce the viscosity.

The properties of various candidate advanced fuel components are shown in Table I along with the desired properties of an endothermic-vaporizing fuel given in a study performed by Shell in the late 60's and early 70's (1). The properties of the laboratory fuel sample produced in this study are also shown.

Preliminary work suggested concentrating on the mixture of decalins only in this program, for the following reasons:

1. The 50/50 decalin mixture is very close to the final properties desired. The only drawback is a viscosity of 13.0 centistokes at -30°F compared to a desired level of 11.5. However, the decalin mixture meets the specification for JP-5 fuel and should perform satisfactorily in existing fuel system equipment.
2. There already exists a wealth of literature data on the dealkylation and hydrogenation of single ring compounds. The chemistry of dicyclic compounds is more important and less well known. An opportunity exists to add useful information.
3. The dicyclic product offers the significant safety advantages of a high flash point and the performance advantage of a high density without sacrificing freeze point or heat of combustion.

4. Next to cyclohexane, which is not a practical fuel, the decalin mixture has the highest heat sink potential of any readily produced fuel, and thus the highest performance.
5. Unlike benzene, naphthalene which is the raw material for decalin production is not in great demand, and supplies and prices may be favorable.

The heat of combustion of cis-decalin is 1502.5 Kcal/mole, while that of trans-decalin is 1499.5 Kcal/mol. Commercial decalin is said to range from 40% trans to 100% trans in line with the greater thermodynamic stability of the trans isomer (2). The analysis of a 99% pure grade of decalin in (3) found it to be a 37.3% cis-62.7% trans mixture.

Cis-decalin will isomerize into trans in the presence of aluminum chloride or aluminum bromide (4). From a purely thermal point of view, the trans-isomer would make a better endothermic fuel, but the difference is small. The viscosity of the trans-isomer is lower than the mixtures, but the freezing point is higher. Figure 1 provides a means of approximately estimating the viscosity of various mixtures and of the pure isomers as a function of temperature.

### The Effect of Alkyl Groups

Ideally, one would like unsubstituted decalins as advanced fuels to obtain the greatest endothermic effect from dehydrogenation and to avoid dealkylation reactions. The latter are unfavorable since they are exothermic, reducing the heat absorbing capability of the fuel. The presence of an alkyl group increases the molecular weight of the fuel relative to the amount of hydrogen that can be recovered by dehydrogenation, and the hydrodealkylation reaction consumes a mole of hydrogen per mole of alkyl substituents removed.

This subject was discussed on a visit to AFWAL on October 21, 1986. The review of fuel properties was broadened to include the following questions:

- Do alkyl groups matter, and if so, how much?
- What is the influence of heteroatoms?
- Are JP-10 analogues desirable?
- Does residual tetralin matter?

Table 1 characterizing alternative advanced fuels has been extended to include cyclohexane, methyl cyclohexane and alkyl decalins. The endothermic heat uptake has been calculated on the basis that the dehydrogenation reactions are much faster than the dealkylation reactions, and that the latter do not occur to an appreciable extent.

Dehydrogenation of endothermic fuels resembles catalytic reforming of hydrocarbons to make high octane aromatic gasoline. The catalyst of choice is a noble metal supported on alumina, and the conditions of high temperatures and low pressures are similar. Data on catalytic reforming (5) suggests that under these conditions dealkylation will in fact be negligible. The effect of alkyl groups is expected to be limited to the fact that they increase the mass of the molecule without increasing the available hydrogen.

Since dehydrogenation resembles catalytic reforming, it is likely to be extremely sensitive to heteroatoms. Reformer feedstock must be hydrotreated to reduce both sulfur and nitrogen to the low parts per million range to avoid poisoning the noble metal catalyst. The stability of the fuel in the non-catalytic heat exchangers of the

aircraft system will also be adversely affected by at least some sulfur, nitrogen and oxygen compounds as well as by oxygen from the air.

Bridged ring compounds such as terpenes and JP-10 should be less attractive than alkyl naphthenes because they are geometrically unable to convert to the corresponding aromatic, and the hydrogen release per pound will be less.

Residual tetralin is undesirable because it represents a loss in endothermic heat absorption capability and a loss of 60% of the potential hydrogen availability from the corresponding decalin. Normally it would be undesirable because it increases smoke and radiative heat transfer to the combustor, which has an adverse effect on liner life. Endothermic fuels are a special case, however, since they will all burn as aromatics.

### Luminosity

A potential drawback of decalins as an endothermic fuel for advanced aircraft is that the hydrocarbon will actually burn as naphthalene, which is known to produce highly luminous flames. This may increase the heat load on the supersonic combustor and offset some of the advantage of endothermic fuel cooling.

A short literature survey has been conducted to assess the severity of this problem. Much of the required chemistry and combustor data was presented at a symposium on Aircraft Research and Technology for Future Fuels at NASA Lewis on April 16-17, 1980 (Reference 6).

Howard and co-workers discussed the basic chemistry of soot formation in hydrocarbon flames. The process is generally believed to involve polymerization of acetylene and its derivatives to form polynuclear aromatic hydrocarbons, which grow to microspheres of approximately 200 Angstroms diameter. These then agglomerate into larger particles if their number is sufficiently large.

Formation of benzene from smaller compounds is a slow reaction sequence, as pointed out by Ruth and Blazowski. Addition of vinyl acetylene to naphthalene and acetylene to methyl naphthalene are fast condensation reactions. This accounts for the fact that the smoking tendencies of monoaromatics are greater than those of aliphatic hydrocarbons, and dicyclic aromatics are smokier still.

Ruth and Blazowski divided the fuels which they investigated in a well stirred reactor into three categories:

<u>I. Like ethylene</u>	<u>II. Like toluene</u>	<u>III. Worse</u>
Hexane	Xylene	1-methyl naphthalene
Cyclo-hexane	Cumene	
n-Octane	Tetralin	
iso-Octane	Dicyclopentadiene	
iso-Octene		
Cyclo-octane		
Decalin		

Category I fuels produce large amounts of unburned hydrocarbons prior to reaching the critical equivalence ratio at which soot begins to form. Category II fuels produce soot at the same equivalence ratio ( $\phi = 1.4$ ) as that at which unburned hydrocarbons first appear. Methyl naphthalene produces soot at a still lower equiv-

alence ratio, and more of it.

The behavior of naphthenes such as cyclohexane and decalin is anomalous. Naegeli and Moses found decalins to behave like alkyl benzenes in a combustion rig similar to an engine. On the one hand, these compounds can fragment to light hydrocarbon gases from which the reassembly of aromatic rings is a slow process. On the other hand, they can dehydrogenate directly to aromatics and contribute to smoke production by a fast reaction sequence. Most test methods show the naphthenes to be intermediate between aromatics and paraffins.

Naegeli and Moses tested a number of fuels at the same hydrogen content to establish the effect of hydrocarbon type on flame radiation. Their conclusion was that radiation correlates best with the percentage of the carbon in the fuel which is in polycyclic rings.

Rosfjord (7) performed a similar test series on naphthalene doped fuels and correlated the results against (100-N) to the -0.4 power. This is a rather weak dependence on naphthalene content, however, since the maximum value of N in these tests was 13%.

Vogel, Troth and Verdouw (8) studied the effect of various fuels on the TF-41 engine and concluded, "Statistical evidence indicates that the influence of multi-ring aromatic content is equal to and sometimes greater than the influence of hydrogen content."

On the other hand, a number of GE authors (9, 10, 11) have found that for the J-79, the smokeless J-79 and the F101 engines, "within the range tested, fuel aromatic type (predominantly monocyclic xylenes or dicyclic naphthalenes) had relatively little effect on combustion characteristics."

Pressure has a significant effect on luminosity. Modern turbofan engines with pressure ratios of 25 have essentially black body conditions in the combustor. Flame radiation under these conditions is also independent of fuel type, since no amount of carbon can make the flame blacker than black.

Early specifications for hypersonic aircraft operating at Mach 8 and 100,000 ft. altitude quoted by Nixon and co-workers (12) suggested a combustor pressure of about 0.5 bar, corresponding to a combustor Mach number greater than 4.0. At Mach 2 the combustor radiation is high and still affected by hydrocarbon type. The actual combustor Mach number will be in excess of 2.5 to preserve a reasonable inlet temperature, so fuel composition effects could be significant.

Martel and Angello (13) originally proposed that hydrogen content was the dominant influence on the combustion characteristics of fuels, and Jackson and Blazowski (14) confirmed this approach more recently, concluding that hydrogen content was the dominant effect relative to hydrocarbon type and volatility. They also pointed out that newer combustor designs with air blast fuel nozzles and lean primary zones were much less sensitive to hydrogen content than earlier combustors with pressure atomizing nozzles and fuel-rich primary zones.

Our conclusion from this is that there is a valid chemical reason to expect fuels high in naphthalene to burn with a more luminous flame than those of other hydrocarbons (and much more luminous than hydrogen), but that the actual luminosity will be determined by the details of the combustion system. The conditions in a Scramjet combustor are favorable for reducing the luminosity, in that the fuel is prevaporized and premixed with air in an air blast fuel nozzle carried to the ultimate extreme.

The recommended fuel for advanced aircraft and engine systems is a mixture of cis- and trans-decalin. The addition of alkyl decalins will probably decrease performance only by "diluting" the endothermic fuel with methyl groups, reducing the endothermic effect by 10 or 20%, and the overall heat sink by 5-10%. Heteroatom content should be in the low parts per million range. Tetralin and other aromatics should be minimized, as they have a relatively large effect on the heat sink capability. Naphthenes which cannot dehydrogenate to six membered ring aromatics are unfavorable for the same reason.

## TASK 2. FEEDSTOCK SURVEY

This program is concerned with advanced fuels which can be produced from currently available or near-term refining feedstocks or petrochemical products. The program has been focused on petroleum derived feedstocks. The refinery feedstocks of most interest are catalytic reformer bottoms, aromatic extracts from kerosene products and light cycle oil from catalytic crackers.

The petrochemical feed of interest is naphthalene. Coal derived naphthalene is a potential feedstock but less desirable than petroleum naphthalene because of lower purity, a high content of difficult to remove heteroatoms, and uncertain supply in view of the current state of the steel industry.

The feedstocks of interest are shown in Table 2, along with analytical data obtained from the literature or in this program and data on price and availability obtained from suppliers or the literature. Other potential feedstocks such as ethylene cracker tar have not been pursued because of low quality and uncertainty of supply. Since the emphasis in this program is on near-term feedstocks, we feel that ample supplies of high quality petroleum based feedstocks will be available.

### Naphthalene

As discussed in succeeding sections, naphthalene hydrogenation is the simplest route to advanced fuels for hypersonic aircraft. Naphthalene with a melting point of  $80.5^{\circ}\text{C}$ , which is equal to the literature value, is available as an article of commerce based on petroleum. This material is essentially chemically pure.

Coal derived naphthalene has a melting point of  $78^{\circ}\text{C}$  and contains substantial quantities of ring bound nitrogen and sulfur. The feedstock is cheaper than petroleum naphthalene, but the processing is likely to be more expensive. Since the cost of fuel from naphthalene is dominated by the feedstock price, however, and coal derived naphthalene will presumably always be available independent of the petroleum industry, this route to advanced fuels should not be ignored.

### Catalytic Reformer Stripper Bottoms

Reformer bottoms could probably be used as feedstock as received. The catalytic reforming process uses the same platinum catalyst as the hydrogenation to the final fuel product. Consequently the reformer feedstock has to be hydrosulfurized and denitrogenated to an acceptable degree, and the reformer product is exceptionally clean.

Currently, no refiners are making heavy reformate which could serve as a feedstock to produce decalin type fuels directly, although Ashland Oil Co. and others have done this in the past to produce naphthalene feedstock (15) and recommended it as a route to produce JP-4 and JP-8 from shale oil (16). It is unlikely that refiners will be willing to run reformers on heavier feedstocks because they are all operating at maximum severity to produce high octane unleaded gasoline, and heavier feeds increase coke, which is the limiting factor now.

There is, however, a significant amount of product from gasoline boiling range reformate which boils in the naphthalene range above  $218^{\circ}\text{C}$ . We have stripped a 100 ml sample of heavy reformate with a nominal boiling range of  $129$  to  $189^{\circ}\text{C}$  and obtained a yield of approximately 5% of product boiling above  $218^{\circ}\text{C}$ . The apparatus used for this

procedure is shown in Figure 2. The approximate boiling range measured in the liquid, not the vapor, was as follows:

Recovered	Temperature
IBP	160°C
5%	162
10	163.5
20	172
50	178
90	210
92	218

The semi-quantitative GC-MS results on naphthalenes and methyl naphthalenes of the heavy reformat and the stripped product are given in Table 2. the gas chromatograms themselves are shown in Appendix B.

A sample of full range reformat which has been received will allow us to compare the yields and analyses of reformat from an operating refinery with those from the laboratory sample of heavy reformat at a later time.

Following up on a suggestion from Chevron Research, a sample of gasoline has been stripped to determine how much naphthalene boiling range product is available from this source. The apparatus and procedure were the same as for the heavy reformat except that 200 ml of 87 octane regular unleaded gasoline were charged due to the lower anticipated yield. The approximate boiling range was as follows:

Recovered	Temperature
40%	101°C
60	140
80	179
85	191
87.5	203
89.5	218

The 218°+ liquid recovered was 2.5% of the charge and the loss, primarily light hydrocarbons, was 8%. The analysis of the recovered material is shown in Table 2.

The yield from gasoline is small, but the quantities produced are prodigious. The total production of gasoline in the United States is approximately 100 billion gallons per year. If 40% of this is reformat containing 3.4% of 218°C+ material usable as feedstock for advanced fuels, the potential supply is 90,000 bbl/day. If, in addition, stripping the high boiling material from gasoline increases octane number without causing a significant loss in gasoline yield, refiners might have a real incentive to supply this product. Reformat stripper bottoms should have approximately the desired 220-250 C (425-475 F) boiling range and be almost completely free of heteroatoms. This will be the feed of choice for making very clean aircraft fuels.

There appears to be some inconsistency between the yields of naphthalenes found in reformat and in stripped reformat. The high boiling naphthalenes should be concentrated in the stripper bottoms by a factor of 10 to 20, but the measured concentration is only 3 times higher in the bottoms. If the actual concentration is this low, the total supply of feedstock from this source may only amount to 13,000 bbl/d. This question should be resolved in future work.

### Kerosene Extracts

An almost equally clean source of feedstock for advanced aircraft fuels will be aromatic extracts from kerosene products such as Jet A, diesel fuel #1 and kerosene itself. Total production of these products amounts to approximately a billion barrels per year in the United States, most of it as Jet A commercial aviation fuel. Again, removing the aromatic constituents will increase the quality of the raffinate and relieve pressure on the refiners who are pressing the specification limits on aromatics content and smoke point for jet fuel.

To determine the characteristics of such an aromatic concentrate, a sample of Jet A was extracted with Sulfolane (tetramethylene sulfone). A 50 ml sample of jet fuel was shaken in a separatory funnel with 50 ml of Sulfolane for one minute. The Sulfolane layer was drawn off and steam distilled in the apparatus shown in Figure 3.

The steam distillation was continued until a total of 100 ml of distillate was recovered. This contained approximately one ml of aromatic extract, for a yield of 2% on the initial charge of Jet-A. The GC-MS analysis of the extract is given in Table 2.

If 2% is a representative yield and 10% of this is naphthalenes, the total supply of feedstock from this source will be approximately 5,500 bbl/d in the United States. This feed will not be as clean as the gasoline stripper bottoms and may require hydrotreatment to reduce sulfur prior to hydrogenation. However, since the feedstock is primarily virgin distillate from relatively sweet crudes which may have been hydro-treated already, the amount of post treatment will be minimal.

### Light Cycle Oil

Light Cycle Oil from catalytic crackers is the largest source of petroleum derived highly aromatic feedstock for advanced aircraft fuel. The total production of this material in the United States is approximately 450,000 bbl/d.

LCO will contain sulfur and nitrogen and will probably be deficient in aromatic content as well. A sample of LCO has been received from the Chevron refinery in El Segundo, California, which is running on highly naphthenic California crudes. This should be an optimum feed for production of advanced fuels from LCO. The GC-MS analysis of this material is shown in Table 2.

LCO will be the cheapest feedstock and is available in the greatest quantity. At a 9% yield, the total feedstock for advanced jet fuel could amount to 40,000 bbl/d. It will probably have to be topped to provide the desired boiling range and extracted with Sulfolane to provide a highly aromatic feed consisting primarily of alkylnaphthalenes. Extensive further processing will be required to prepare an acceptable final product, but since feedstock cost has such a dominant influence on product cost, this may be acceptable. This question is addressed in Task 5.

### TASK 3. EVALUATION OF PROCESSING ALTERNATIVES

The processing alternatives which have been found to be most attractive in this study are shown in Table 3.

#### Hydrogenation

The conventional process for producing advanced aircraft fuels consisting of mixtures of decalins is total hydrogenation of an aromatic hydrocarbon feedstock such as naphthalene.

The process chosen for the hydrogenation data was the Smoke Point Improvement process offered by Shell described in Reference 17. This is a process for upgrading kerosenes over platinum on alumina catalyst at 50 to 70 bars hydrogen pressure, 230 to 300°C, and a liquid hourly space velocity of 2.5 to 4.5. A single stage reactor is capable of reducing the aromatics content of a typical feed from 17% to 1.5%.

A number of other commercial processes are available for hydrotreating petroleum feeds of varying degrees of contamination. To achieve complete saturation, however, it is necessary to operate with an active Group VIII B (platinum) catalyst under conditions where the equilibrium strongly favors aromatic saturation, namely at temperatures lower than 350°C. This in turn implies a very clean feedstock, since the noble metal catalysts are poisoned by even ppm levels of sulfur. Thus the final step in producing the advanced aircraft fuel is probably determined and is well known commercial technology. The unknown steps in the fuel production sequence involve preparing a suitably clean feed for the hydrogenation step.

An alternative which may relieve this restriction is the Unisar Process of Union Oil Co. (18). It is similar to other hydrogenation processes, but the AS-100 catalyst used is stated to be resistant to sulfur poisoning. Even with this process, however, it is likely that exceptionally clean feeds will be required because of the requirement for exceptional thermal stability of the final fuel. Heteroatoms are known to degrade thermal stability (19), and a successful advanced fuel will have to be thoroughly desulfurized and denitrogenated.

It is worth noting the central role played by noble metal catalysts in the preparation and use of advanced aircraft fuels. This is shown schematically in Figure 4.

#### Dehydrogenation. (Reforming)

The aircraft system will include a platinum or bimetallic platinum-rhenium catalyst essentially identical to a catalytic reforming catalyst (20) to dehydrogenate the naphthenic fuel, provide cooling to the airframe, and generate hydrogen. Viewing the situation in this way means that the tremendous background in catalytic reforming technology can be used to provide guidance in the design of the aircraft system. In particular, the requirements on the naphthene fuel used as a feed to the on-board catalytic system will be the same as those for reformer feed, namely a few parts per million of sulfur and nitrogen.

Starting with reformat as a feedstock for the fuel production process ensures that this requirement is met in line with the general principle that to make a clean product it is advantageous to start with a clean feed. It also means that there is no need to pretreat the feed to the hydrogenation unit, which will saturate the aromatic feedstock and reduce the heteroatom content still more. This process sequence is our

second preferred route for the early 1990's. The major uncertainty in this sequence is whether it will be necessary or desirable to remove the alkyl substituents on the aromatic product of the reformat stripper by hydrodealkylation. HDA processes are also important to this study since they are the process route to petroleum naphthalene (21), which is a potential feedstock in the 1980's.

### Hydrodealkylation

Because the presence of alkyl side groups is not helpful to the functioning of endothermic fuels, and may be harmful, a major part of this Phase I program has been to investigate the dealkylation of various feedstocks to naphthalene which can be hydrogenated to a mixture of decalins as the final fuel.

Most naphthalene up to the early 1970's was derived from coal tar middle oil. In 1961 Ashland brought on the first plant for producing petroleum naphthalene, followed by several others (22). All were based on hydrodealkylation processes using catalytic reformer bottoms or cat cracker light cycle oil as feedstocks. A full 75% of the naphthalene produced historically went into phthalic anhydride manufacture. With the emergence of processes based on ortho-xylene, naphthalene production has been declining, and no new plants have been built. DuPont has converted some naphthalene into decalins for use as solvents and chemicals.

There are three classes of dealkylation processes which have been commercialized:

non-catalytic dealkylation,  
catalytic dealkylation, and  
disproportionation,

in which part of the feed is dealkylated and part is doubly alkylated, as in production of xylenes and benzene from toluene.

Examples of the first type are the HDA and THD processes and proprietary processes developed by Standard Oil of Indiana and Sun Oil Co. They operate at 1250 to 1350° F and at pressures above 500 psi, with a substantial excess of hydrogen. Cold hydrogen is used to control the exothermic heat release of the dealkylation reaction as well as to provide the reagent. The product is very pure benzene or naphthalene and light hydrocarbon gases, principally methane.

Hydeal and Unidak are catalytic processes. Dealkylation proceeds by a free radical mechanism catalysed by group VIB and group VIII metals at high temperature. Carbonium ion formation is undesirable, so acid catalyst supports are avoided. Active hydrogenation catalysts and conditions should be avoided to minimize ring saturation and cracking.

The Hydeal catalyst is a low activity hydrodesulfurization catalyst operating at 1250° F and at 500-1000 psi with a 5:1 hydrogen-to-feed ratio. The Unidak process operates at 1000-1100° F and at 500-1000 psi with 2-5 moles of steam and 4-10 moles of hydrogen per mole of hydrocarbon. The catalyst is eg. cobalt molybdate on silica-stabilized alumina. Steam has been found useful in preventing loss of aromatic rings. Otherwise, conditions are very similar to the thermal processes, including the high temperature.

Disproportionation or trans alkylation processes are the ARCO Xylenes Plus process and the Tatoray process (23) licensed by UOP. Both are vapor phase catalytic processes using non-precious metal catalysts. Mobil has a similar process based on

ZSM-5 zeolite catalyst. These processes are more economic than dealkylation because the alkyl group is preserved and the yield of valuable aromatics is higher. They have been successfully applied to monoaromatics but not to dicyclic aromatics, as far as we know now.

Disproportionation may be a possible route to the desired naphthalene feedstock, but for fuel production it will involve separating the naphthalene from dimethyl naphthalene and finding a use for the latter. The yield of fuel will be low and the economics not as favorable as the petrochemical process for monoaromatics.

A more favorable route appeared to be hydrodesulfurization accompanied by mild hydrocracking to clean up the feedstock and eliminate alkyl substitution simultaneously. Friedman and Kovach (24) have studied mild hydrocracking of light cycle oil to convert it to gasoline. They have found steam helpful in preventing loss of aromatic rings in the presence of an alkalized Co Mo on alumina catalyst. Alkalized chromia-alumina has also been found to be effective. Naphthalene feeds give rise to some carbon deposition which will require regeneration periodically.

Patzer, Farrauto and Montagna (25) published a paper on "Characterization of Coal Liquefaction Catalysts Using 1-Methyl-Naphthalene as a Model Compound" which shows conversion of up to 96.9% of the feed into dealkylated products. Further confirmation of this important result was a major objective of the experimental work carried out in Task 4 of this program. If this route were practicable, the three-step process for producing vaporizing-endothermic fuel from available feedstocks proposed for this program could be reduced to two steps of combined feed pretreatment and dealkylation followed by hydrogenation to the final product. Furthermore, the conditions were expected to be well within the capabilities of available hydrocrackers and the Fuel Hydrogenation Reactor at AFWAL.

Alternatively, if the rate of dealkylation can be shown to be much lower than that of dehydrogenation, then the presence of alkyl groups will have a minimal effect on the performance of an endothermic fuel, since the dealkylation reaction will not diminish the yield of hydrogen or the endothermic heat absorption. The only effect of alkyl groups will be to increase the molecular weight of the naphthalene based fuel and lower the endothermic heat abstraction by 5 or 10% on a weight or volume basis. Thus the measurement of the rates of dealkylation was an important objective of the present program.

### Hydrodesulfurization

Again there are a number of commercial processes which have been developed to hydrotreat feeds containing sulfur and nitrogen to reduce the concentrations of these heteroatoms. In some cases these have been used as a first stage with a noble metal second stage to desulfurize and saturate difficult feeds. Examples are DPG Hydrotreating by Lummus, Pyrolysis Distillate Hydrogenation by IFP, and Pyrolysis Gasoline Hydrogenation by BASF (26). These units are used primarily with ethylene steam cracker tar from ethylene furnaces running on liquid feeds, and the saturation is of olefins only, not aromatics.

The more conventional HDS processes are typified by Distillate HDS by IFP, Hydrofining by Exxon and Unionfining by Union Oil (27). The first two of these mention that significant hydrogenation and smoke point improvement are accomplished. The latter two are specifically designed to provide feedstock to a catalytic reformer which has the same type of catalyst and the same cleanliness requirements as the catalyst system for saturating the naphthenes and the system for dehydrogenating them on board the

aircraft. This provides confidence that these processes can provide feedstocks of acceptable quality to the hydrogenation unit and fuels of acceptable cleanliness for the aircraft system.

### Aromatics Extraction

Extraction of an aromatic concentrate from refinery streams may be an important source of feedstock for endothermic fuel. Two potential process routes relying on extraction are shown in Table 3. The first of these depends on the use of extraction to derive a high aromatic stream from clean products in the kerosene boiling range. Typical feeds would be kerosene itself, No.1 diesel fuel and Jet A which is by far the biggest. Extraction of the two ring aromatics from these streams would improve their cetane number and smoke point. The resulting quality improvement might be enough to offset the cost of processing.

The other source of feedstock is the extraction of aromatics from cat cracker light cycle oil. In this case the feed is of poor quality and extraction is a means of upgrading it. Some light cycle oils may be sufficiently aromatic that extraction is unnecessary. Otherwise aromatic extraction will produce a more valuable product from a low value feed which will pay for the cost of the extraction step.

There are several processes for aromatics extraction of which the Sulfolane process developed by Shell Oil and licensed by UOP is the most popular (28). The hydrocarbon stream is contacted with cyclic tetramethylene sulfone (Sulfolane) in a counter current extractor, and the rich solution is stripped of light hydrocarbons and Sulfolane in successive distillation columns. The aromatic extract is taken overhead from the second column and the associated water is separated and used to wash residual Sulfolane out of the raffinate. The plant equipment is similar to that used in the earlier Udex process and a number of Udex plants have been converted to Sulfolane. Very high purity, (99+%), aromatic streams can be produced by Sulfolane extraction.

The Tetra process licensed by Union Carbide is similar to Sulfolane and is based on the use of tetraethylene glycol as the extractant. Data on plant costs and utilities are given in Reference 29 which were used in Task 5 to estimate the costs associated with providing an extract stream from kerosene and from light cycle oil.

The Unisorb process was described in 1962 (30). It used a proprietary absorption process which could extract only the naphthalene aromatics while leaving the monoaromatics behind. This would be a useful capability for the production of advanced fuels. With the lessening of interest in petroleum naphthalene it appears not to have been commercialized, but the technology may still be available.

### Catalytic Cracking

Catalytic cracking is the last process step to be described. It is not used directly in the preparation of advanced fuels, but the light cycle oil produced by cat cracking is a potential long term source of feedstock. There have been proposals to use cycle oil after hydrotreatment as jet fuel directly (31), but this is very difficult because of the high aromaticity of LCO. The alternative route, which may be important in the long run, is the extraction of aromatics from the LCO (rendering the raffinate more valuable for other applications such as diesel fuel) and the total hydrodesulfurization and hydrogenation of the extract.

The attraction of LCO as a feed arises from the fact that there is a tremendous amount of it, and that it is a low cost product. Typically catalytic cracking produces

15% light cycle oil and 5% heavy decant oil (32) while being operated at high severity to make gasoline in 70% yield. The yield of LCO increases to 45% and gasoline falls to a similar level when the cat cracker is run at low severity to make heating oil. The low severity operation is not of much interest to the present study, because the product is low in aromatics and is all sold as No. 2 heating oil. In the high severity mode, however, the product is very aromatic and is a byproduct.

Approximately 35% of the gasoline produced is cat cracker product (33), and the total LCO byproduct is of the order of 450,000 barrels per day. Something like 9% of this is naphthalene and alkyl naphthalenes. This source of feedstock could provide a major source of advanced fuel. Unfortunately it would require the most extensive upgrading of any of the feedstocks recommended in this study.

## TASK 4. PREPARATION OF LABORATORY SAMPLES OF FUELS

### Experimental Plan

In the proposal for this program we had planned to produce the required samples of fuels from monoaromatic and diaromatic feedstocks using the Fuel Hydrogenation Reactor Facility of the Aero Propulsion Laboratory at Wright Patterson Air Force Base.

This facility consists of twin trickle bed reactors of 400 ml volume capable of operation to 3000 psi and 950 F. It is equipped with a sophisticated feed and product handling system and is microcomputer controlled for unattended operation. Complete analytical facilities are available for characterizing the feeds and products.

With the elimination of mono-cyclic naphthenes as fuel candidates and the search for a simplified process route to a mixture of decalins, the experimental plan became more focused, but at the same time more of a research project. As a result, we proposed to eliminate the runs which were originally planned to be devoted to monoaromatic feeds and products, and replaced them with more runs devoted to dicyclic aromatics in two campaigns.

The first campaign consisted of a run to hydrogenate naphthalene to decalins, investigating a catalyst and conditions, and the second campaign consisted of two runs to hydrogenate, hydrodenitrogenate, and hydrodealkylate a feedstock of alkyl naphthalenes to naphthalene, tetralins and decalins. These two runs comprised the research program to identify a promising catalyst and conditions for the novel first step in the two-step route.

### Hydrogenation of Naphthalene to Decalin

Introduction: Based on a literature study of prior work, decalin appears to be one of the most promising candidates for scramjet fuel. To produce such a fuel from commercially available, inexpensive petroleum or coal derived streams, the following steps are necessary:

1. Selection of a stream rich in naphthalene and alkylnaphthalenes, such as catalytic reformer bottoms, or catalytic light cycle oil.
2. Hydrodesulfurization, hydrodenitrogenation, hydrodealkylation, and hydrogenation of the selected stream to produce a mixture containing mainly naphthalene, tetralin, and decalins.
3. Complete hydrogenation of the treated stream to decalins using a Pt on alumina catalyst.

The earliest known reference (34) to the hydrogenation of naphthalene mentions tetralin as the end product. In a review of the subject, Smith (35) mentioned that hydrogenation stops at the tetralin stage over various types of nickel catalysts, depending on temperature, pressure, and catalyst activity. Other catalysts that were said to stop saturation at the tetralin stage included copper chromite, various forms of reduced copper, and tungsten sulfide. Baker and Schuetz (36) found the overall rates of hydrogenation of naphthalene and tetralin to be about equal on Adams's catalyst in acetic acid solution at ambient temperature and high hydrogen pressure (1700 - 1800 psi). However, the initial rate of disappearance of naphthalene was about twice that of tetralin. Rylander and Steele (37), in studies with palladium,

platinum, rhodium, and iridium, found that only the palladium reduction stopped spontaneously at the tetralin stage. In a second experiment, with a more active palladium-on-charcoal catalyst, the hydrogenation was followed to completion. The rate of disappearance of naphthalene was roughly 25 times that of the resulting tetralin. Naphthalene and tetralin hydrogenation reactions were observed to follow zero-order reaction kinetics.

Hydrogenation of naphthalene to decalin was investigated in the first step of the present experimental R&D program.

**Objective:** The objective of this R&D program was to determine convenient operating conditions for complete hydroconversion of naphthalene to decalin using Pt on alumina catalyst.

**Experimental:** A schematic diagram of the Hydrogenation Reactor System is shown in Figure 5. The reactor is a fixed bed downflow reactor. Figure 6 shows the reactor packing. The preheating zone of the reactor is packed with 1/8" alumina balls and sand. The catalytic bed consists of a mixture of 100 c.c. Pt on alumina catalyst (Engelhard AE12) and 60 c.c. of 1/8" alumina balls. The end zone was packed with alumina balls and sand. Product gas was analyzed by an on-line Gas Chromatograph.

The feed was a solution of approximately 21.0 w% naphthalene in decalin. The feed tank was heated to 160° F to avoid recrystallization of naphthalene. Inspections on the feedstock are presented in Table 4.

The hydrogenation catalyst was 0.5 w% Pt on alumina (Engelhard AE-12). Inspections on the catalyst are presented in Table 5.

The liquid products were subjected to gas chromatographic, elemental and density analyses. Pure decalin and hydrogenated fuel samples were subjected to freezing point, flash point, viscosity, mid-boiling point, and JFTOT analyses.

Experiments were conducted and products analysed at the following five operating conditions:

Temperature, ° F	Pressure, psia.	LHSV / (HR), (catalyst volume basis)
396	500	1.04
450	500	1.16
647	500	1.10
462	500	1.94
450	500	1.48

During these runs, the pump for liquid feed stopped five times and had to be reset and restarted. Since the hydrogen flow was on all the time, no damage to the catalyst was expected.

### **Results and Discussion**

Results on naphthalene hydrogenation experiments are presented in Table 6. The results show that naphthalene can be completely converted to decalin by selection of the proper operating conditions.

In all cases the naphthalene is substantially converted in a single pass. The real issue is the conversion of the intermediate product tetralin to the desired final product decalin, and the ratio of decalin isomers produced. It can be seen that at a

temperature of 450° F and a space velocity near 1, the tetralin is converted and the product is an approximately 50-50 mixture of cis- and trans-, which is desirable for freezing point and viscosity.

Higher temperatures yield more trans- isomer without improving conversion, while higher space velocities decrease conversion of tetralin.

Our tentative conclusion is that it is possible to produce the fuel of choice in a simple hydrogenation at 450° F, 500 psia and LHSV = 1.0.

Approximately 2.5 w% tetralin and 0.12 w% naphthalene in the product stream of Run 1-3 are due to attainment of equilibrium between the reversible hydrogenation of naphthalene and dehydrogenation of decalin at 647 F temperature. For exothermic, reversible reactions, the equilibrium composition at lower temperature is more favorable to the forward reaction; however, the rate of reaction is slower. The mechanism of naphthalene and tetralin hydrogenation reaction is stepwise addition of hydrogen.

For Run 1-3, naphthalene hydrogenation, the equilibrium constant

$$K = [\text{decalin}] / [\text{naphthalene}] [\text{hydrogen}]$$
$$= 720 @ 647^{\circ} \text{F}$$

where concentrations are in gram moles / liter, and the concentration of hydrogen is 1.0.

Assuming constancy of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  with temperature change,

$$\ln K = -\Delta H^{\circ} / RT + 23.08, \text{ and}$$
$$K = 3.2 \times 10^8 @ 450^{\circ} \text{F}, 505^{\circ} \text{K}.$$

At temperatures < 450° F, the equilibrium concentration of naphthalene should be negligible.

The equilibrium constant for tetralin hydrogenation can be calculated using data from Run 1-3.

$$K = 36.75 @ 647^{\circ} \text{F}$$
$$K = 12,590 @ 450^{\circ} \text{F (est.)}$$
$$K = 2.3 \times 10^5 @ 396^{\circ} \text{F (est.)}$$

and at temperatures < 450° F, the concentration of tetralin in equilibrium should also be negligible.

The results show that run conditions 1-4 and 1-5 are not at equilibrium with respect to tetralin conversion to decalin. Results for run condition 1-1 show that equilibrium has not been reached for naphthalene as well as tetralin conversion.

Rylander and Steele (37) observed that tetralin hydrogenation follows zero order reaction kinetics. Naphthalene hydrogenation follows first order reaction kinetics. Using the data from Runs 1-1, 1-4 and 1-5, the following rate constants were calculated:

$$k(\text{tetralin-decalin}) = 0.156 \text{ g mole/ liter hr. @ } 396^{\circ} \text{ F}$$

$$= 1.856 \quad " \quad @ 450^{\circ} \text{ F}$$

$$= 2.582 \quad " \quad @ 462^{\circ} \text{ F}$$

$$k(\text{naphthalene-tetralin}) = 1.01 / \text{hr @ } 396^{\circ} \text{ F}$$

At  $396^{\circ} \text{ F}$ , the naphthalene conversion rate is 6.5 times faster than the tetralin conversion rate.

Using the rate constant data for tetralin conversion, the following rate constant expression was derived assuming no catalyst deactivation (see Fig. 7):

$$k(\text{tetralin-decalin}) = 2.3 \times 10^{16} \exp(-37,170 / RT) \text{ g mole/ liter hr.}$$

with an activation energy  $E = 37 \text{ Kcal/mole}$

Special properties of selected samples of the fuel samples produced are presented in Table 1. The freezing point of the isomeric mixture of decalin produced is extremely low ( $< -73^{\circ} \text{ F}$ ). The JFTOT thermal stability test (ASTM D3241) of the product from Run 1-5 shows that it will make a good jet fuel. Other properties, such as viscosity, flash point, smoke point and density, are satisfactory for a scramjet fuel.

#### Reaction Kinetics of Isomerization of Cis-Decalin to Trans-Decalin

Decalin is produced in two isomeric forms -- cis- and trans-. The trans-fused ring system is represented by I, and cis- by II.



I



II

The 3 KCal/mole by which the heat of combustion of cis-decalin (1502.92 kcal/mole) exceeds that of trans-decalin (1500.23 kcal/mole) reflects energy required to isomerize the relatively unstrained trans isomer to the more compact cis configuration. Calculations of non-bonded interactions in the decalins revealed that trans-decalin is more stable than cis-decalin by about 2.7 kcal/mole.

Due to the compact configuration, the density of cis-decalin (0.896) is about 3% higher than that of trans-decalin (0.870). Cis-decalin has a significant advantage in heat of combustion on a volume basis that can be exploited for greater range.

The equilibrium constant for the isomerization of cis-decalin to trans-decalin was measured by Allinger and Coke (38) in the liquid phase under hydrogen pressure in the temperature range  $531\text{-}641^{\circ} \text{ K}$ . From these data the thermodynamic quantities for the isomerization were calculated as  $\Delta H = -2.72 \text{ Kcal / mole}$  and  $\Delta S = -0.55 \text{ e.u.}$

Results on naphthalene hydrogenation feedstock analyses and experiments are presented in Tables 4 and 6. The data show that both the isomers are present in the feeds and products in different ratios. The following table gives the ratio of trans- to cis-isomers in Run 1 and the ratio at equilibrium:

Run No.	Ratio of trans-/cis-	Approximate equilibrium ratio
1-1	0.89	13
1-2	1.20	11
1-3	5.8	6
1-4	0.98	11
1-5	1.08	11

It appears that only in Run 1-3 has the system reached equilibrium.

In the first step in naphthalene hydrogenation over Pt catalyst, tetralin is formed, which is hydrogenated mainly to cis-decalin, which in turn is converted to more stable trans-decalin. In calculating an isomerization rate constant from the experimental data of Run 1, it is necessary to consider two simultaneous reactions:



Tetralin hydrogenation to decalin follows zero order reaction kinetics. Because of limited data, the isomerization reaction is also assumed to follow zero order kinetics. The rate of conversion of cis-decalin to trans-decalin is then given by

$$-d[\text{cis-decalin}] / dt = k(\text{cis-trans}) - k(\text{tetralin-decalin}) \text{ g mole / liter hr.}$$

Using the data from Runs 1-1, 1-4 and 1-5 including  $k(\text{tetralin-decalin})$  values calculated earlier, the following zero order rate constants were calculated:

$$\begin{aligned} k(\text{cis-trans}) &= 0.034 \text{ gmole/liter hr at } 396^\circ\text{F} \\ &= 1.285 \text{ gmole/liter hr at } 462^\circ\text{F} \\ &= 0.716 \text{ gmole/liter hr at } 450^\circ\text{F} \end{aligned}$$

Using these rate constant data, the following rate constant expression was derived from the Arrhenius plot shown in Figure 8, assuming no catalyst deactivation:

$$k = 2.05 \times 10^8 \text{ Exp}(-19,160 / RT) \text{ g moles/ liter hr.}$$

with an activation energy  $E = 19 \text{ Kcal / mole.}$

Because of limited data, the accuracy of the expression is difficult to determine.

### Hydrotreating of Methyl and Dimethyl Naphthalenes

Introduction: The combined hydrodesulfurization, hydrodenitrogenation, hydrodealkylation, and hydrogenation of the selected stream to produce a mixture containing mainly naphthalenes, tetralins, decalins, and alkyl cyclohexanes may be approached in two

ways:

- 1) Hydrotreating of the stream to remove heteroatoms and unsaturation followed by catalytic (alkalized chromia-alumina catalyst), or noncatalytic hydrodealkylation at high temperature ( $> 1100^{\circ}\text{F}$ ) and moderate hydrogen pressure followed in turn by saturation of the aromatics produced.
- 2) Hydrotreating and hydrocracking of the stream for hydrodenitrogenation, hydrodesulfurization, hydrodealkylation, and hydrogenation simultaneously.

The first approach has not been tested because of the  $950^{\circ}\text{F}$  temperature limit of the available experimental unit at the Air Force Wright Aeronautical Laboratories and the fact that literature data are available. Since the second approach requires an operating temperature  $< 900^{\circ}\text{F}$ , the Hydrogenation Reaction System at AFWAL could be used for experimentation to determine whether combined processing is a feasible route and to produce fuel samples.

Hydrodealkylation reactions occur through an atomic free-radical mechanism. Catalysts for this type of reaction include the elements of Groups VIB and VIII, their oxides, and/or their sulfides. Catalytic activity of these substances is attributed to unfilled "d" orbitals, and ability to accept electrons one at a time.

Hydrotreating catalysts such as Co-Mo on alumina or Ni-Co-Mo on alumina are proven for heteroatom removal and hydrogenation. Theoretically hydrocracking activity of a hydrotreating catalyst should facilitate hydrodealkylation, at severe operating conditions, particularly at high temperatures. Cracking activity may or may not be strong enough at  $< 900^{\circ}\text{F}$  for hydrodealkylation. Also, at high temperature there is the possibility of cracking hydrogenated ring structures which decreases the yield of saturated compounds. A major advantage of the second approach is that a contaminated but inexpensive feedstock can be processed in one step rather than the three steps required for the conventional HDS - HDA - hydrogenation processing sequence.

Patzer, et. al. (25) reported that 1-Methylnaphthalene could be hydrodealkylated and hydrogenated to decalin using a hydrotreating Ni-Co-Mo on alumina catalyst (0.5% Ni, 1% Co, 8% Mo) at  $650^{\circ}\text{F}$  and moderate hydrogen pressure. Sapre and Gates (39) used Patzer's data to derive a mechanism and projections for the dealkylation of methyl naphthalene and its conversion to tetralin and decalin. Based on these reports, it appeared that dimethyl naphthalenes might be hydrogenated and hydrodealkylated to decalins using a similar catalyst under somewhat more severe operating conditions. Even if the dealkylation does not proceed under these conditions, the product might still be an acceptable advanced fuel if the heteroatoms are removed and the aromatic rings are saturated.

Based on the above considerations, the second approach was chosen for experimentation with alkylnaphthalenes feedstocks using American Cyanamid HDS-20 (Co-Mo on alumina) catalyst in Run 2 and 1.25 w% NiO-impregnated HDS-20 in Run 3.

**Experimental:** The reactor is a fixed bed downflow reactor. The preheating zone of the reactor was packed with 1/8" alumina balls and sand as before. The catalytic bed in Run 2 consisted of 200 cc of a trilobe Co-Mo on alumina catalyst (American Cyanamid HDS-20). For Run 3, the HDS-20 catalyst was impregnated with 1.25 w% NiO (from Aldrich Chemical Co. Gold Label 99.999% nickel nitrate). Properties of the HDS-20 catalyst are presented in Table 7. The end zone was packed with alumina balls and sand. The catalyst bed was presulfided using dimethyl disulfide. Product gas was analyzed by an on-line Gas Chromatograph.

The feed for Run 2 was a mixture of dimethyl naphthalene isomers contaminated with nitrogen compounds, (Aldrich Chemical Co. dimethyl naphthalene, mixture of isomers). Semiquantitative GC-MS analyses of the feed show its composition to be 77.16 w% dimethyl naphthalene isomers, 7.83 w% methyl quinoline, 2.86 w% methyl indole, 8.95 w% monomethyl naphthalenes, and no sulfur compounds. The feed was doped with 0.2 w% dimethyl disulfide in order to maintain the desired sulfided condition of the catalyst.

The gaseous and liquid products were subjected to gas chromatographic and semi-quantitative GC-MS analyses, respectively. Run 2 experiments were conducted at the following four operating conditions:

Run No.	Temperature, ° F	Pressure, psi	LHSV, / hr.
2-1	658	1000	1.22
2-2	798	1000	1.01
2-3	839	1000	0.57
2-4	844	2000	0.47

Two major upsets of the reactor system occurred -- once before reaching Run condition 2-2 and once before reaching Run condition 2-3. During these upsets hydrogen flow was maintained through the catalyst bed.

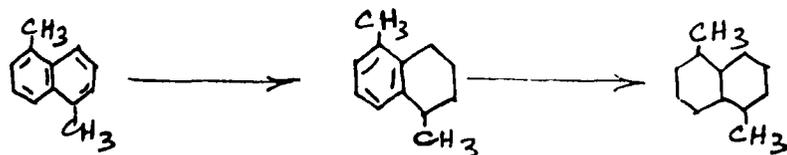
Run 3 experiments were conducted at the following operating conditions:

Feed	Temperature, ° F	Pressure, psi	LHSV / hr
1-Methyl naphthalene	839	1000	0.55
Liquid Product from Run 2-2	833	2000	0.46
Liquid Product from Run 2-2	872	2500	0.43
Dimethyl Naphthalene mixture	877	2500	0.54

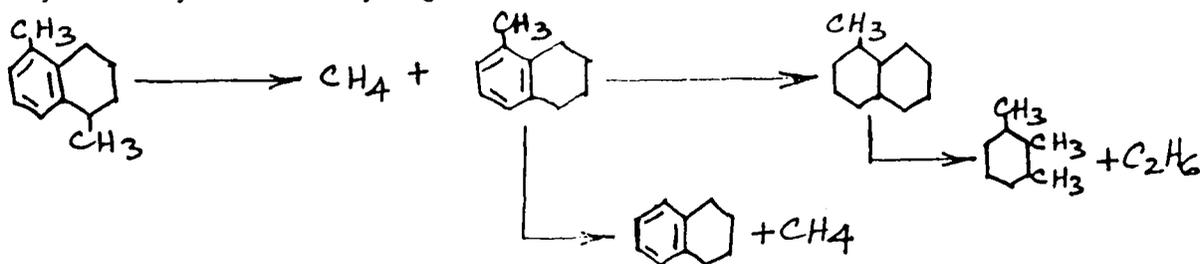
Two major upsets of the reactor system occurred during Run 3.

**Results and Discussion:** Before presentation of the results, different possible isomers and a few possible reactions should be discussed. Dimethyl naphthalene may consist of 10 isomers. These dimethyl naphthalenes can be hydrogenated to twenty isomers of dimethyl tetralins and 68 isomers of dimethyl decalins. All these isomers have different reactivities. A few possible reactions in hydrotreating of the dimethyl naphthalene feed may be described as follows:

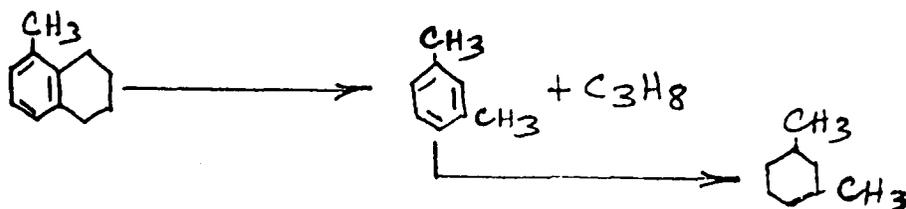
Hydrogenation:



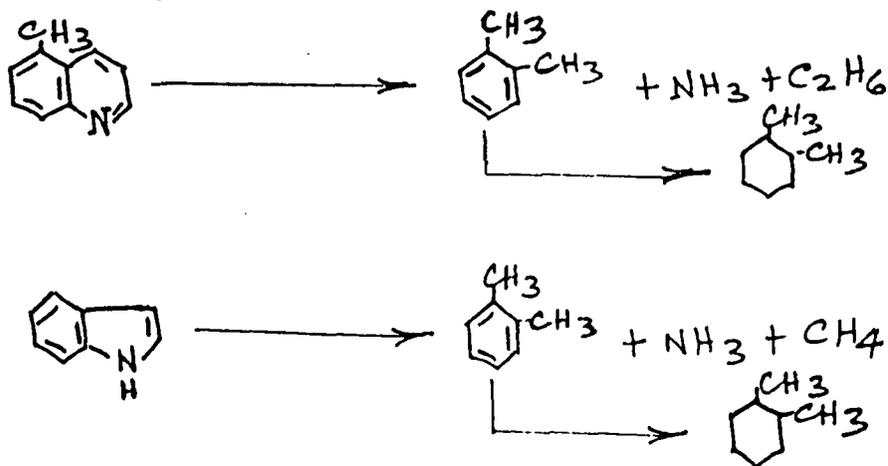
Hydrodealkylation and Hydrogenation:



Ring Cracking:



Hydrodenitrogenation:



Run 2: Table 8 shows the complete results on Run 2 in which the yields of gas and liquid products have been normalized based on the hydrogen content from analysis. Hydrogen contents of selected periods have also been calculated from the GC-MS analysis of the product and agree with measured hydrogen contents within half a weight percent hydrogen on the average.

The results for methylindane, ethylindane, alkylbenzene and alkyl cyclohexane for Run 2.2 were not measured but were estimated from the results for Run 2.1 on the basis that these compounds result from denitrogenation of the nitrogen compounds in the feed, and the distribution will be similar in each case.

Run 2-1 was conducted at a mild operating condition of 658° F, 1.22 LHSV, 1000 psi hydrogen pressure. Analyses of the liquid products show that approximately 44 w% of the dimethyl naphthalene is converted mainly to dimethyl tetralin. Since the analyses

of the liquid product do not detect any organic compounds containing nitrogen, the methyl quinoline and methyl indole in the liquid feed must have been converted to alkyl benzene, alkyl cyclohexane, methyl indan, and ammonia. However, the gas analyses by on-line GC could not detect any ammonia, possibly due to the type of column used. Liquid product analyses suggest that complete denitrogenation can be achieved at the operating conditions of Run 2-1. Since denitrogenation is much more difficult than desulfurization, it is likely that complete heteroatom removal can be achieved at the operating conditions of Run 2-1. Since the percentages of methane and other hydrocarbon gases are very low with respect to feed, there was no significant hydrodealkylation in Run 2-1.

In Run 2-2, the reactor temperature was increased to 800° F in order to increase the severity for hydrogenation and hydrodealkylation of dimethyl naphthalenes. Liquid product analyses show that approximately 63.4 w% dimethyl naphthalenes are converted to dimethyl tetralin, dimethyl decalin, and ethyl tetralin. Monoalkyl naphthalenes in the feed are hydrogenated to methyl tetralin and ethyl tetralin. Gaseous products containing 1.02 w% methane, 2.73 w% ethane, and 0.76 w% propane indicates some hydrodealkylation as well as ring cracking as in the case of nitrogen containing compounds. There are no nitrogen containing organic compounds in the product, indicating complete heteroatom removal. These compounds are converted to alkyl benzenes and alkyl cyclohexanes.

In Run 2-3, the severity of the operating condition was increased by increasing the reactor temperature to 839 F and by reducing the liquid hourly space velocity from 1.0 to 0.5. Analyses of the liquid product show that approximately 54.2 w% of dimethyl naphthalene was converted to dimethyl tetralin, dimethyl decalin, methyl naphthalene, and methyl tetralin. Lower conversion, compared to Run 2-2, suggests that the catalyst was deactivated due to a major upset of the reactor system before reaching Run condition 2-3. Nitrogen containing compounds, methyl quinoline and methyl indole, are converted to alkyl benzene, alkyl cyclohexane, methyl indan, and ammonia. Absence of any nitrogen containing organic compound suggests complete heteroatom removal. Significant amounts of light gaseous hydrocarbon products indicates some hydrodealkylation and minor cracking of hydrogenated ring structure.

Reduction in liquid hourly space velocity did not make any significant change in product yield except more gas production due to some hydrodealkylation. However, catalyst deactivation during upset of the unit may have caused this insignificant change as well as low conversion of dimethyl naphthalenes.

In Run 2-4, the severity of the operating condition was increased by increasing the hydrogen pressure from 1000 psi to 2000 psi. A significant improvement in performance was observed. Approximately 95.7 w% dimethyl naphthalenes was converted to hydrogenated products. Approximately 32 w% alkyl decalins and 13.45 w% alkyl cyclohexanes, the desirable components of a Scramjet fuel, were formed. The liquid product also contained 5.18 w% tetralin, 4.53 w% methyl tetralin and 18.08 w% dimethyl tetralin. No nitrogen containing organic compounds were detected, indicating complete denitrogenation and complete heteroatom removal. Methyl quinoline and methyl indole in the feed must have been converted to alkyl cyclohexanes and ammonia. The high percentage of alkyl cyclohexanes and significant amounts of tetralin and methyl tetralin in the liquid product suggest significant hydrodealkylation and hydrogenated ring cracking. The high percentage of light hydrocarbon gaseous products also suggests considerable ring cracking and hydrodealkylation.

The results of Run 2-4 indicate that at higher hydrogen pressure and with proper choice of operating conditions, the feed can be converted mainly to alkyl

tetralins, alkyl decalins and alkyl cyclohexanes without any heteroatom impurity. A better selection of catalyst might improve hydrogenation and hydrodealkylation and might prevent ring cracking. This will probably be necessary for this process route, to provide an attractive yield of the desired advanced fuel.

Conclusions: Hydrotreating of a contaminated feed of dimethyl naphthalenes using Co-Mo on alumina catalyst can remove heteroatoms and hydrogenate to a considerable extent.

The results show that relatively severe conditions of 2000 psi, 844°F and a space velocity of 0.5 are required to achieve high conversions of the dimethylnaphthalene feedstock. Even under these very severe conditions, the product still contains a relatively high content of dimethyl tetralin, and conversion to dimethyl decalin is not complete.

The amount of dealkylation achieved in these runs is very small. As conditions become increasingly severe, cracking of the decalin product to alkylcyclohexane and gas is more likely than dealkylation of methyl and dimethyl decalin.

Run 3: In Run 3 three feeds were hydrotreated. They were:

1-Methyl naphthalene (Run 3-1),  
a feed made up of liquid product from Run 2-2 (Runs 3-2 and 3-3), and  
dimethyl naphthalenes (Run 3-4).

All the feeds were treated over 1.25 w% Ni-impregnated HDS-20 catalyst. The 1-methyl naphthalene was Aldrich Chemical Co. 99% grade. GC-MS analyses of the liquid product feed from Run 2-2 are presented in Table 9.

Run 3 was conducted to serve the following purposes:

1. To find the catalytic effect of nickel on hydrodealkylation.
2. Processing 1-methyl naphthalene to compare hydrodealkylation results with those of earlier work (Reference 25).
3. Processing with feedstock containing no nitrogen compounds in order to find hydrodealkylation results in the absence of nitrogen compounds. The 1-methyl naphthalene and liquid product from Run 2-2 do not contain any nitrogen compounds.
4. To find the effects of severe operating conditions, high temperature and high hydrogen pressure, on hydrodealkylation and hydrogenation.

Elemental analyses of liquid products are presented in Table 10. Table 11 shows the normalized yields and operating conditions.

The results show that nickel does not have any special catalytic effect on hydrodealkylation. Also, the nitrogen compounds in the feed did not affect the hydrodealkylation activity of the catalyst. 1-methyl naphthalene was not hydrodealkylated even at higher temperature than used by Patzer and coworkers (25). This result suggests that their hydrodealkylation results are not a reliable guide to process opportunities.

Overall results of Run 3 are essentially the same as those of Run 2. Due to severe operating conditions, the conversion of feedstock is relatively high, but

again, the conversion of tetralins to decalin is slow and the dealkylation reactions are not significant except in Run 3-4. Our hopes, based on literature results, that hydrogenation and dealkylation could be combined in one process, have not been realized.

Kinetic rate constants derived from Runs 2 and 3 are shown in Table 12. The rate constants for the hydrogenation of dimethyl naphthalene and 1-methyl naphthalene are based on the disappearance of the respective feedstocks. The rate constants for hydrogenation of alkyltetralins; cracking of alkyldecalins to alkylcyclohexanes; cracking of alkyltetralins to alkylbenzenes; and hydrodealkylation are derived from the rate of appearance of the respective products.

The rate constants are plotted in Arrhenius form in Figure 9. They are not strictly comparable from run to run due to differences in hydrogen pressure and to catalyst deactivation. Fortunately, literature data suggests that, except for the hydrodealkylation which is half order, the other reactions are zero order in hydrogen. The dealkylation rate constants have been corrected for the assumed half order pressure dependence in Figure 9.

Due to the uncertainty in reaction order and catalyst activity, no attempt has been made to extract quantitative activation energies from the data. Qualitatively, one can see that cracking reactions are much more temperature sensitive than hydrogenation, as expected.

Comparisons between rate constants are also clouded by differences in reaction order with respect to hydrocarbon. Comparing naphthalene hydrogenation with naphthalene hydrodealkylation both of which have the same assumed order with respect to hydrocarbon and the same substrate, the dealkylation has a similar temperature dependence but is about 25 times slower in rate.

### Process Implications of Runs 2 and 3

These results have been used to estimate the process conditions required to hydrogenate a contaminated alkyl naphthalene feedstock to the advanced fuel we desire to produce. The objective of this process sequence is complete denitrogenation, desulfurization and hydrogenation of the feedstock with partial dealkylation and no cracking. The conditions chosen on the basis of the results of runs 2 and 3 are temperature of 800°F, pressure of 1000 psi and the HDS-20 catalyst. For 99% hydrogenation to decalin, the overall liquid hourly space velocity will be 0.1, and the dealkylation achieved will amount to 20 mole %. A four-stage reactor sequence with a 0.4 LHSV per stage and a 0.5 recycle ratio is required.

This is a relatively complex and expensive reactor system to accomplish the objective of cleaning up a dirty feed and hydrogenating it. Our hopes of demonstrating a simpler alternative to conventional process routes for heteroatom removal and aromatics saturation have not been realized.

### Prospect of Using Alkyl Decalins as Scramjet Fuel

Further kinetic analysis of available data is being done to evaluate the relative rates of dehydrogenation and dealkylation of fuels in advanced aircraft systems. Our expectation is that the dealkylation rate will be slow enough that dehydrogenation will be essentially the only reaction. The consequence of this is that the presence

of alkyl groups on advanced fuels is not a significant consumer of hydrogen in the endothermic fuel heat absorption process; they simply act as a diluent to reduce the heat absorption capacity of the fuel. This means, for example, that 1-methyl naphthalene based fuels suffer only a 10% penalty in endothermic heat absorption capability relative to pure decalins. Based on literature data, the 1-methyl decalin/1-methyl naphthalene system also suffers a penalty in heat of vaporization and heat capacity relative to decalin/naphthalene. This results in a reduction of about 10% in the overall heat absorption capabilities of the fuel. For dimethyl naphthalene derived dimethyl decalins, the penalty in endothermic heat is about 20% and in total heat sink capability it will be about 10%. This is not a severe penalty provided that there are offsetting advantages in yield and cost of product or other aspects of fuel performance.

The following table shows the heat sink capacity of cis-trans, methyl and dimethyl decalins based on literature data and assuming no dealkylation. Because of significant inconsistencies in literature data, these numbers need to be verified.

	50/50 Cis/Trans Decalin	Methyl Decalin	Dimethyl Decalin
Net Heat, BTU / gallon	135669	135180	135040
Endothermic Heat Sink, BTU / lb	935	856	749
Total Heat Sink @ 1200°F, BTU / lb.	1931	1720	1700

The situation for alkylbenzene fuels is rather different. If it is desired to achieve a relatively high flashpoint or low volatility with alkylbenzenes, the degree of substitution will have to be much higher than the naphthalene based fuels, and in this case the endothermic heat sink capability of the fuel is severely affected. The choice then lies between a JP 4 type high volatility fuel based on benzene, toluene and xylenes, and a JP 8 type low-volatility fuel based on naphthalene and 1-methyl and dimethyl naphthalenes.

The presence of alkyl side chains can permit the hydrodealkylation reaction to take place, which is exothermic to the extent of 8.75 kcal per methyl group. It also consumes a mole of hydrogen per mole of methyl groups, producing a mole of methane. This will seriously degrade the performance of endothermic fuels.

If, on the other hand, the dealkylation reaction can be suppressed in the aircraft system, the costly hydrodealkylation step can be avoided in producing the fuel from a feedstock of alkyl naphthalenes. Success in the use of alkyl-decalins as endothermic fuel depends on the relative reaction rates for the following four processes at the scramjet engine conditions:

1. Catalytic dehydrogenation
2. Dealkylation
  - a. Thermal
  - b. Catalytic
3. Cracking of Naphthenes
4. Heat transfer from the fuel system

To be successful, catalytic dehydrogenation and heat transfer must be very fast, and at the same time, dealkylation and cracking must be negligible. The following data from prior work has been analyzed to find some of these rates.

Tables 13 and 14 show that a temperature  $> 980^{\circ}\text{F}$  is required to have any significant thermal cracking of decalin and methyl cyclohexane. Significant thermal dealkylation of methyl cyclohexane occurs at  $> 1125^{\circ}\text{F}$  temperature as revealed by benzene yield.

Table 15 shows that catalytic cracking of decalin is insignificant at  $< 870^{\circ}\text{F}$  temperature. This should be true for methyl cyclohexane also.

The data in Tables 16 and 17 show that rates of dehydrogenation of decalin and methyl cyclohexane are very fast and that dehydrogenation can be accomplished at a temperature  $< 850^{\circ}\text{F}$ .

The data in Table 18 show that very high temperature and high pressure are required for thermal hydrodealkylation of alkyl naphthalenes.

The data in Table 19 show that catalytic hydrodealkylation of methyl cyclohexane is very slow, even at  $837^{\circ}\text{F}$  temperature.

The data in Table 20 reveal that dehydrogenation reactions are very fast but hydrodealkylation reactions are very slow, giving a maximum yield of 10 w% of dealkylated products.

Based on all of the above results, it may be concluded that complete catalytic dehydrogenation of methyl cyclohexane and decalin can be accomplished with very little cracking or hydrodealkylation if the catalyst bed is maintained at  $< 850^{\circ}\text{F}$  temperature and proper pressure and space velocities are used. However, at present sufficient data on methyl decalin and dimethyl decalin are not available to justify a similar conclusion.

## TASK 5. FUEL AVAILABILITY SCENARIOS THROUGH THE YEAR 2000

A hierarchy of process options to produce advanced fuels is shown in Table 3.

The simplest of these is to buy petroleum naphthalene and hydrogenate it to a mixture of cis- and trans-decalin, as we did in Run 1. Conditions are mild, many refineries and petrochemical plants have hydrotreaters which could perform the reaction, and the feedstock is probably available, since the major market for naphthalene has been taken over by synthesis of phthalic anhydride from ortho-xylene. The feedstock could even be supplemented by coal tar naphthalene with some purification to reduce heteroatom content, although this is a diminishing source of supply. The naphthalene route could provide something like 4000 bbl/day of fuel if all the petroleum naphtha capacity were devoted to providing feedstock. Some of this capacity may no longer be operational, however.

The next easiest source to tap is catalytic reformer gasoline. Reforming is known to increase the end point of naphthas by approximately 30 °F. We have found that there is a high boiling tail containing dicyclic aromatics even in reformate intended as 100% gasoline blending material. That tail is primarily naphthalene, with smaller amounts of 1-methyl naphthalene and still smaller amounts of dimethyl naphthalene isomers. The tail could be cut off in a stripper column and could serve as feedstock for hydrogenation to c-t decalin and alkyl decalins. This route has the advantage that the process steps are simple, the feedstock is very clean, and the removal of the naphthalene will actually improve the gasoline product.

This product improvement is an even greater advantage of the next route to advanced fuel feedstock. This is to extract aromatics from distillate fuels followed by hydrodesulfurization, if required, and hydrogenation. In this boiling range the amount of dicyclic aromatics is greater than in gasoline. Since the dicyclics are primarily alkyl derivatives, it will be necessary to follow extraction with hydrodealkylation if a pure c-t decalin fuel is to be produced.

Extraction of the aromatics could be particularly beneficial to the quality of the distillate fuels left behind, and extraction is already practiced commercially. Limiting aromatics is critical to insuring the quality of jet fuel with regard to aromatic content, hydrogen content and smoke point. Methyl naphthalene is zero on the cetane index scale for diesel fuels.

The final source of very large quantities of advanced fuels is light cycle oil from fluid catalytic crackers. FCC units are present in most refineries, and all of them produce LCO amounting to approximately 14% of feed when operating in a high severity mode to produce gasoline. 10% or more of the light cycle oil consists of dicyclic aromatics. Unfortunately, the feedstock quality is poor, and the process route to produce advanced fuels is more complex than for cleaner feeds. It requires severe hydrotreatment to remove heteroatoms followed by hydrogenation to the final saturated product containing alkyl decalins. Alternatively, it can be followed by hydrodealkylation and hydrogenation to c-t decalin.

The time scenario is envisaged as naphthalene feed in the 1980's, gasoline stripping in the early 90's, distillate extraction by the mid 1990's and LCO processing in the late 1990's-post 2000 time period. Approximate estimates have been prepared for the cost of the various process steps. These are shown in Tables 21-25. The results are summarized in Table 26 to compare the alternative process sequences.

From these results it can be seen that the economics of fuel production is dominated by feedstock cost. Even the most complex processing route is less expensive than the cheapest feed by a factor of two. The cost of naphthalene was taken from current quoted prices for petroleum derived chemical naphthalene. Lower prices might be obtained for larger quantities on long term contract, but it is likely always to be an expensive starting material.

The price of reformat is an estimate based on current gasoline prices from the Oil and Gas Journal. The price of kerosene is set equal to gasoline, which is approximately true, despite its higher heating value. No credit is taken for the value of upgrading the gasoline or kerosene by extracting the dicyclic aromatics.

The price of light cycle oil is arbitrarily set equal to crude oil. LCO is a less desirable product than No. 2 home heating oil but can always find a home in fuel oil blends. It is valued accordingly.

It should be noted that while the cost of naphthalene would probably go down on a large scale long term contract, the cost of advanced fuels by the other routes will probably be higher than estimated above. The estimates are based on costs and do not include contingencies and profits other than the return on the directly associated investment. Nevertheless, the results are sufficiently clear that conclusions can be drawn.

Naphthalene hydrogenation offers a simple and short term route to test quantities of decalin fuels, but is a very expensive source for the long term.

Reformat stripping and kerosene extraction are about equivalent. The choice would be made on the basis of refiners interested in producing the product and individual circumstances.

Light cycle oil offers the lowest cost route to advanced fuels as well as the largest source for the long term. The processing sequence is complex and the range of compounds in the product is greater than from the other sources, but it is worth development for the long term because it is ultimately the best source.

Hydrodealkylation is treated as an adder because it is not clear that it will be required. It is clearly something to be avoided if possible. It is expensive and causes a loss of 10% in yield which adds substantially to the cost of producing a barrel of product, especially for the higher priced feeds.

#### Available Refining Capacity

A survey of the Oil and Gas Journal refining report of March, 1983, pp. 1332-150 shows the refineries listed in Table 27 which have capabilities relevant to the production of advanced fuels.

A total of sixteen refineries have potential aromatics saturation capacity. Six have solvent extraction capability. Ashland at Catlettsburg, Exxon at Baton Rouge and Baytown, and Pennzoil at Shreveport have both.

Thus there are a number of potential sources of advanced fuels, some of which are major refiners with substantial capacity.

## CONCLUSIONS AND RECOMMENDATIONS

1. A cis-trans-decalin fuel which substantially meets the desired properties for advanced aircraft fuels has been made by hydrogenating naphthalene over a noble metal catalyst under mild conditions.
2. Such a fuel could not be produced from contaminated feeds under hydrocracking conditions over Co-Mo type catalysts. The dealkylation reactions are slow. Cracking reactions are comparable to dealkylation reactions, reducing yields, and hydrogenation is incomplete, reducing conversion of aromatics to naphthenes.
3. The data suggest, however, that it may not be necessary to dealkylate the fuel to maintain most of its heat sink capability because the dealkylation reactions are slow relative to the endothermic dehydrogenation.
4. There is a high boiling tail in gasoline and reformat which may be a suitable feedstock.
5. Aromatics can be extracted from kerosene which may also provide a suitable feedstock.
6. The high boiling end of both these feedstocks are high in naphthalene and alkyl naphthalenes
7. Light cycle oil and similar low cost but low quality feedstocks may not be required as a feed until 21st century, but
8. Process economics are dominated by feedstock cost.

## RECOMMENDATIONS

The following points should be confirmed by further work.

1. Catalytic dehydrogenation technology can probably be extended to decalin fuels to provide near quantitative hydrogen yields in aircraft cooling systems with acceptable size and weight, similar to results achieved with methylcyclohexane.
2. Alkyl groups on the fuel probably don't matter very much. The dealkylation reactions are so slow, even over noble metal catalyst in the aircraft system, that the alkyl groups simply dilute the endothermic effect by increasing the molecular weight of the fuel. This widens the selection of feedstocks for producing the fuel and reduces the processing required.
3. Reformat stripper bottoms may provide a very desirable feedstock for advanced fuels due to its cleanliness and competitive cost. The amounts of such feedstock that can be made available should be confirmed as well as the feasibility of producing and saturating it.
4. Some kerosene extracts could provide almost equally suitable feedstocks requiring minimal processing. The amounts available and the processing requirements of such extracts should be confirmed.

5. Saturated compounds which cannot dehydrogenate to six membered rings, (JP-10, RJ-5) are less desirable than decalins because of lower endothermic effect and lower hydrogen yield.
6. Heteroatoms, S, N and O, in at least some of their compounds, are unacceptable above the ppm level because they lead to heat exchanger deposits and catalyst poisoning.
7. Tricyclic and higher polynuclear aromatics are undesirable because of an increased tendency to coke formation, higher boiling point and higher freezing point.
8. Decalin fuels will probably exhibit exceptional thermal stability and permit use of the fuel for cooling to temperatures of 600°C or more.
9. Fuel system inerting may be required to preserve the thermal stability of the fuel. Conventional antioxidant additives may be an acceptable substitute.
10. The behavior of other additives should be tested to determine whether they are compatible with vaporizing-endothermic fuel systems.

FIGURE 1

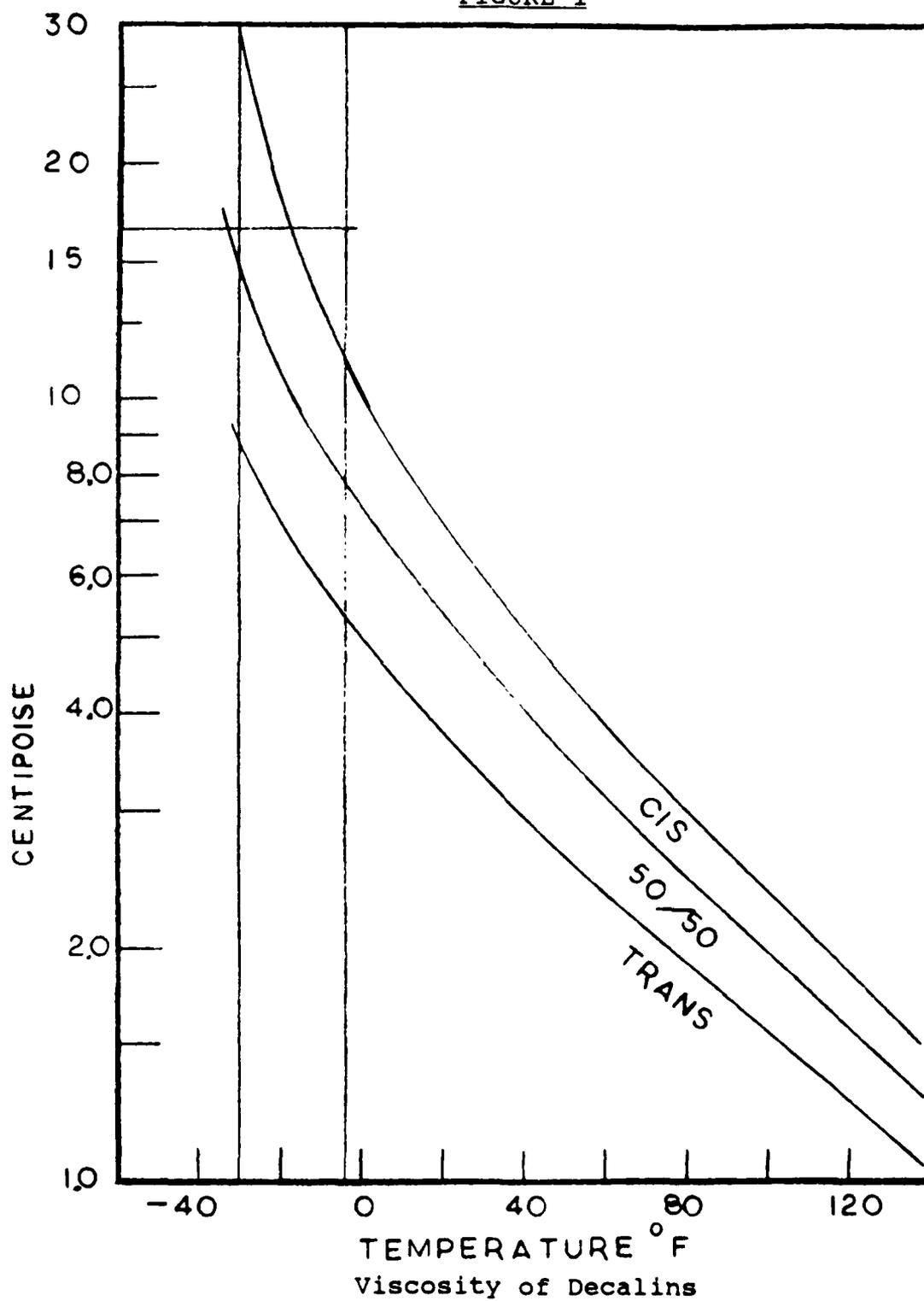
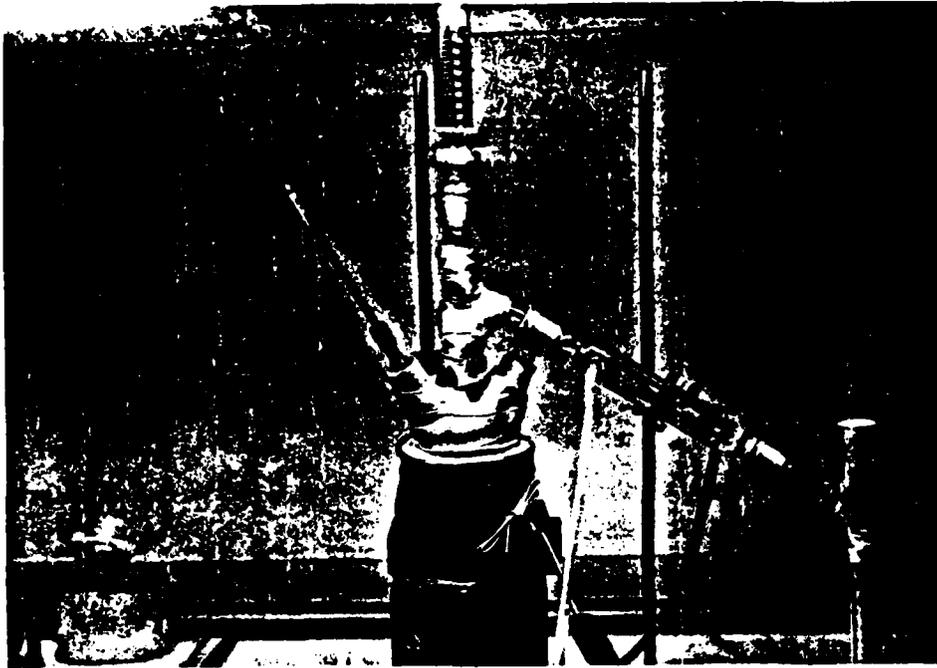
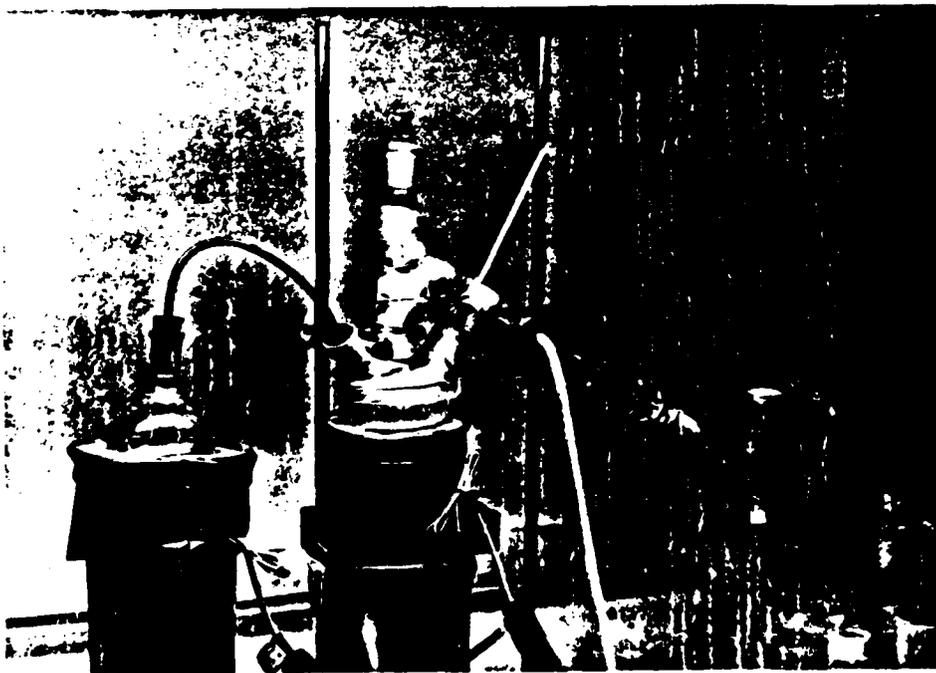


FIGURE 2.



Apparatus to strip reformate and gasoline.

FIGURE 3.



Apparatus to steam distill kerosene extracts.

FIGURE 4. ROLE OF NOBLE METAL CATALYSTS IN ADVANCED FUEL SYSTEMS

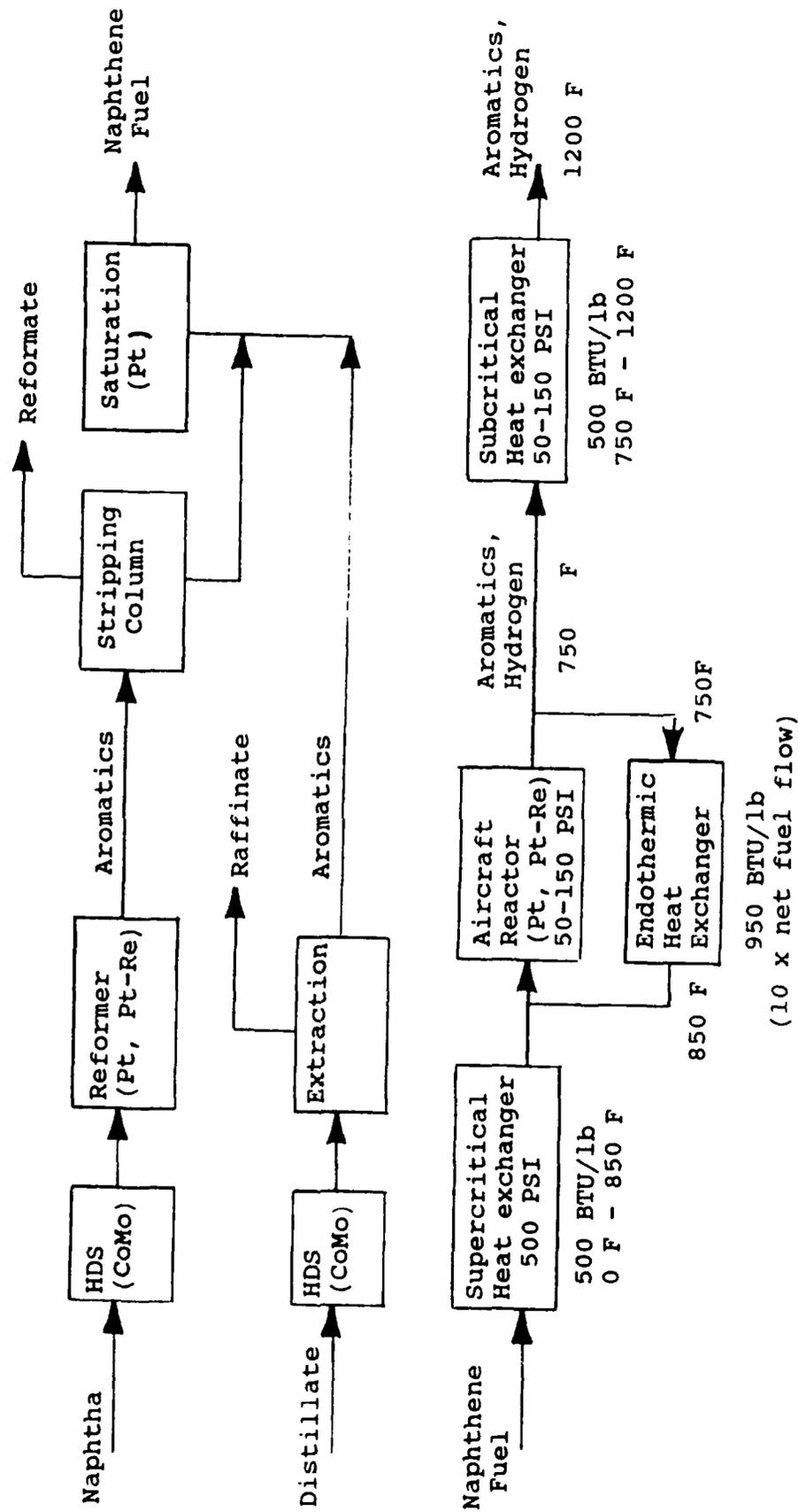


FIGURE 5.

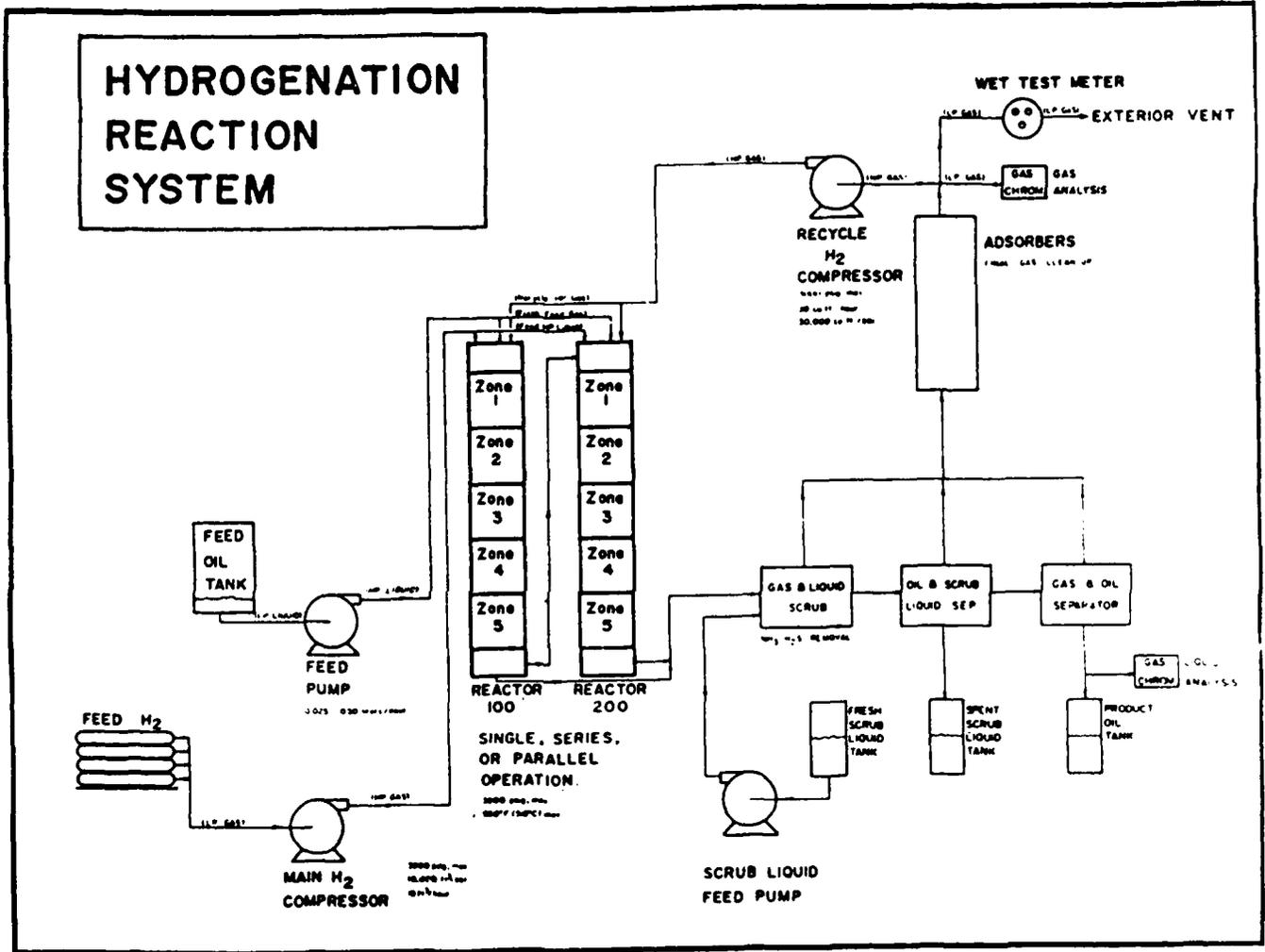
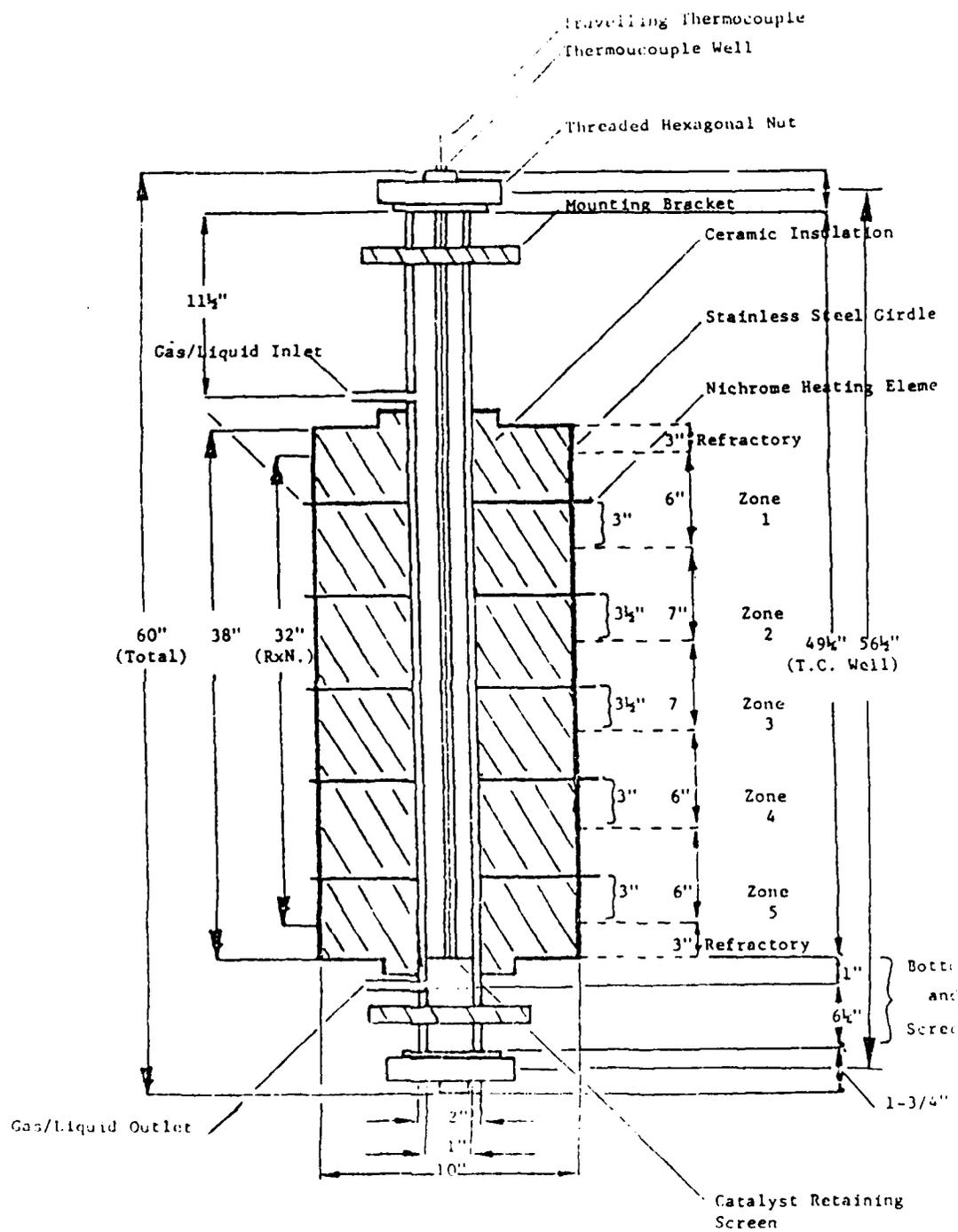
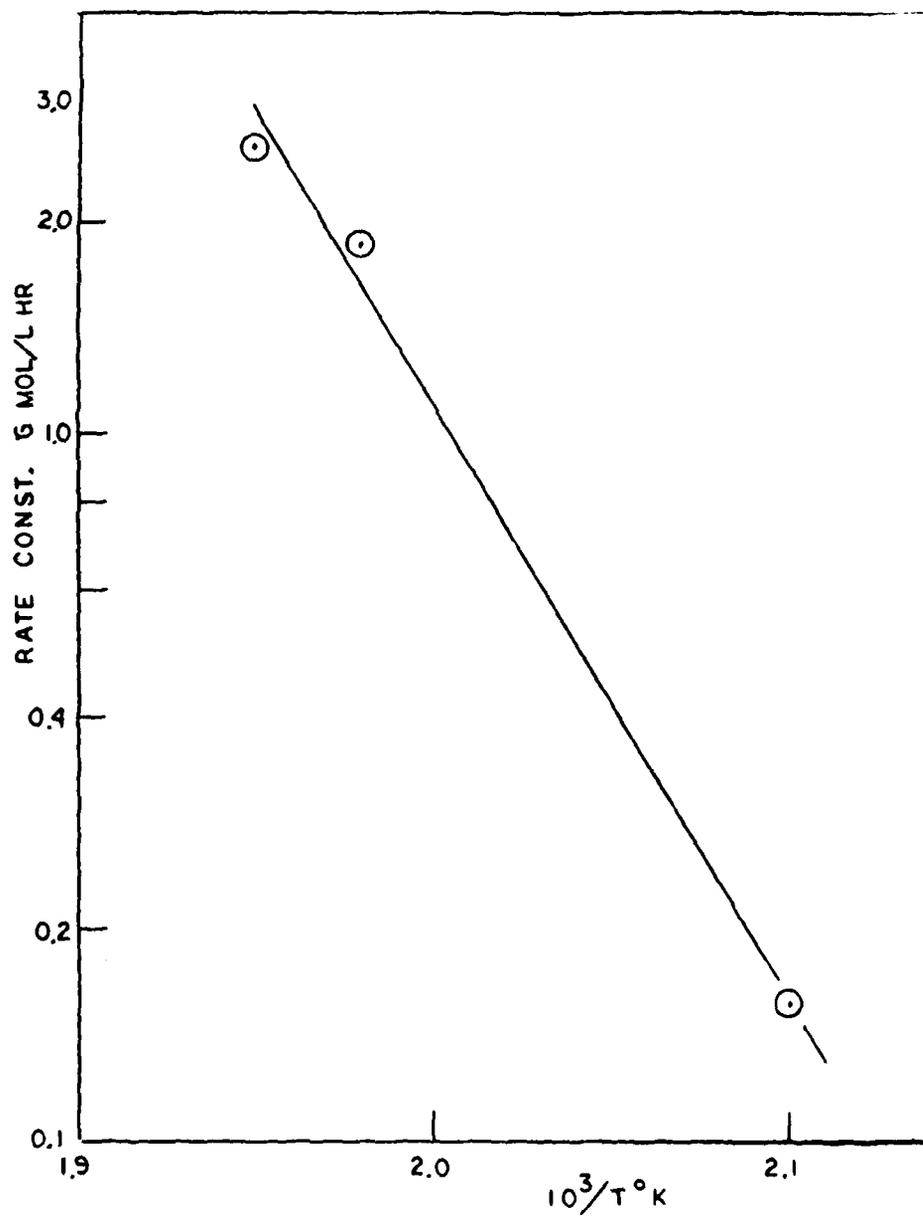


FIGURE 6.



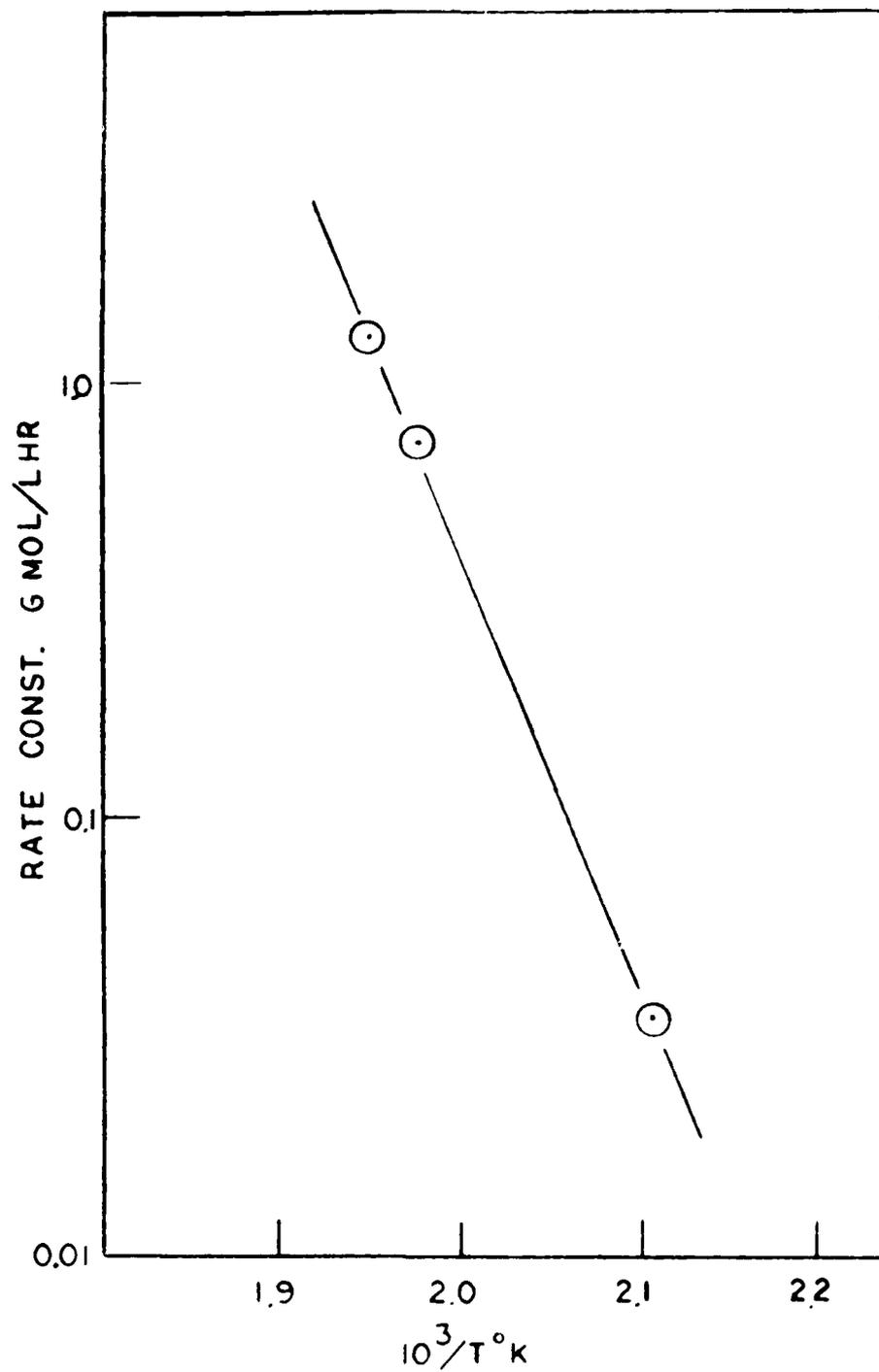
Reactor and furnace dimensions

FIGURE 7



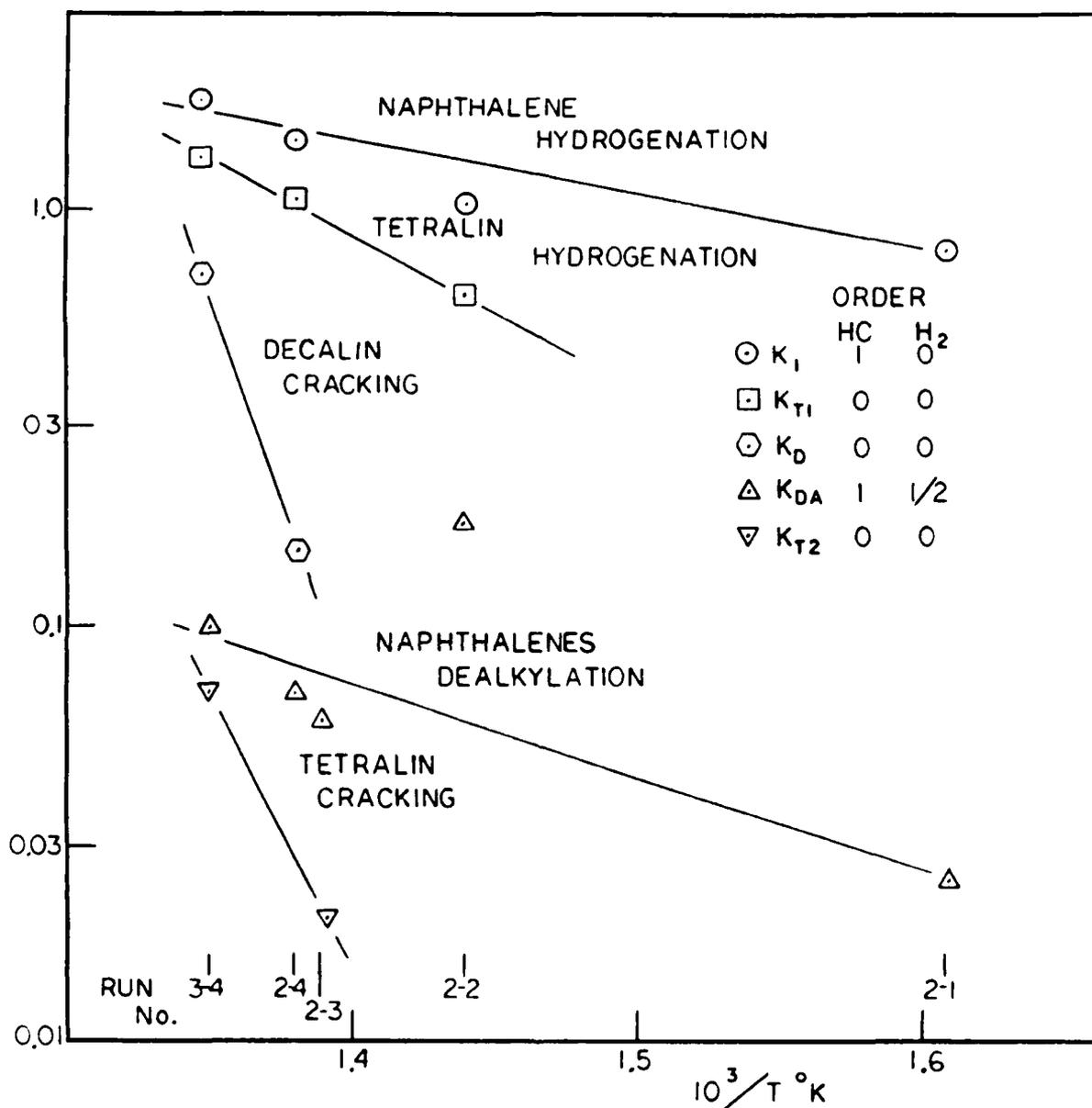
Arrhenius plot for tetralin hydrogenation.

FIGURE 8.



Arrhenius plot for cis-decalin to trans-decalin isomerization.

FIGURE 9.



Rate constants for hydrogenation, cracking and dealkylation of dicyclic hydrocarbons measured in Runs 2 and 3. Reaction order for hydrocarbons and hydrogen is assumed based on literature data. Dealkylation rate constants have been corrected for the assumed square root dependence on pressure.

TABLE 1. ADVANCED FUEL PROPERTIES

	-----Literature-----										--Phase I--
	Desired	Cyclo- Hexane	Methyl Cyclo- Hexane	100% cis- Decalin	50/50 c-t Decalin	100% Trans- Decalin	1- methyl Decalin	Di methyl Decalins	Kyd *		
Density g/l	0.779	0.769	0.898	0.885	0.871	(0.88)	(0.88)	0.881			
Viscosity @ -30° F, cst.	11.5	(solid)	1.2	(16.8)	(solid)	(12.73)					
-4° C, cst.		(solid)	(9.6)	(7.9)	(6.0)	7.67					
Flash° C	65	-17	-4	58	52	57					
Freeze° C	-51	6.5	-126	-43	-31	<-73					
Net heat											
BTU/lb	18,800	18,790	18,860	18,410	18,393	18,450	(18,430)	(18,409)			
BTU/gal	124,000	121,950	120,740	135,669	133,515	135,180	(135,040)	(135,120)			
Endo Heat											
BTU/lb.	1,000	1,049	894	917	935	(856)	(749)	(936)			
Total Heat, BTU/lb.											
@1200° F	2,000	2,000	1,830	1,913	1,948	(1,720)	(1,700)	(1,932)			
JFTOT											
Code #	3								1A		
P, mm	25								0		
S, max. w%	0.4								20 ppm.		
H, w%									13.12		

\* JFTOT done on product from Run 1-5. Other inspections done on product from Run 1-2.  
( ) Estimated value.

TABLE 2. FEEDSTOCKS

<u>Analytical Data</u>		<u>Availability</u>	<u>Price</u>
Monsanto and other petroleum naphthalene suppliers. Freezing point 80.5°C, FOB		\$0.30-0.32.5	per lb.
Allied and other coal processors. Crude naphthalene, Freezing point 78°C, Tanks, wks (Significant nitrogen content.)			\$0.22 per lb.
Phthallic grade		Tanks, wks.	\$0.235 per lb.

Refinery Feedstocks

Boiling range, nom. °C	Naph- 1-methyl thalene	dimethyl	trimethyl	Total		
				weight percent		
Hvy. Reformate 129-189	1.9	1.0	0.5	--	--	3.4
Stripped Ref. 218+	3.3	2.9	1.9	0.9	1.6	10.6
Stripped 87 oct. 218+ Gasoline	2.6	1.7	0.7	--	--	5.0
Kerosene Extract Jet A 200-290	2.8	3.0	2.4	1.6	1.6	11.4
Light Cycle Oil 200-350	0.6	2.0	1.1	1.3	1.9	8.9

TABLE 3. PROCESSING ALTERNATIVES

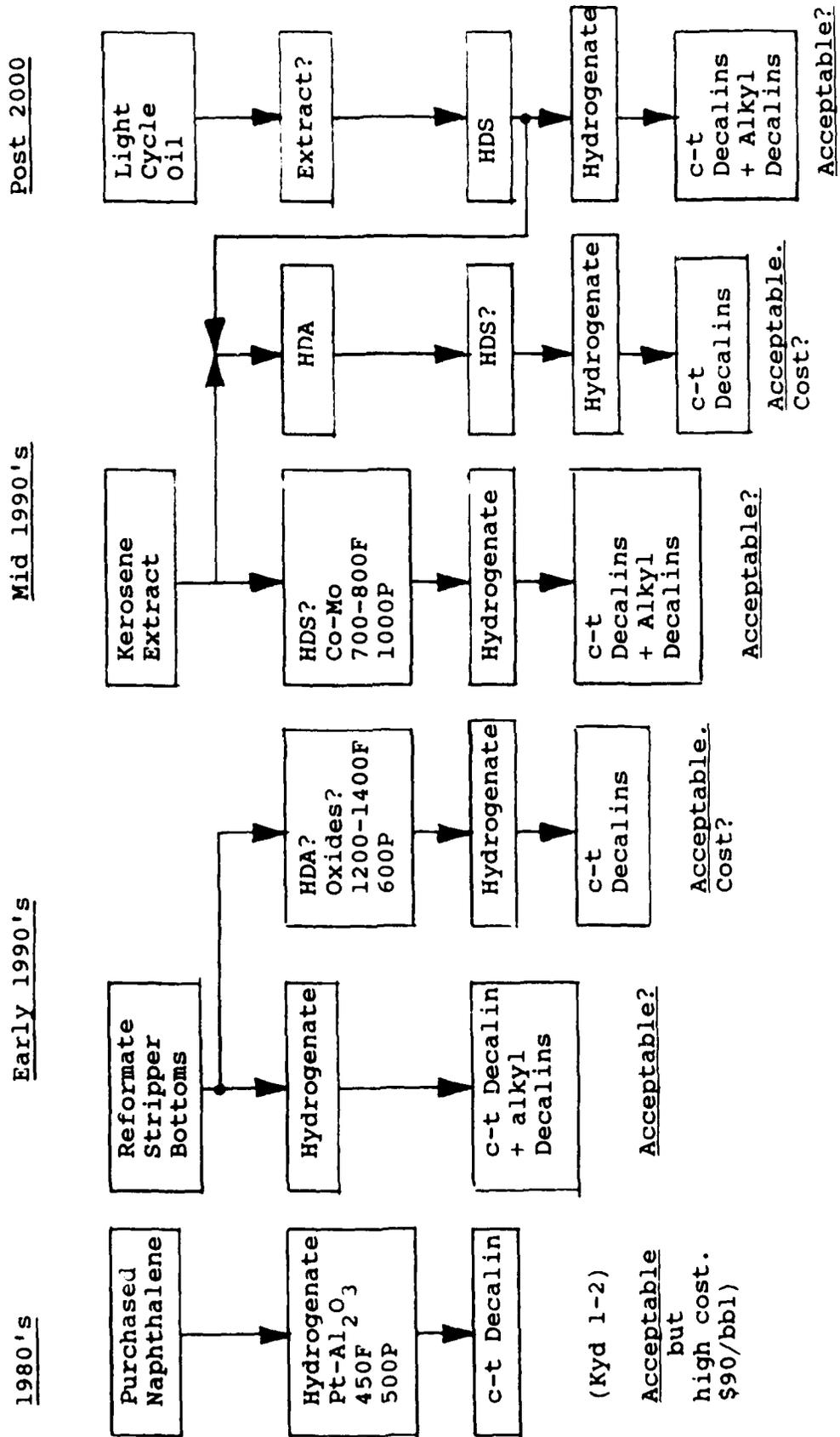


TABLE 4. FEEDSTOCK INSPECTION

<u>COMPOUNDS</u>	<u>RUNS 1-1, 1-2, 1-3, 1-4</u>	<u>RUN 1-5</u>
	<u>w%</u>	
Trans-Decalin	37.1	41.78
Cis-Decalin	41.4	36.52
Tetralin	0.1	0.75
Naphthalene	21.4	20.95
<u>Elements</u>		
Carbon, w%	(88.35)	
Hydrogen, w%	(11.65)	
Sulfur, PPM	50-70 PPM	

( ) ESTIMATED

Decalin was Aldrich Chemical 98% mixture of cis- and trans-isomers. Analysed 99.9% by GC-MS.

Naphthalene estimated 99.9% based on feed analysis.

TABLE 5. CATALYST INSPECTIONS

Designation	Engelhard AE12
Nominal Size	1/16" Extrudates
Substrate	Alumina
Pt, w%	0.5
Compacted Bulk Density, lb/cu.ft.	43
Pore Volume, cc/g	0.57
Surface Area, m <sup>2</sup> /g	220

TABLE 6. RESULTS ON NAPHTHALENE HYDROGENATION EXPERIMENTS

FEED: 21.4w% Naphthalene in Decalin  
 CATALYST: 0.5w% Pt on Al<sub>2</sub>O<sub>3</sub> (Engelhard AE12)

RUN NO.	1-1	1-2	1-3	1-4	1-5
<u>OPERATING CONDITIONS</u>					
Temperature, °F	396	450	647	462	450
Pressure, psia	500	500	500	500	500
Liquid Hourly Space Velocity	1.04	1.16	1.16	1.94	1.48
Hydrogen Flow Rate, SCFH	9.3	5.5	6.3	4.8	6.7
<u>PRODUCT ANALYSES</u>					
Trans-Decalin, w%	38.0	54.55	83.04	48.7	50.3
Cis-Decalin, w%	42.7	45.38	14.31	49.83	46.44
Tetralin, w%	18.5	0.00	2.53	1.47	3.26
Naphthalene, w%	0.8	0.00	0.12	0.00	0.00
<u>NORMALIZED PRODUCT ANALYSES, w% OF FEED</u>					
Trans-Decalin	38.30	55.51	84.34	49.486	51.073
Cis-Decalin	43.02	46.14	14.53	50.63	47.15
Tetralin	18.64	0.00	2.57	1.49	3.31
Naphthalene	0.81	0.00	0.12	0.00	0.00
TOTAL	100.77	101.68	101.56	101.61	101.54
Naphthalene Conversion, w%	96.2	100	99.44	100	100
Hydrogen Consumption, w%	0.77	1.68	1.56	1.61	1.54

TABLE 7. CATALYST PROPERTIES

Designation	HDS-20 (American Cyanamid)	
Shape	Trilobe	
Nominal Size, inch	1/16	
Substrate	-Alumina	
CoO, w%	5.0	
MoO <sub>3</sub> , w%	16.2	
Por <sub>e</sub> Volume, cc/g	0.52	
Surface Area, m <sup>2</sup> /g	230	
Bulk Density, lb/ft <sup>2</sup>	46	

TABLE 8. RESULTS OF HYDROTREATING DIMETHYL NAPHTHALENES  
OVER HDS-20

RUN-PERIOD	<u>2-1</u>	<u>2-2</u>	<u>2-3</u>	<u>2-4</u>
Temperature, °F	658	798	839	844
LHSV, (hr)	1.22	1.01	0.57	0.47
Pressure, psi	1000	1000	1000	2000
Off Gas Flow Rate, SCFH	13.3	19.7	14.0	20.6
<u>Normalized Yield, w% of Feed</u>				
Methane	0.21	1.02	2.72	1.73
Ethane	0.41	2.73	6.94	14.33
Propane		0.76	1.01	7.84
Butane				3.48
Pentane			0.81	
Ammonia	1.21	1.21	1.21	1.07
Liquid Product	100.06	97.87	91.31	79.11
Dimethyl Naphthalene	43.19	28.22	35.36	3.24
Methyl Ethyl Naphthalene	0.43			
Ethenyl Naphthalene	4.22	1.83	0.98	
Methyl Naphthalene	0.75		4.81	
Ethyl Naphthalene			0.89	
C-16	0.61	0.56		
Dimethyl Tetralin	40.47	36.36	29.26	18.09
Methyl Tetralin		1.13	5.6	4.53
Ethyl Tetralin		10.26		
Tetralin	1.04			5.18
Dimethyl Decalin		10.15	2.87	29.98
Methyl Decalin				1.84
Methyl Indane	0.94	0.92	1.68	
Alkyl Benzene	6.11	5.98	8.41	2.80
Alkyl Cyclohexane	2.3	2.25	1.47	13.45
Total Product	101.89	103.59	104.00	107.73
Hydrogen Consumption, w%	1.89	3.59	4.00	7.77
Dimethyl Naphthalene Conversion, w%	44.0	63.4	54.2	98.7

TABLE 9. GC-MS FEED ANALYSIS

	Runs 2 and 3-4	Runs 3-2 and 3-3
	w%	
Dimethyl Naphthalene	77.16	34.62
Dimethyl Tetralin		51.69
Ethyl Tetralin		1.97
Methyl Ethyl Naphthalene	0.71	
Ethyl Naphthalene	4.13	
Ethenyl Naphthalene	3.93	2.06
Methyl Naphthalene	0.89	0.81
Methyl Tetralin		1.93
Tetralin		0.31
Methyl Indane		0.58
Alkyl Benzene		1.22
Alkyl Cyclohexane		1.75
Dimethyl Decalin		2.01
C-16	0.52	0.53
Methyl Biphenyl	0.51	
Methyl Quinoline	7.83	
Methyl Indole	2.86	

TABLE 10. DENSITY AND ELEMENTAL ANALYSES OF LIQUID PRODUCTS  
FROM RUN 2 AND RUN 3

Liquid Product From Run No.	Density, GM/CC	Hydrogen, W%	Nitrogen,* W%	Sulfur,* W%
2-1	0.9464	9.171	0.02	0.1384
2-2	0.9279	9.972	0.023	0.1035
2-3	0.9236	9.876	0.007	0.1086
2-4	0.8607	12.379	0.004	0.047
3-1	0.9402	(9.86)	0.0005	NES
3-2	0.8634	12.292	0.0001	0.055
3-3	0.8389	12.769	0.000	0.048
3-4	0.848	12.442	0.010	0.057

\* Small values of sulfur and nitrogen are apparently due to dissolved H<sub>2</sub>S and NH<sub>3</sub> in the liquid products.

NES--Not Enough Sample.

( )--Estimated value.

TABLE 11. RESULTS OF HYDROTREATING METHYL AND DIMETHYL NAPHTHALENES

CATALYST: HDS-20 IMPREGNATED WITH 1.25w% NiO

RUN-PERIOD	<u>3-1</u>	<u>3-2</u>	<u>3-3</u>	<u>3-4</u>
FEED	1-Methyl Naphthalene	Liquid Product From Run 2-2	Liquid Product From Run 2-2	Dimethyl Naphthalene
Temperature, °F	839	833	872	877
LHSV, (hr) <sup>-1</sup>	0.55	0.46	0.43	0.54
Pressure, psi	1000	2000	2500	2500
Off Gas Flow Rate, SCFH	23.0	25.5	15.1	19.6
<u>Normalized Yield, w% of Feed</u>				
Methane	3.86	2.01	3.77	5.42
Ethane	5.46	8.65	5.44	12.01
Propane		1.64	1.36	1.45
Butane			1.24	1.79
Pentane			0.55	0.58
Hydrogen Sulfide	0.02	0.23		
Ammonia		0.29		1.21
Liquid Product	95.01	90.38	91.66	85.17
Dimethyl Naphthalene		4.75	1.88	3.13
Methyl Naphthalene	22.94			1.52
Dimethyl Tetralin		23.12	10.29	10.73
Methyl Tetralin	39.90		8.78	10.62
Tetralin			1.34	
Dimethyl Decalin		37.19	15.13	16.20
Methyl Decalin	11.39	2.08	8.05	6.81
Ethyl Indane	3.38		2.14	3.45
Alkyl Benzene	12.64	5.43	7.61	11.02
Alkyl Cyclohexane	4.75	17.80	36.44	21.69
Total Product	104.35	103.2	104.55	107.63
Hydrogen Consumption, w%	4.35	3.2	4.55	7.63
Dimethyl Naphthalene Conversion, w%		86.3	94.6	95.9
Methyl Naphthalene Conversion, w%	76.8			

TABLE 12. REACTION KINETIC RATE DATA, RUNS 2 AND 3

	2-1	2-2	2-3	2-4	3-1	3-2	3-3	3-4
Dimethyl naphthalene								
hydrogenation								
1-Methyl naphthalene								
hydrogenation								
Alkyl tetralin								
hydrogenation								
Alkyl decalin cracking								
Alkyl tetralin cracking								
Dimethyl naphthalene								
Product or dimethyl tetralin								
Product or methyl tetralin								
Alkyl decalin + alkyl benzene + alkyl cyclohexane Alkyl cyclohexane								
Alkyl benzene								
Dealkylated products								
RUN-PERIOD	2-1	2-2	2-3	2-4	3-1	3-2	3-3	3-4
Temperature, °F	658	789	839	844	839	833	872	877
Pressure, psi	1000	1000	1000	2000	1000	2000	2500	2500
$k_1$ , (hr) <sup>-1</sup>	0.79	1.02	0.50	1.48	0.95	0.95	1.25	1.82
$k_2$ , (hr) <sup>-1</sup>					0.84			
$k_{T1}$ , g mole/liter hr	0	0.62	0.09	1.06	0.55	1.31	1.44	1.34
$k_D$ , g mole/liter hr	0	0	0	0.15	0.16	0.42	0.91	0.69
$k_{T2}$ , g mole/liter hr	0	0	0.02	0	0.44	0.10	0.14	0.07
Dealkylation mole %	-2	16.1	-10	18.7	0	0	26.2	
$k_{DA}$ , (hr) <sup>-1</sup>	0.025	0.177	0.06	0.097			0.164	
$k_{DA}(P/1000)^{-0.5}$	0.025	0.177	0.06	0.069			0.104	

TABLE 13 THERMAL CRACKING OF DECALIN

From Nixon, A. C. ;Ackerman, G. H. ; Project AF-54-84730  
Quarterly Progress Report No. 11, February, 1966, Table 1.

Temperature, °F	986	1072	1136
LHSV	20	20	20
Pressure, atm	10	10	10
Decalin conversion, w%	0.6	4.1	31.8
Liquid lighter than decalin, w%	0.6	3.9	12.9
Light gas, w%	0	0	9.5
First_order rate constant, k sec <sup>-1</sup>	--	0.010	0.095

TABLE 14 THERMAL CRACKING OF METHYL CYCLOHEXANE

From Nixon, A. C. et al.; AFAPL-TR-67-114-PT-3-VOL-1, Feb. 1970  
Table 13

Temperature, °F	1036	1126	1125	1226
Pressure, atm	10	10	30	10
LHSV	12	14	14	16
MCH conversion, w%	0.6	3.3	39.8	48.7
Benzene	0	0.1	2.3	4.2
Cracked liquid	0.2	1.2	5.7	19.6
Light gas & coke	0.0	0.0	17.4	11.5
First_order rate constant, k sec <sup>-1</sup>	--	0.0075	0.037	0.18

TABLE 15. CATALYTIC CRACKING OF DECALIN

From Nixon, A. C. ;Ackerman, G. H. ; Project AF-54-84730  
Quarterly Progress Report No. 11, February, 1966, pp. 11,17.

Catalyst: 1 w% Pt on Al<sub>2</sub>O<sub>3</sub>

Temperature, °F	660-729	700-802	750-1067	690-729	870
LHSV	100	100	100	100	30
Pressure, atm	10	10	10	10	10
Decalin conv., w%	41.9	50.0	41.3	71.7	82.0
Cracked liquid, w%	0	0	2.2	0.7	0.2
Cracked gas	0	0	5.9	0	0
Selectivity to naphthalene	80.4	88.6	62.4	--	98.8
Selectivity to tetralin	19.6	11.4	9.0	--	--
k, sec <sup>-1</sup>	0.553	0.737	--	--	1.925

TABLE 16. DEHYDROGENATION OF DECALIN

From Nixon, A. C. et al.; AFAPL-TR-67-114-PT-3-VOL-1, Feb. 1970  
Table 92

Catalyst: Shell 113 - Pt on Al<sub>2</sub>O<sub>3</sub>

Temperature, °F	780-847	740-770
LHSV	118	118
Pressure, psig	890-618	780-900
Heat, BTU/Hr.(Ft <sup>2</sup> )	33,000	14,700
Decalin conversion, w%	82.3	37.7
Selectivity to naphthalene	74	35
Selectivity to tetralin	26	65

TABLE 17. DEHYDROGENATION OF METHYL CYCLOHEXANE

From Nixon, A. C. et al.; AFAPL-TR-67-114-PT-3-VOL-1, Feb. 1970  
Table 91

Catalyst: Shell 113 - Pt on Al<sub>2</sub>O<sub>3</sub>

Temperature, °F	780-850	735-781
LHSV	128	128
Pressure, psig	886-590	881-696
Heat, BTU/Hr.(Ft <sup>2</sup> )	31,000	16,900
MCH conversion, w%	89.2	48.1
Selectivity to toluene	98.6	99.2

TABLE 18. THERMAL HYDRODEALKYLATION OF ALKYL NAPHTHALENES

From Ballard, H. D., Jr; Adv. in Petroleum Chemistry and Refining  
Vol 10, CH. 6, 1960, p. 267.

Temperature, °F	1200 - 1350
Pressure, psig	500 - 1000
Contact time, sec.	10 - 140
Conversion, w%	35 - 100

TABLE 19. CATALYTIC HYDRODEALKYLATION OF METHYL CYCLOHEXANE

From: Bonnifay, P.; et al.; Oil and Gas Journal, 74(3), 48, (1976)  
Encyclopedia of Chemical Technology, Vol 3, Wiley, NY, p. 752.

Temperature, °F	772-837	682-795
LHSV	5	15
Pressure, atm	1	1
MCH conversion, w%	97.8	87.2
Benzene (or dealkylation), w%	2.1	0.3
Selectivity to toluene	97.9	99.7

TABLE 20. CATALYTIC HYDRODEALKYLATION OF ALKYL NAPHTHENES

From Nixon, A. C.; et al.; AFAPL-TR-67-114-PT-3-VOL-1, Feb. 1970.  
Table 126

Catalyst: Pt-chloride and Rh-chloride on Al<sub>2</sub>O<sub>3</sub>

Preheating temperature, °F	800 - 1000
Pressure, psig	100 - 700
Dehydrogenation, w%	100
Hydrodealkylation, w%	5 - 10

TABLE 21.

Hydrogenation Shell Smoke Point Improvement

(Data from Hydrocarbon Processing, September, 1984, p 89)

Capital, \$1000/bbl/sd (similar to other 1 stage hydrotreaters)

Size 2080 bbl/sd to match supply of petroleum naphthalene  
303 metric tons/d

Electricity 30Kwh/ton, 330 days/yr, \$0.075/Kwh	\$225,000
Fuel, 198 scf/ton @ \$2.50/ Mscf	49,500
Hydrogen, 2000 scf/ton @ \$1.00/Mscf	200,000
Operations, maintenance, taxes, insurance @ 7%	140,000
DCF return @ 20%, 10 years	398,000
Total	\$1,012,500
\$1,012,500/687,000 = \$1.47/bbl	\$ 0.035/gal.

TABLE 22.

Hydrodesulfurization Exxon Hydrofining (for bimetallic reformer)

(Data from Hydrocarbon Processing, Sept, 1986, p. 86)

Capital \$1,000/bbl/sd, (Midrange of \$90-\$1,500), size 2080 bbl/d

Electricity, 0.25 Kwh/bbl @\$0.075	\$ 12,900
Steam, 9 lb/bbl @ \$2.50/million BTU equivalent	193,000
Fuel, 1,000 BTU/bbl @ \$2.50/million	1,700
water, 35 gal/bbl @ \$0.05/thousand gallons	1,200
Operations, etc.	140,000
DCF return, 20%, 10 years	398,000
Total	\$746,800
\$1.09/bbl	\$0.026/ gal.

TABLE 23

Hydrodealkylation HRI/Arco, non catalytic, 2080 bbl/D feed  
(Data from HRI HDA brochure)

Capital estimated by analogy with pyrolysis distillate hydrotreating which has a similar vessel count, \$1500/bbl/D.

Hydrogen, for toluene 638 lb/hr	
for naphthalene 319 lb/hr, 63,000scfh @ \$1.00	\$499,000
Power, 540 Kw @7920 Hrs/yr, @ \$0.075/ kwh	320,800
Water, 700 GPM @ \$0.05/ thousand gal	16,300
Fuel, 25 MMBTU less 63MMBTU light gas produced	(752,000)
Steam, net 1,700 lb/hr	420,700
Operations, etc.	210,000
DCF return @ 20%, 10 years	597,000
Total	\$1,311,400

\$2.12/ bbl accounting for a 10% loss in weight and volume for dealkylating naphthalene.

\$0.051/ gal.

TABLE 24

Reformate Stripping

Reformers have stabilizing columns to remove light ends. At most stripping requires addition of an additional column to provide reboil to the stabilizer and take off a heavier product. Utilities should be unchanged, and in any case there is ample heat rejection in cooling the reformate from reactor temperature.

The cost of the stripper column is estimated at \$100/bbl/D.

Operations, etc. per bbl/day/year	\$7.00
DCF return @20%, 10 years	23.85
Total	\$30.85

\$0.09/ bbl

\$0.002/gal.

TABLE 25.

Extraction Union Carbide Tetra Process  
 (Data from Hydrocarbon Processing, September, 1982, p.195)

Capital \$330/bbl/d, 2080 bbl/SD

Steam, 157lb/bbl, 158 scf gas, @\$2.50	\$271,000
Electricity, 0.03 Kwh @ \$0.075	1,500
Solvent, @ 0.003/bbl	2,000
Cooling water, 350 gal / bbl @ \$0.05/ thousand gallons	22,300
Operations, etc.	48,000
DCF return @ 20%, 10 years	163,600
Total	508,400
\$0.74/bbl	\$0.018/gal.

TABLE 26. COAT COMPARISON OF ALTERNATIVE ROUTES TO ADVANCED FUELS

Feedstock	Naphthalene	Reformate	Kerosene	Cycle Oil
Price	\$2.50	\$0.60	\$0.60	\$0.40
Stripping		0.002		
Extraction			0.018	0.018
HDS			(0.026)	0.026
Hydrogenation	0.035	0.035	0.035	0.035
Processing	0.035	0.037	0.053	0.079
Total per gal.	\$2.53	\$0.637	\$0.653 (0.0679)	0.479
HDA		0.051	0.051	0.051
Extra feed		0.060	0.060	0.040
Total per gal.	\$2.53	\$0.748	\$0.764 (0.790)	\$0.570

TABLE 27. REFINERIES WITH PROCESS UNITS RELEVANT TO ADVANCED FUELS

(Capabilities in bbl/d)

State	Refiner	Location	Hydro-refining Mid-dist.	Hydro-Treating Arom-sat.	Solv-extract
AL	Hunt Oil	Tuscaloosa	4000	1500	
	Louisiana	Saraland	12000		
CA	Chevron	El Segundo	14000		
		Richmond	65000		50000
	Mobil	Torrance		15000	
	Pacific	Paramount	7000		
	Powerine	Martinez		6000	
	Shell	Martinez		10000	
		Wilmington		12000	
HI	Chevron	Barber's Pt.		3500	
IL	Union	Lemont		4000	
KS	Farmland	Coffeyville	4500		
	Getty	El Dorado		4300	
KY	Ashland	Catlettsburg		6500	10000
LA	Pennzoil	Shreveport		2000	7100
	Cities	Lake Charles	34000		
	Exxon	Baton Rouge		2500	6900
	Marathon	Garyville	35500		
	Shell	Norco		35000	
	Tenneco	Chalmette	18000		
MS	Chevron	Pascagoula	30000		
MT	Cenex	Laurel	14000		4000
	Simmons	Gt. Falls	1300		
OH	Ashland	Canton		23000	
	Sohio	Lima	20000		
		Toledo	35000		
PA	Arco	Philadelphia	50000		
TX	Petrofina	Pt. Arthur	30000		
	Arco	Houston	88000	8000	
	Chevron	El Paso	18000		
	Crown	Houston	10000		
	Exxon	Baytown		29300	45000
	Shell	Deer Park	37000		
	Texas City	(Same)	29000		
	Union	Beaumont		6000	
UT	Chevron	Salt Lake	5500		
WA	Arco	Ferndale	15000		

## APPENDIX A

Analytical results on purchased decalin (Aldrich gold label 99+% anhydrous) and on fuel samples produced in Phase I, Run 1.

ENERGY MANAGEMENT LABORATORY  
WET 15, BARFIELD/SPTLA  
WRIGHT-PATTERSON AFB, OH 45433-5000

PAGE 1 OF 1  
LAB SAMPLE NBR: 86-F-1322  
REPORT DATE: 25 SEP 86

TURBINE FUEL TEST REPORT  
NOT LISTED AND/OR UNKNOWN

REASON FOR SUBMISSION :  
AFWAL/POSF

SUBMITTED BY:

AFWAL/POSF  
WRIGHT PATTERSON AFB, OH 45433-5000

SUPPLIER:

Insufficient information  
Data required:  
Company Name  
Address  
City, State Zip Code

DATE RECEIVED: 25 SEP 86  
SUBMITTER'S NBR: DECAHYDRONAPHALENE

TEST RESULTS:-

02622 Sulfur, Total Wt %	0.00
01322 Smoke Point, mm	23.3
01740 Luminometer Number	49
093 Flash Point, Deg C	60
0445 Viscosity @ -20 Deg C, cs	8.67
0445 Viscosity @ -34.4 Deg C, cs	14.71

REMARKS:

Data reported for information purposes only.

*A. Vanecko*  
QUALITY INSPECTION SPECIALIST

*Thomas J. O'Shaughnessy*  
THOMAS J. O'SHAUGHNESSY  
CHIEF, ENERGY MANAGEMENT LABORATORY  
DIRECTORATE OF ENERGY MANAGEMENT

FUEL ANALYSIS LABORATORY  
13, BARRETT STREET  
WRIGHT-PATTERSON AFB, OH 45433-5000

PAGE 1 OF 1  
LAB SAMPLE NBR: 16-7-1021  
REPORT DATE: 25 SEP 86

TURBINE FUEL TEST REPORT  
NOT LISTED AND/OR UNKNOWN

REASON FOR SUBMISSION :  
FWAL/POSF

SUBMITTED BY:  
  
AFWAL/POSF  
WRIGHT PATTERSON AFB, OH 45433-5000

SUPPLIER: .  
  
Insufficient information  
Data required:  
Company Name  
Address  
City, State Zip Code

DATE RECEIVED: 25 SEP 86  
SUBMITTER'S NBR: KID EXP 1-2

TEST RESULTS:-

2622 Sulfur, Total Wt %	0.00
2386 Freezing Point, Deg C	BELOW -73
1322 Smoke Point, mm	23.0
1740 Luminometer Number	52
93 Flash Point, Deg C	57
445 Viscosity @ -20 Deg C, cs	7.67
445 Viscosity @ -34.4 Deg C, cs	12.75

REMARKS:

data reported for information purposes only.

*L. Vance Ryall*  
L. VANCE RYALL  
QUALITY INSPECTION SPECIALIST

*Thomas J. O'Shea*  
THOMAS J. O'SHEA  
CHIEF, ENERGY MANAGEMENT LABORATORY  
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**APPENDIX B**

Analytical results on feedstock samples prepared in Phase I, Task 2.

# Gollob Analytical Service

MOLININI/GOLLOB (A DIVISION OF) ENSECO (INCORPORATED)

47 INDUSTRIAL ROAD, BERKELEY HEIGHTS, NEW JERSEY 07922 • TEL. (201) 464 3331

TO Dr. Paul H. Kydd, Pres.  
Partnerships Limited  
P.O. Box 6503  
Lawrenceville, NJ 08648

G.A.S. REPORT No. 62654-11/23/86  
62672-11/30/86  
62715-1/8/87  
Date Requested 1/22/87  
Date Reported: 1/23/87  
P.O. No. Verbal

MATERIAL SUBMITTED 5 (Five) Liquid Samples

INFORMATION REQUESTED Organic Mass Spectrometry I Analysis

NOTEBOOK REFERENCE OMSI 1220, Pg. 41 & 42

#### RESULT OF INVESTIGATION

Subject samples, hand delivered to G.A.S., have been analyzed for the presence of naphthalene and for higher boilers with concentration higher than naphthalene.

The five liquid samples, submitted at different times, have been analyzed by gas chromatography/mass spectrometry. The chromatographic separation was achieved on a SPB-35 fused silica capillary column, 30m x 0.32mm I.D., temperature programmed from 40 to 250°C at 10°/minute.

All data are presented in the attached table.

n 12387

By

  
GOLLOB ANALYTICAL SERVICE

Dr. Paul H. Kydd, Pres.  
Partnerships Limited

Page 2

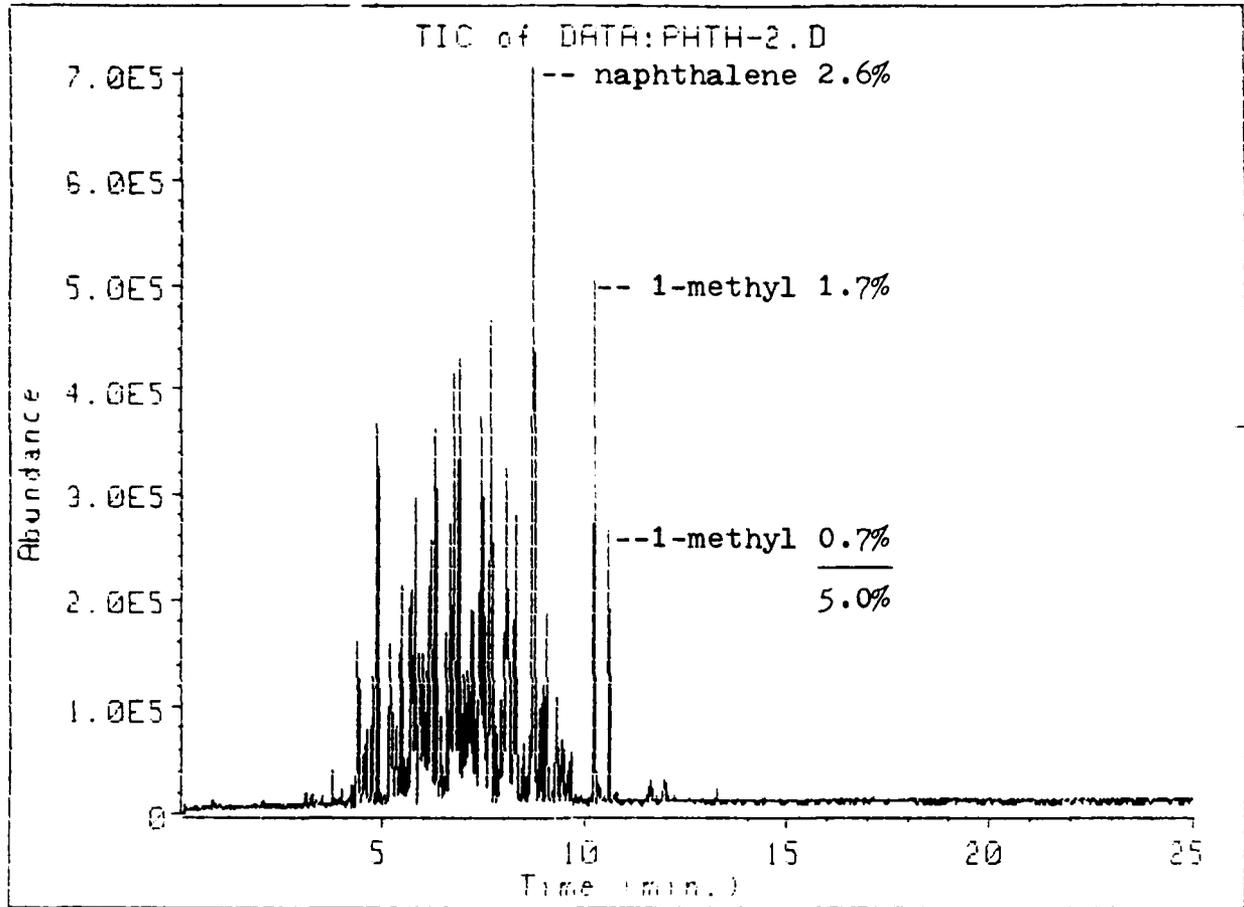
G.A.S.#62654,  
62672 & 62715

<u>Sample Identity:</u>	<u>A-218</u>	<u>E87218A</u>	<u>A</u>	<u>Pet. Distillate</u> <u>SL6192-E</u>	<u>Extract #1</u>
<u>Constituents Detected</u>		<u>Concentration, milligrams/ml</u>			
Naphthalene	33.4	26.1	19.2	5.6	27.7
Methyl Naphthalene	28.8	17.0	9.7	20.2	29.8
Methyl Naphthalene	19.4	7.3	4.8	10.6	23.5
Dimethyl Naphthalene	8.9	ND	ND	13.2	16.3
Dimethyl Naphthalene	15.6	ND	ND	18.9	16.3
Trimethyl Naphthalene	ND	ND	ND	13.1	ND
Trimethyl Naphthalene	ND	ND	ND	4.1	ND
Trimethyl Naphthalene	ND	ND	ND	2.9	ND

63

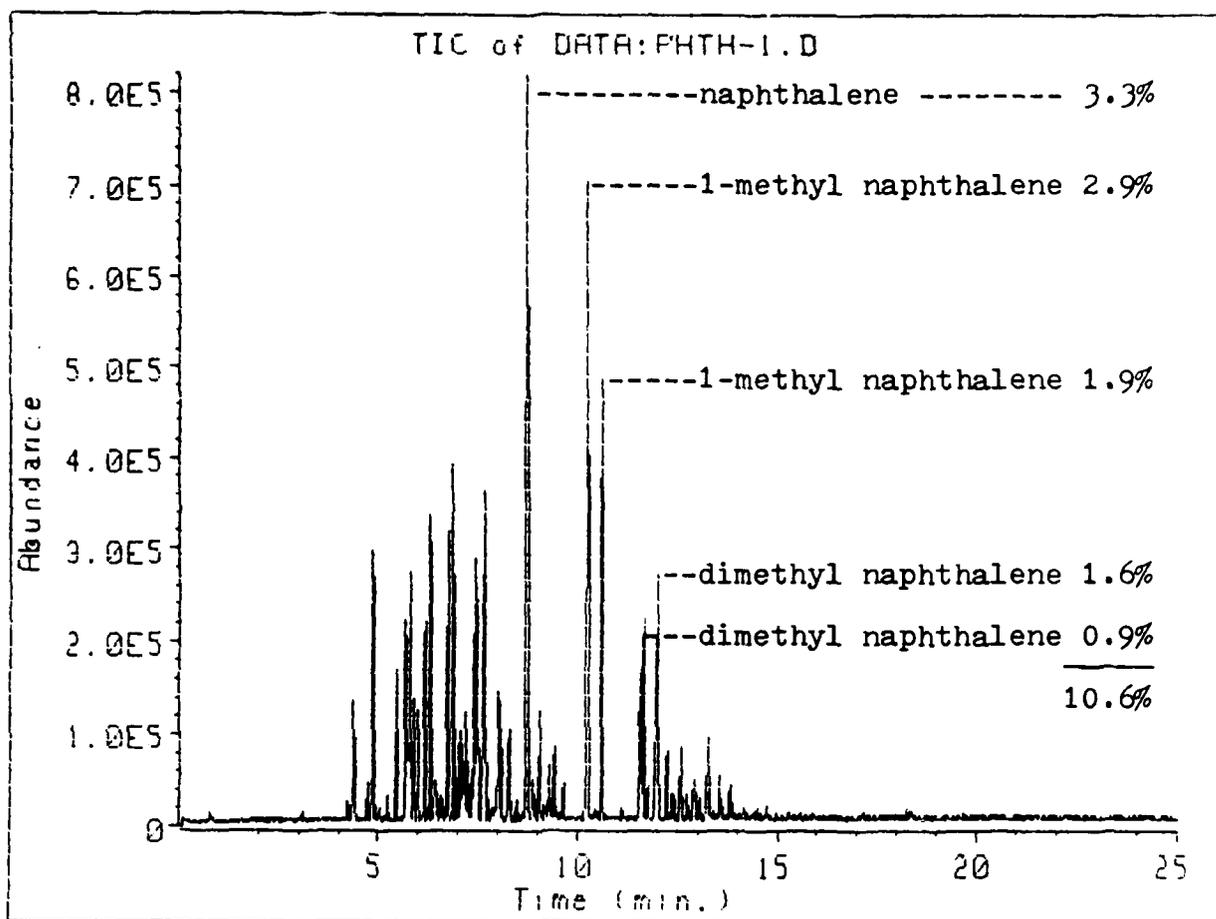
ND=None detected

FIGURE B-1



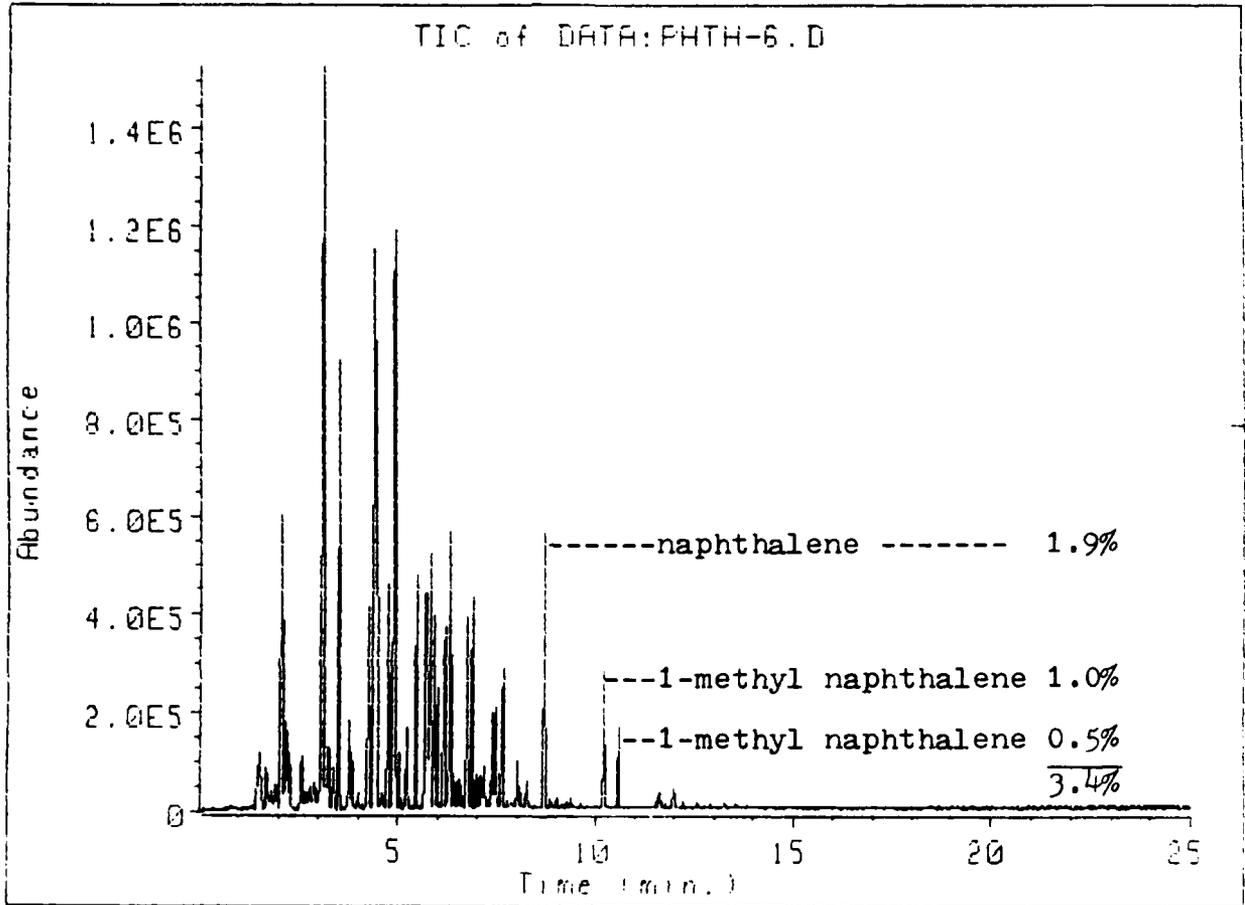
Gas Chromatograph 218°C + Gasoline Stripper Bottoms.  
(87 octane unleaded)

FIGURE B-2



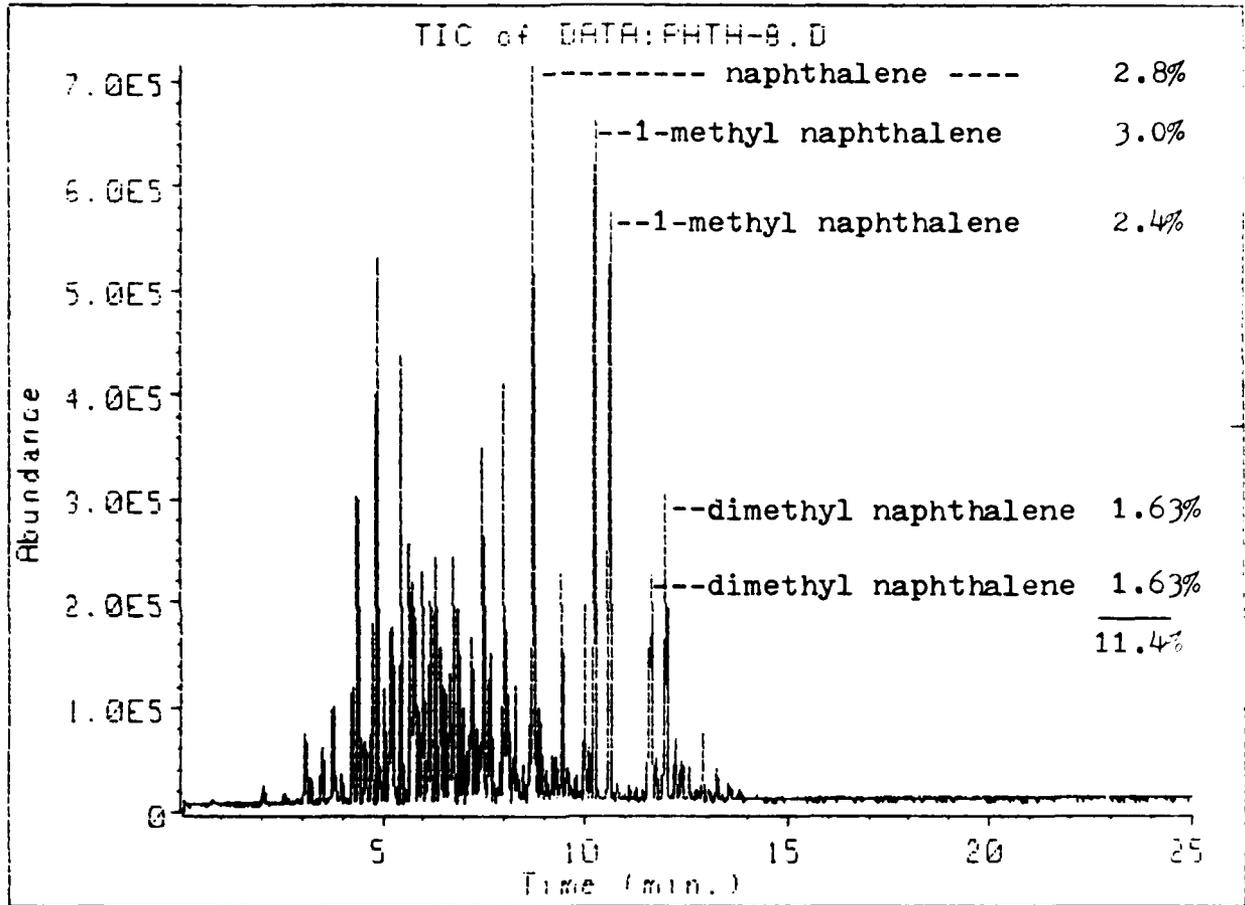
Gas Chromatograph 218°C + Heavy Reformate

FIGURE B-3



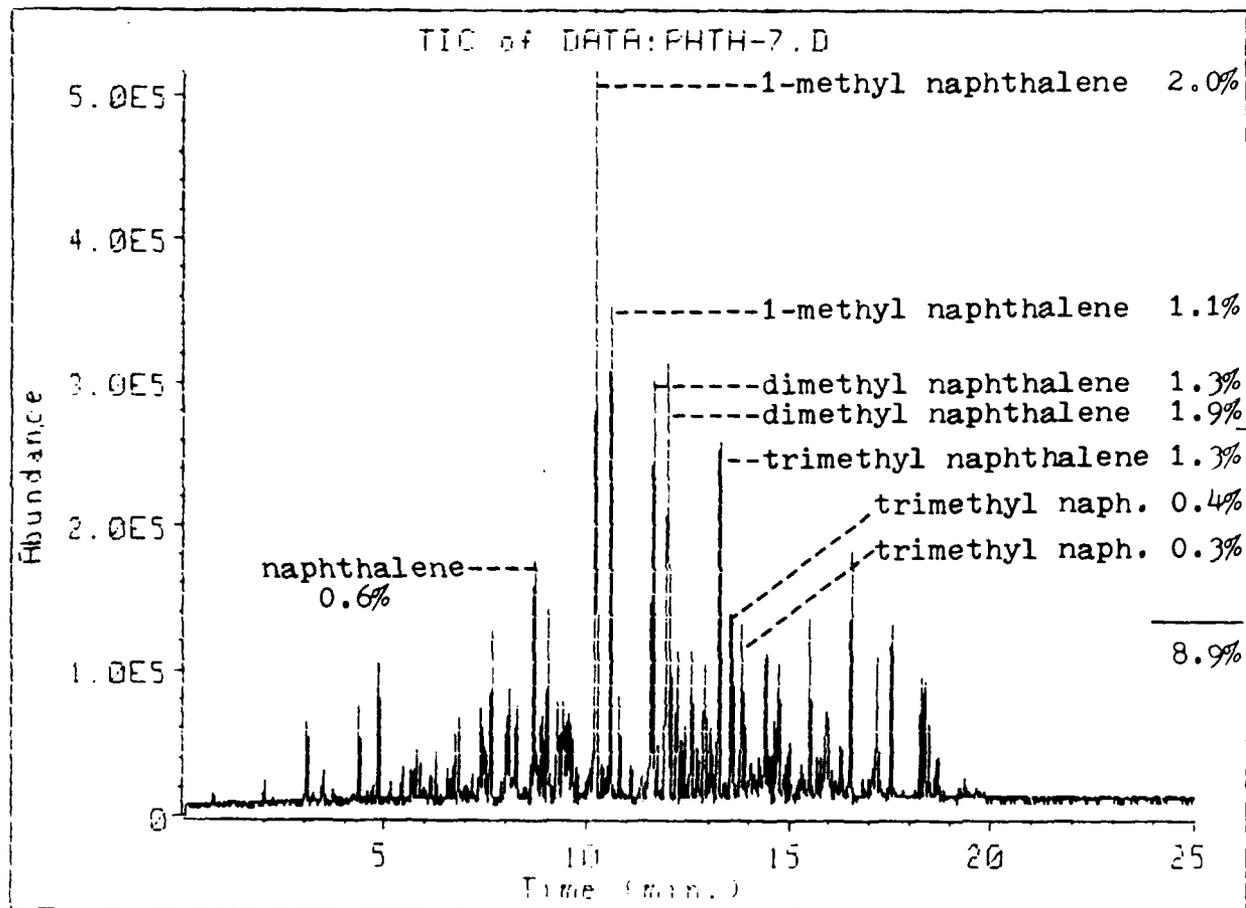
Gas Chromatograph Full Range Heavy Reformate

FIGURE B-4



Gas Chromatograph Jet A Aromatic Extract

FIGURE B-5



Gas Chromatograph Light Cycle Oil

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