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ORGANIC COOLANT RECLAMATION AND COOLANT CHEMISTRY

Fourth Annual Report — December 15, 1961 to
December 14, 1962

By
Daniel A. Scola
John S. Adams
Charles C. Richiusa
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May 10, 1963

Boston Laboratories
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Everett, Massachusetts

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I. INTRODUCTION AND SUMMARY

This report represents the results of exploratory research and development on organic coolant reclamation and coolant technology under United States Atomic Energy Commission contract AT(10-1)-1088 for the twelve month period, 15 December 1961 to 14 December 1962.

A. OBJECTIVES AND SCOPE

The overall objective of this research program is to develop an economical process to reclaim the decomposed terphenyl coolant in order to decrease coolant make-up costs for organic cooled or moderated reactors.

Other obejctives are to evaluate reclaimed products as coolant, to determine economic feasibility of several reclamation processes by cost calculations, and to study polyphenyl derivatives in an effort to determine how terphenyl degrades and forms films, and to provide information about reclaimed products.

The scope of the work included:

1. Process of optimization of the solvent treatment method to reclaim coolant.
2. A pilot plant distillation of high boiler.
3. Studies on two chemical methods to reclaim high boiler:
    (a) catalytic hydrocracking and
    (b) partial hydrogenation.
4. Technical evaluation of reclaimed products.
5. Economic evaluation of potential reclamation processes.
6. A fundamental study of polyphenyls and polyphenyl derivatives such as the thermal decomposition of biphenyl, radiolytic and thermal stability of alkylpolyphenyls, and thermal behavior of polyphenyl dienes.

B. RESULTS

The solvent treatment method for reclaiming high boiler was further refined to include OMRE* core IIIA high boiler and spent coolants with varying high boiler concentrations. The solvent types that can be used were defined. Centrifugation was shown to be a good technique for separating the soluble and insoluble fractions.

---

*OMRE is the Organic Moderated Reactor Experiment at the National Reactor Test Station in Idaho.

The results from formulated spent coolants containing varying high boiler concentrations showed that a solvent system can effect the fractionation of the soluble and presumably low molecular weight fraction from the insoluble high molecular weight fraction. Fractionation of Core III HB, a lower moleculare weight mixture compared to Core I and II HB, was achieved using Varsol-1 and -2, and n-decane to give 87, 95 and 60 wt % respectively reclaimed HB. Solvents containing a small concentration of aromatic hydrocarbons gave greater yields than was experienced with Core I and II HB.

The centrifugation technique to separate the soluble and insoluble fractions was successful. Large quantitites of spent coolant-solvent process mixture could be processed without blocking of the precoat filters used in the filtration process.

Results from the electron radiolysis and reactor irradiation of reclaimed high boiler and spent coolant definitely show that the reclaimed coolants have good radiation resistance and can be used as reactor coolant.

A pilot plant distillation using a Kontro centrifugal wiped-film still to effect gross fractionation of Core II HB gave only 27% yield of reclaimed coolant. This was accomplished at 323°C/0.5 mm Hg at a feed rate of 12 lbs/hr. Further development in this type of distillation equipment could prove fruitful.

Hydrocracking of Core II HB was demonstrated to be a feasible reclamation process. Product yields of 61-83% were obtained and conversions were of the order of 20 to 40%.

Results of the irradiation of hydrocracked high boiler indicate that these products have good radiation resistance and therefore have possible use as reclaimed reactor coolant. All other properties are superior to those of the starting high boiler. The economics of the process is not good even for 80% yields, however.

Hydrocracking of partially reduced high boiler is a technically feasible process but, again, it is not economically feasible. Products with high concentration of alkyl polyphenyl (25%) show lesser resistance to irradiation than those with a low concentration of alkyl polyphenyls (10%).

Results of the partial hydrogenation of o-, m-, and p-terphenyl with Girdler copper chromite (G-13) catalyst at temperatures of 260-290°C and 2500 pounds hydrogen pressure showed that the o- and m-isomers are selectively hydrogenated at the center ring, while the rings in p-terphenyl are hydrogenated either randomly or at the outer ring. The degree of central ring reduction follows the order o->m->p-terphenyl.

The nickel catalysts, Girdler G-49 and Harshaw 0500P, at 195-225°C and 1200-2000 pounds hydrogen pressure, promoted outer ring reduction of m-terphenyl and p-terphenyl, but center ring reduction of o-terphenyl.

Extension of this work to HB gave PRHB of much lower viscosity compared to high boiler, and product from the copper chromite reduction showed a marked decrease in viscosity compared to product from the nickel reduction. From the model studies, it is concluded that the copper chromite HB reduction product contained a greater concentration of single ring reduced terphenyl, thereby causing a large decrease in the viscosity. In addition to lowering the viscosity, partial hydrogenation provided a "built-in" weak link in the polyphenyl molecules and cracking to lower molecular weight compounds proceeded with greater ease than experienced with HB.

Electron radiolysis of high boiler reduced at various levels indicated that the highly reduced high boiler (55% hydrogenation) underwent radiation-induced cracking. The relative radiolytic polymer yield was 0.31 compared to 1.00 for m-terphenyl. Samples of HB reduced to lower levels (11-29%) gave values of 0.41 to 0.63. There is some indication that partially reduced HB might be inhibiting terphenyl degradations since solutions of PRHB in Santowax* OMP gave low values (0.18) compared to Santowax OMP itself. Partially reduced high boiler may therefore have some value for use in terphenyl coolant mixtures as an inhibitor.

Several alkylpolyphenyls were synthesized and their thermal and radiolytic stability were measured. These included 4-ethylbiphenyl, 3-methyl-m-terphenyl, 2-ethyl-m-terphenyl, 4-methyl-p-terphenyl, and 1,3-diphenylcyclohexadiene-1,3. All these compounds have thermal decomposition temperatures greater than 400°C and gave relative radiolytic polymer yields varying from 0.48 to 0.76, compared to 1.00 for m-terphenyl.

The reaction rate constants for the thermal decomposition of biphenyl at 350, 427, 482, and 510°C were determined. The decomposition appears to follow a first-order rate expression over the temperature range investigated. An activation energy of 67 ± 2 kcal/mole was calculated from the rate data.

A re-evaluation of the cost evaluations of the various reclamation processes was made. Economic comparison of the processes indicate that the solvent treatment process is the most economical of the processes which have been demonstrated to be technically feasible.

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II. FRACTIONATION OF OMRE HIGH BOILER AND OMRE SPENT COOLANT

A. INTRODUCTION

Separation of OMRE high boiler and OMRE spent coolant into low and high molecular weight fractions has been studied in this laboratory by two techniques. The first, and most extensively studied and developed, is a solvent treatment method. Extensive data have previously (ref. 1,2) been reported on this method and additional laboratory work done in the past year has shown that this method is technologically and economically feasible.

The second fractionation technique, investigated on a single trial basis, is wiped-film distillation using a Kontro commercial pilot plant "Ajust-o-Film" still. This unit was capable of separating high boiler into low and high molecular weight fractions, but the upper temperature limit (615°C) of the heat transfer fluid used in distillation kept the yield of reclaimed material below 30%. It is felt that a unit of this type would give adequate yields at higher temperatures.

B. SOLVENT FRACTIONATION STUDIES

1. Introduction

The overall objectives of this work were (1) to separate high boiler arising from terphenyl polymerization into high and low molecular weight fractions using appropriate blends of hydrocarbon solvents, (2) to evaluate the low molecular weight fractions for reuse as reactor coolant moderator materials, (3) to develop a technically and economically feasible reclamation process on a laboratory scale. A detailed topical report on the solvent treatment process is in preparation. The specific objectives during this calendar year have been directed toward (1) laboratory generalization of the solvent treatment processes to include coolants of varying high boiler concentrations and solvents of varying composition, (2) solvent treatment of high boiler of lower average molecular weight (Core IIIA HB), (3) further study of process techniques and variables, (4) evaluation of reclaimed materials, including radiolytic (electron and reactor) stability, and (5) an economic analysis of the solvent distribution process on spent coolant containing 5 to 30 wt-% high boiler.

2. Results and Discussion

a. Spent Coolant Reclamation: Spent Coolant with Various HB Concentrations

Spent coolant samples of various high boiler concentrations were reclaimed by solvent treatment. Samples of 5, 10, 30, 40, and 50 wt-% high boiler in Santowax OMP were reclaimed using Esso VM and P Naphtha. Runs were made using two aromatic:aliphatic solvent ratios, 20:80 and 30:70. The experiments were designed to show that the solvent distribution technique is applicable as a reclamation procedure over a wide range of coolant composition. Table 1 gives product yields as well as concentration of spent coolant and high boiler reclaimed in each run.

Table 1

PRODUCT YIELDS FROM RECLAMATION OF FORMULATED SPENT COOLANTS OF VARYING HIGH BOILER CONCENTRATION

Aromatic/ Aliphatic Wt Ratio	HB[a] conc. in Santowax-omp	Wt SC[b] reclaimed per liter solvent, g	Wt HB reclaimed per liter solvent, g	Yields, Wt %	
				Reclaimed SC	High Mol Wt Fraction
20:80	5	198	9.9	99.5	1.0
20:80	10	210	21	91.0	2.4
20:80	22[c]	241	53	87.2	9.7
20:80	30	270	81	91.5	6.3
20:80	40	315	126	90.8	5.6
20:80	50	378	189	89.2	10.0
30:70	5	340	17	99.0	1.0
30:70	10	360	36	96.0	1.5
30:70	22[c]	414	91	84.5	10.1
30:70	30	449	135	94.0	4.8
30:70	40	540	216	90.0	6.9
30:70	50	648	324	88.0	7.9

---

[a] HB is high boiler (Core II)

[b] SC is spent coolant (Core II HB in Santowax omp)

[c] Core II spent coolant

Table 1 shows that yields obtained at a given high boiler concentration do not change significantly when the aromatic:aliphatic solvent weight ratio is increased from 20:80 to 30:70. Since the weight of spent coolant reclaimed per liter of solvent (VM and P Naphtha) is increased markedly at the 30:70 ratio with no loss in fractionation efficiency, this solvent ratio is more economical. At a ratio of 40:60 no fractionation is achieved. Table 1 also shows that even when a 30:70 aromatic:aliphatic reclaiming mixture is used, the weight of the high boiler reclaimed per liter of solvent is only 17 grams at 5% HB concentration and 36 grams at 10% HB concentration. At the decomposition rates expected at these high boiler concentrations and to maintain the high boiler concentrations at 5 to 10% the rate of coolant processing would be 40,000-17,000 lb/hr, respectively (ref.3).

Products were evaluated for degree of separation achieved between high and low molecular weight fractions, thermal stability, and the film forming capacity of the low molecular weight fractions. These data are given in Table 2.

Table 2

EVALUATION OF RECLAIMED SPENT COOLANTS AND HIGH MOLECULAR WEIGHT FRACTIONS

Initial HB Conc. in Santowax-OMP	Reclaimed Spent Coolant			High Mol Wt Fraction		
Wt %	C/H	Thermal Decomp Temp, °C[b]	PCFT[c] value mg film	C/H	No Ave Mol Wt	Wt % ϕ_3 Unrecovered
5	-	-	5	1.40	1159	0.7
10	1.31	476	-	1.43	584	0.2
22	-	-	8	1.55	525	2.9
30	-	438	4	-	1770	0.1
40	-	445[a]	4	-	566	1.8
50	1.35	366	9	1.49	748	1.7

---

[a] Run on sample from 20:80 solvent ratio; all other data from 30:70 ratio samples.

[b] Defined as the temperature at which 1 mole percent per hour decomposes.

[c] Pyrolytic capsule fouling test.

In general, it appears from the C/H ratios and molecular weights cited in Table 2 that the high molecular weight fractions separated are roughly equivalent in each case. The rather high molecular weights for the 10 and 30% runs could result from the presence of undissolved solute in the diphenyl ether used as solvent in the cryoscopic molecular weight determination. The total amount of terphenyl hold-up by the high molecular weight fractions is between 0.1 and 2.9%. This loss is influenced highly by the efficiency of the washing operation of the filter cake. In 12 out of 15 runs it was held below 2%, and in 9 out of 15 below 1% using a single-leaf laboratory filter. The PCFT data of these reclaimed coolants show values generally an order of magnitude lower than those obtained with Core II spent coolant (~50 mg) and 30% Core II high boiler in Santowax (42 mg). From a coolant management standpoint, solvent distribution could offer a means of reducing coolant fouling ability. As expected, the thermal decomposition temperatures show a gradual increase with decreasing high boiler concentration. Reclaimed spent coolant from spent coolant containing 10% high boiler, has a thermal decomposition temperature of 476°C. This is nearly as stable as Santowax OMP (490°C) evaluated under the same experimental conditions.

b. Generalizations of Solvent Types for Solvent Treatment Process

The solvent distribution process should be related not only to complex mixtures of currently available commercial solvents such as Esso VM and P Naphtha, but more generally to blends of specific hydrocarbons. These simpler blends can then be related to petroleum compositions commercially available at any future time. Thus, if a particular petroleum brand name becomes unavailable later, a satisfactory substitute can easily be found using the data reported. In the Third Annual Report (ref. 4), several factors involved in the selection of particular petroleum cuts were described. Among them, aromatic-aliphatic-alicyclic hydrocarbon ratio was found to be significant. In addition, trace amounts of high boiling components in certain solvents were nearly impossible to remove, and contributed to heavy film formation in the PCFT (pyrolytic capsule fouling test) unit. These factors were taken into consideration in formulating blends of known hydrocarbons for reclamation experiments. The hydrocarbon ratios were chosen on the basis of FIA* and mass spectral data obtained on commercially available solvents which gave the best reclamation process (ref. 5). All reagents showed 98-99+% purity as measured by vapor phase chromatography (VPC). The boiling points ranged from 99°C (2,2,4-trimethylpentane) to 174°C (n-decane). Solvent blends used and yields obtained with Core II HB and spent coolant are given in Table 3.

---

*Fluorescent Indicator Analysis

Table 3

PRODUCT YIELDS FROM RECLAMATION OF CORE II SPENT COOLANT AND HIGH BOILER USING FORMULATED SOLVENTS

Run No.	Solvent Composition, Vol %	Aromatic: Aliphatic Ratio	High Boiler		Spent Coolant	
			Wt % Reclaimed HB[c]	Wt % HMWF[d]	Wt % Rec. SC	Wt % HMWF[d]
1	n-Decane (100%)	30:70[a]	----	----	91.8	8.2
2	2,2,4-Trimethylpentane (100%)	30:70	----	----	77.2	22.8
3	n-Decane (70%) p-Xylene (30%)	30:70[b]	72.5	27.5	----	----
4	n-Decane (47.1%) p-Xylene (11.6%) Cycloheptane (41.3%)	30:70	----	----	90.3	9.7
5	n-Decane (28.3%) 2,2,4-Trimethylpentane (18.8%) p-Xylene (11.6%) Cycloheptane (41.3%)	30:70	----	----	87.5	12.5

---

[a] For spent coolant runs, aromatic solvent is taken as total weight of terphenyls present and aliphatic as total weight of formulated solvent added.

[b] Aromatic:Aliphatic Volume Ratio in added solvent.

[c] Initial weight of HB used was 50 grams in 150 ml solvent or 333 grams per liter.

[d] HMWF = High Molecular Weight Fraction.

Results obtained from these runs are similar to those obtained with complex petroleum mixtures with the same aromatic-aliphatic-alicyclic composition. The data serve not only as a basis upon which to choose solvents or solvent mixtures if a particular commercial solvent becomes unavailable, but also serve to eliminate certain hydrocarbons that give low yields. For example, 2,2,4-trimethylpentane (isooctane) gives a yield of 77.2% reclaimed spent coolant (run 2).

n-Decane alone (run 1) gives a yield of 91.8%, a 14.6% increase over isoöctane. The addition of isoöctane to solvent mixtures has the effect of decreasing the yield even in the presence of alicyclics that are good solvents for the process (runs 4 and 5). Therefore, in order to obtain maximum yield with a solvent having a 30:70 aromatic:aliphatic solvent ratio, excessive amounts of isoöctane and similar branched-chain compounds should be avoided. If they are present, the aromatic content should be increased to a point where maximum yield and fractionation are obtained.

The yield results obtained on high boiler with a 30:70 p-xylene-n-decane ratio are about equal to those obtained with xylol-kerosene solvent pair (ref. 6) and Esso Varsol-2 (ref. 7), but greater than with benzene-hexane solvent pair all of the same aromatic-aliphatic composition. The yield from benzene-hexane at this ratio is 58% (ref. 8).

Some general comments concerning the process can be made.

1. High boiling solvents (> 175°C) should be avoided because these are difficult to separate from the reclaimed spent coolant and also are potential sources of fouling (ref. 4).

2. Straight-chain aliphatics and alicyclics containing 8 to 10 carbon atoms are good solvents for the process.

3. Isoöctane and similar branched-chain aliphatics decrease the yield and should not be used in excessive amounts.

4. C_6 to C_9 hydrocarbons (straight-chain and alicyclics) also give low yields (ref. 8).

c. High Boiler Reclamation: Core IIIA Fractionation

High boiler compositions differ depending on the composition of the virgin coolant and the exposure time of the coolant to radiation and heat. Core I and II high boiler and spent coolant samples have been studied in detail with respect to reclamation by solvent distribution. The virgin coolant used in the Core I loading was Santowax OM while that used in Core II was Santowax R. The major differences between these coolants are that Santowax OM has a ratio of ortho-to meta-to para-terphenyl of 8:5:1 (ref. 9) while Santowax R has a ratio of 1:5:2.5 (ref. 9) and contains about 10% pyrolytic high boiler. Santowax OMP, with an O:M:P ratio of 1:5:2.2 (ref. 9) and about 1.5% pyrolytic HB was used in Core IIIA. In addition, since the high boiler concentration was kept at about 5% or less during operation of Core IIIA, the high boiler was subjected to a shorter reactor exposure time than that from either Core I or II, and therefore had a low average molecular weight. The terphenyl content of Core IIIA HB (16 wt %) is slightly higher tan that of Core II (~12 wt %).

To adapt the solvent treatment process to high boiler with different histories, reclamation of Core IIIA HB with Varsol-1 (12% aromatic), Varsol-2 (30% aromatic), and n-decane was carried out. The results are given in Table 4.

Table 4

COMPARISON OF CORE II AND IIIA HIGH BOILER FRACTIONATION
(Temp ~100°C)

High Boiler Source	Solvent	% Yields	
		RHB	HMWF
Core II	Varsol 2 (30:70 $\frac{\text{aromatic}}{\text{aliphatic}}$)	75	23
Core IIIA	Varsol 2 (30:70 $\frac{\text{aromatic}}{\text{aliphatic}}$)	95	3
Core IIIA	Varsol-1 (12:85 $\frac{\text{aromatic}}{\text{aliphatic}}$)	87	8
Core IIIA	n-Decane (100% aliphatic)	60	30

With Varsol 2, a yield of 95% Core IIIA RHB and 3% high molecular weight discard fraction was obtained. The yield of reclaimed coolant from Core I and II under the same conditions is 75%. The effect of the lower average molecular weight (460) of Core IIIA high boiler can readily be seen. A run using Varsol-1 solvent (ca 12% aromatic, 85% aliphatic) gave 87% yield of Core IIIA RHB. The yield of high molecular weight fraction was 8.0%. n-Decane gave 60% soluble high boiler and 30% insoluble fraction.

Because of the apparent decrease in the concentration of high molecular weight polyphenyls (shown by the lower average molecular weight) in Core IIIA HB, compared to Core I and II HB, yields of Core IIIA RHB at 100°C are higher.

Unexpectedly, however, Core IIIA HB appears to show a lower solubility in p-xylene at room temperature than does Core I and II HB. For instance, fifty grams of Core IIIA HB appears to be completely soluble in 100 g p-xylene but, after standing overnight, a certain quantity of high boiler precipitates. This does not occur with Core I and II HB. It may be that Core IIIA HB has a high concentration of polyphenyls similar to m,m,m-Ø_5 which show a relatively low solubility at room temperature, but have a high temperature coefficient of solubility.

The important fact is that Core IIIA high boiler could be readily fractionated by an aromatic-aliphatic solvent yielding improved reclaimed material. This indicates the solvent distribution process can be readily adapted to high boilers with different compositions.

Comparative properties of Core IIIA reclaimed high boiler and starting material are given in Table 5.

Table 5

COMPARATIVE PROPERTIES OF CORE IIIA HIGH BOILER AND RECLAIMED HIGH BOILER

	Core IIIA HB	Core IIIA RHB
No Avg Mol Wt	450	~300
C/H Ratio	1.43	1.31
Viscosity at 265°C, cp	3.9	3.2
Thermal Decomp Temp, °C	393	378
PCFT value mg	8.7	1.8

d. Process Studies: Centrifugation

Reclamation of organic reactor high boiler and spent coolant by solvent distribution involves a filtration step to separate the high molecular weight fraction from the soluble reclaimed fraction. To assess the feasibility of centrifugal filtration, several runs were made with Varsol-2-high boiler and VM and P Naphtha - spent coolant process mixes using an 8-inch diameter basket centrifuge. The filter cloths were Eimco Saran Cloth S.A. 601 and Wellington Sears terrapin chain-weave. A 1/8 in. thick precoat of Johns-Manville Celite® filter aid was used. Results of these centrifugations are given in Table 6.

Table 6

CENTRIFUGATION OF HIGH BOILER AND SPENT COOLANT PROCESS MIXES

(Speed = 2500 rpm; Temp. = 100 ± 5°C)

Run No.	Filter Cloth	Process mix	Soluble fraction % yield	Soluble fraction No Avg Mol Wt	Insoluble fraction % yield	Insoluble fraction No Avg Mol Wt
1	Terrapin	Naphtha-SC	85.6	---	---	---
2	Saran	Naphtha-SC	77.5	---	8.8	---
3	Terrapin	Varsol-HB	66.9	387	21.4	1672
4	Saran	Varsol-HB	68.6	434	22.6	819
5	Saran (no precoat)	Naphtha-SC	~100	---	0	---
6*	Saran	Varsol-HB	65.1	458	31.7	827

---

* Temperature of process mix = 60°C.

It was found that Core II spent coolant process mix, which previously filtered successfully using a leaf filter apparatus, (ref. 10) also was filtered well in the centrifuge provided a precoat was used. Without precoat, the insoluble fraction passed through the Saran cloth.

Runs 1 and 2 gave lower yields of reclaimed spent coolant relative to the vacuum filtration technique because of losses incurred in pouring from the mixing flask to the centrifuge basket. In these runs, the centrifugation proceeded smoothly without any apparent plugging or blocking of the precoat by the insoluble high molecular weight fractions (cake).

With high boiler-Varsol-2 process mix, some difficulty was encountered before the centrifugation. The process mix filtered readily if the filtration was done immediately after it was prepared. It it was stirred between 90 and 120°C for 5 to 10 minutes, the insoluble high molecular weight fraction agglomerated in the mixing flask and transfer was extremely difficult. This occurred in runs 3 and 4 (Table 6). The yields in these two cases were lower than were obtained in previous work since the agglomerate occluded low molecular weight polyphenyl.

By lowering the temperature of the process mix to between 50 to 80°C, agglomeration did not occur; the fine, black insoluble particles did not agglomerate even after standing for 30 minutes. Decreasing the concentration of high boiler also prevented agglomeration. Run 6, which was carried out at 60°C and with a concentration of 300 g HB/liter illustrates the temperature effect. In this run, the feed stock was 2.61 kg of Core II HB and 8.84 liters of Varsol-1-p-xylene blended to give an aromatic-to-aliphatic solvent ratio (volume) of 30:70. A cake thickness of 1 1/8 inches was built up before the filtration rate decreased, near the last 200 ml of process mix. No agglomeration of the high moleculare weight fraction occurred, resulting in complete transfer of the mixture. On distillation of the solvent from the reclaimed high boiler, 93.9% of the solvent was recovered. The properties of the two fractions from this run (6) are shown in Table 7.

Table 7

PROPERTIES OF HIGH BOILER AND FRACTIONATED PRODUCTS

(Separation by Centrifugation, Run No. 6)

	High Boiler	Reclaimed HB	HMWF (Discard Fraction)
No Avg mol wt	550	458	827
Viscosity at 265°C, cp	10.7	4.2	94.3*
Carbon-to-hydrogen ratio	1.40	1.30	1.46
PCFT, mg film	145	6.5	142.5**

---

*At 348°C

**50 wt % in Santowax OMP

These runs showed that centrifugation is feasible for separating the high molecular weight fraction from the solvent distribution process mix. Possible advantages of a centrifuge over a rotary drum filter are (1) faster filtration rates and (2) less solvent hold up in the cake. A possible disadvantage of the centrifuge could be associated with cleaning out the high molecular weight fractions.

e. Radiolytic Stability of Reclaimed Coolants

Evaluation of various samples of reclaimed high boiler and reclaimed spent coolant for radiolytic stability has been completed. Studies were made using the Van de Graaff electron accelerator at our Dayton Laboratories and reactor radiation from the Materials Testing Reactor facility under the supervision of California Research Corp. Tables 8 and 9 summarize the data obtained in these irradiations.

For electron irradiation, it can be seen that samples of reclaimed high boiler in Santowax OMP show improved relative polymer yields with respect to m-terphenyl. In addition, relative polymer yields obtained from irradiation of neat reclaimed high boiler samples are less than 1.0 with the exception of sample No. 15872D (1.34). Although this is expected, it is seen that the molecular weights of these neat samples are not appreciably changed after irradiation indicating little tendency to undergo further polymerization under these conditions. Furthermore, the lower relative polymer yields indicate that these high molecular weight polyphenyls might be cracking to lower molecular weight polyphenyls.

In Table 9, it can be seen that MTR irradiation of reclaimed high boiler in Santowax OMP gave a relative polymer yield with respect to m-terphenyl of 1.1 while starting high boiler in Santowax showed a comparable value of 1.03. Core II reclaimed spent coolant gave a value of 0.84.

From these irradiations, it can be concluded that reclamation of high boiler or spent coolant results in coolant having properties equal to m-terphenyl. Although solutions of starting high boiler in Santowax also show good radiation stability, the reclaimed materials are superior in other respects including fouling ability (lower), thermal stability (somewhat higher), average molecular weight and viscosity (considerably lower).

f. Solvent Distribution-Experimental

1. Fractionation of 5-50% High Boiler in Santowax with VM+P Naphtha Solvent

In a typical experiment, 250 grams of synthetic coolant containing from 5 to 50% Core II HB was melted in a one-liter Erlenmeyer flask To the molten coolant (at about 125°C) was added, with stirring, a quantity of Esso VM+P Naphtha calculated to give a solvent weight ratio of 30:70 or 20:80 aliphatic (VM+P) to aromatic (total terphenyls). The mixture was stirred while being held at a temperature of 100°C ± 5°C for about 3-5 minutes. At the end of this time, the mixture was filtered by suction through a heated Buchner funnel containing a previously prepared Celite filter material. The filter cake (high molecular weight fraction) was mechanically separated from the Celite, dried on the hot plate and weighed. The filtrate

Table 8

ELECTRON RADIOLYSIS OF RECLAIMED COOLANT

(2 Mev electrons at 400°C, 20 Watt-hr/g)

Sample No.	Solvent Pair Used In Reclamation	Before Irrad. No. Avg Mol Wt	Before Irrad. Polymer Yield, wt %	After Irrad. No Avg Mol Wt	After Irrad. Polymer Yield, wt %	Relative Polymer Yield^{a}
RHB						
17077H	xyl-ker 90:10	541	27.7	-	37.4	0.62
17075B	" " 50:50	468	24.9	-	32.2	0.48
17077K	" " 30:70	444	23.5	-	33.2	0.63
17077B	" " 10:90	437	21.1	-	31.4	0.67
15872A	Benz-Hex (70:30)	500	95.9	361	96.2	0.077
15872E^{e}	" " "	270	28.2	-	34.9	0.43
15872B	" " (50:50)	500	91.1	462	96.3	0.30
15872F	" " "	-	27.1	-	34.9	0.49
15872C	" " (30:70)	460	87.7	449	96.0	0.43
15872G	" " "	-	25.1	-	33.8	0.56
15872D	" " 10:90	425	69.7	390	92.6	1.34
15872H^{e}	" " 10:90	-	22.9	-	30.2	0.47
Core I HB--------		600	34.7	-	38.6	0.18
Reclaimed Spent Coolant (30449)		-	14	-	27	0.56
m-terphenyl--------		230	0	-	15.5^{b} 17.2^{c}	1.0
m-terphenyl--------		230	0	-	21.5^{d}	1.0

a - Δ polymer yield before and after irradiation divided by polymer yield of m-Ø$_3$ after irradiation

b - Standard value for 15872E, F, G and H and 17077H, - 5B, 77K, 77B

c - Standard value for 15872A, B, C, D

d - Value for Core I HB, and RSC (30449)

e - 30 wt % in Santowax OMP

Table 9

RESULTS OF CAPSULE IRRADIATIONS OF RECLAIMED COOLANT SAMPLES
(Materials Testing Reactor, Temp. 245°C; Dosage 4.3 x 10^9 Rads)

Sample No.		Description	Before Irradiation No Avg Mol Wt	Before Irradiation Polymer Yield wt-%	After Irradiation No Avg Mol Wt	After Irradiation Polymer Yield wt-%	Relative Polymer Yield
MRC-14		RHB from 30:70 solvent pair	400	92.8	424	N.A.*	-
MRC-15		RHB in Santowax-OMP	-	29	-	54.2	1.1
MRC-11		Core II HB in Santowax-OMP	-	34.9	-	58	1.03
MRC-12		Core II RSC	260	14	270	33	0.84
MRC-16	178	m-terphenyl	230	0	252	22.8	1.00
	170	"	230	0	-	25.1	1.00
	171	"	230	0	-	24.0	1.00
	173	"	230	0	-	21.9	1.00

---

*N.A. - Not available

was charged to a tared round bottom flask and the solvent stripped in a simple still. Last traces of solvent were removed at 5-20 mm Hg. From these data, material balances were obtained and the products obtained were then subjected to further analysis.

(2) Centrifugation Experiments

The centrifuge employed for these experiments was manufactured by International Equipment Company, Model No. 28754H. It was fitted with an 8-inch diameter basket. The basket was first lined with a tared filter cloth (either Saran or terrapin). The centrifuge was then started and a slurry of benzene and a weighed amount of Celite filter aid was filtered leaving a precoat on the cloth about 1/8" thick. The centrifugation speed was then adjusted to 2500 rpm and one gallon of tetrachloroethylene at its boiling point (110°C) was rapidly fed through the filter material in order to preheat the basket. Immediately following the preheat operation, the spent coolant or high boiler process mix (prepared as described previously) was filtered. The yield of high molecular weight fraction was determined by drying the entire filter cake, including the Celite and cloth, and subtracting the known weights of Celite and cloth. Preparation of this fraction for analysis was accomplished by dissolving in benzene, filtering to remove spent filter aid and subsequent removal of solvent by a rotary evaporator. Isolation of the reclaimed coolant from the centrifuge was done as described above.

C. WIPED FILM DISTILLATION

1. Introduction

Research on fractionation of coolant containing high boiler has also been directed at distillation techniques. Distillation using the CMS-5 centrifugal molecular still was unsuccessful because of major mechanical problems associated with distilling high boiler. However, during this period a successful distillation of high boiler was carried out at Artisan Metal Products, Inc., Waltham, Mass., using a commercial pilot plant Kontro "Ajust-O-Films" still.

2. Apparatus

Figure 1 is a drawing of the still. The still is 1 square foot, horizontal, forward-taper machine (stator) with blade clearance adjusting feature. Inside the stator, a rotor, equipped with blades, is mounted on the center axis. The still operates on a centrifugally wiped, thin-film principle, with minimum clearance between the tips of the rotor blades and the heat transfer wall. The cylindrical body is surrounded by a heating jacket for the heat transfer fluid. As the blades rotate at 1400 rpm, feed material (introduced into the still at the wide end of the stator) is picked up by the blades, and immediately forms a thin film on the inside wall. The volatile materials are quickly vaporized and the less volatile materials flow out at the bottom of the stator. The temperature, pressure, residence time (feed rate), and film thickness can be controlled to vary the distillation conditions.

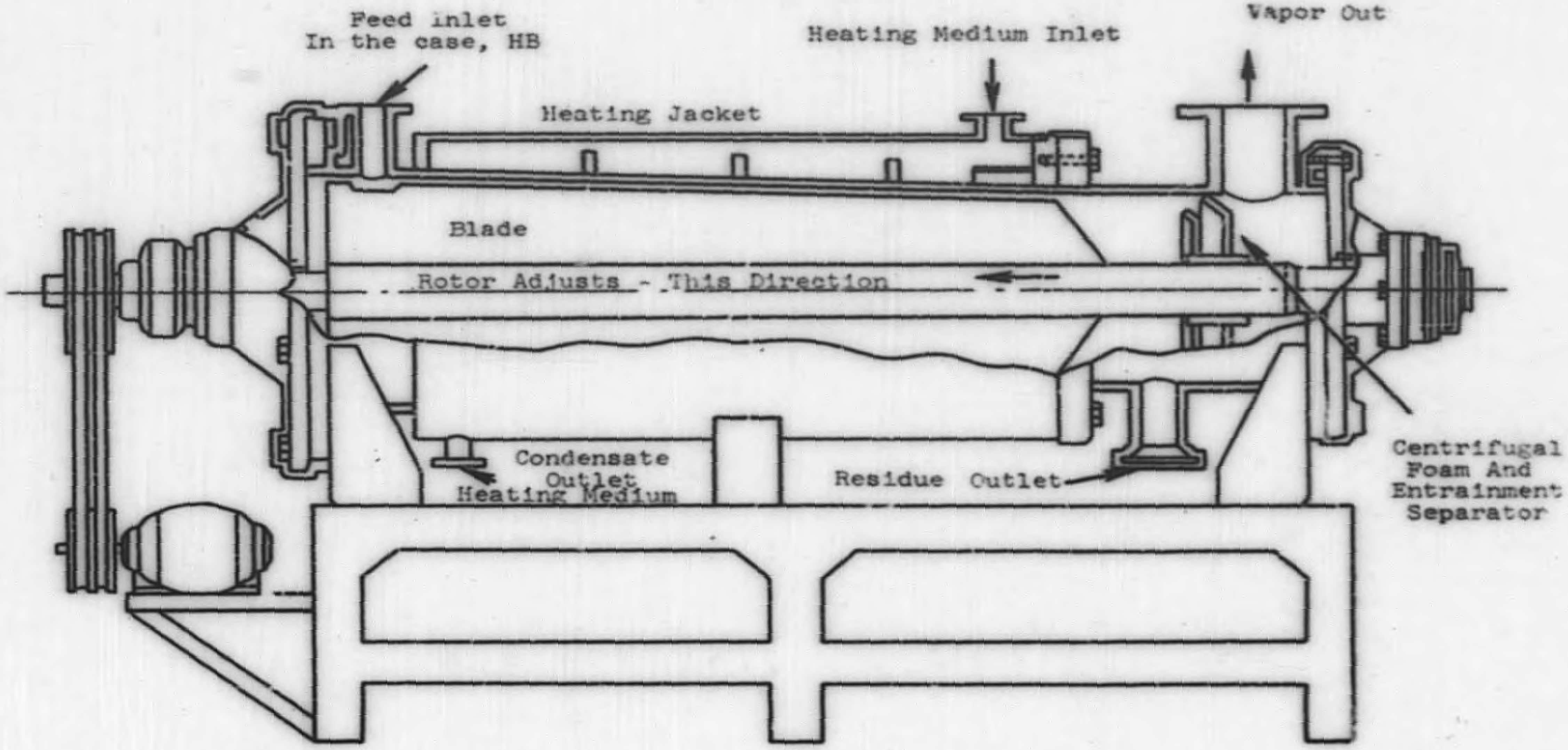


Figure 1. Ajust-O-Film® Horizontal Wiped Film Still

3. Results

The results of the distillation are shown in Table 10. The unit was operated at its maximum temperature (323°C) and minimum pressure (~0.5 mm) with varying feed rates.

Table 10

CONDITIONS USED IN WIPED-FILM DISTILLATION
OF OMRE CORE II HIGH BOILER

Cut No.	Feed Rate lb/hr	Still Temp., °C	Pressure mm Hg	Yield Wt-%
1	40.5	312	0.45	19.2
2	23	311	0.37	23
3	14.6	312	0.34	25.4
4	11.9	317	0.36	26.0
5	12	323	0.39	27.0

Table 10 shows that reducing the feed rate from 23 lb/hr (cut No. 2) to 11 lb/hr (cut No. 5) had only a small effect on the distillate yield. It therefore appears that the still was operating near its maximum efficiency at this temperature (311-323°C). The experiment was a success from a mechanical and operational standpoint, but the yield fell short of the goal (50-70%) set for this type of process. It is felt that higher yields can be obtained if the stainless steel pilot plant is modified for operation at higher temperatures (400-450°C).

Product and residue of two cuts (Nos. 2 and 5) were evaluated. These data are shown in Table 11. The results show that a low molecular weight fraction was separated from a high molecular weight fraction. Average molecular weights of the distillates (297; 343) and residue (690; 741) as well as the carbon-to-hydrogen ratio of the distillates (1.27; 1.38) and residues (1.52; 1.49) provide adequate evidence for the fractionation. Viscosity, thermal decomposition temperatures, and PCFT data provide additional evidence. The viscosities of both distillates were measured at 265°C. The residues were not completely melted at this temperature so that the viscosities reported for them are at 354°C. The difference in viscosity, even at these two temperatures is indeed large. The viscosity of the residue at 354°C is 22.3 cp (cut No. 5) while that of the distillate at 200°C is 3.60 cp. The residue value, however, is still far below the 50,000 cp limit that the Kontro still is reported to be able to handle.

The pyrolytic capsule fouling test (PCFT) values and thermal decomposition temperatures are improved considerably compared with values for the residue and starting high boiler.

The still performance and viscosity of the residue indicate that yields greater than 27% can be achieved with the wiped-film still if it could operate at higher temperatures (400-450°C). An advantage of this type of distillation is that the residence time required for distillation of any substance is extremely short. For distillation at higher temperatures (400-450°C), the short residence time would minimize coolant decomposition during the distillation.

An economic evaluation of this deep cut distillation using results from cut No. 5 gives an incremental profit of $332,000 per year compared to the process where high boiler is discarded and replaced with new terphenyl. The return on investment is 24% (Table 41).

Table 11

PROPERTIES OF DISTILLATE AND RESIDUE FROM WIPED-FILM DISTILLATION OF CORE II HB

		Cut No.2		Cut No. 5	
	HB[a]	Distillate	Residue	Distillate	Residue
Wt-% Yield	-	23	64[g]	27	60[g]
No Avg Mol Wt	550	297	690	343	749
C/H Ratio	1.40	1.27	1.52	1.38	1.49
Viscosity, cp	10.7[b]	2.33[c]	13.5[c]	3.60[c]	22.3[d]
PCFT, mg film	145[i]	4.0[e]	38.5[e]	6.2[f]	47.5[e]
Thermal Decomposition Temperature, °C[h]	360	-	-	402	330
Ø_3 Content, wt-%	10	-	0.6	-	none

---

[a] High Boiler (Core II) placed here for comparison

[b] At 265°C

[c] At 200°C

[d] At 354°C

[e] 37.5% in Santowax OMP

[f] 25% in Santowax OMP

[g] Some terphenyl and volatiles were lost in the lines leading to the vacuum traps. Hence, the distillate and residue yields are lower.

[h] See page 6 for definition

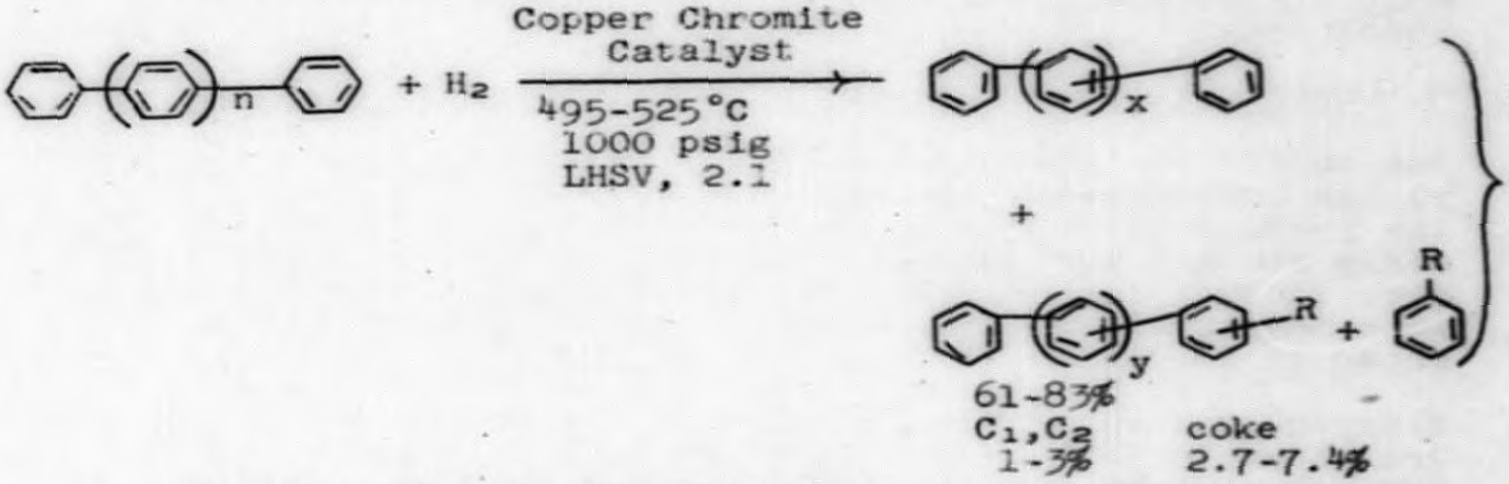
[i] 5% in Santowax OMP

III. CHEMICAL RECONSTITUTION METHODS

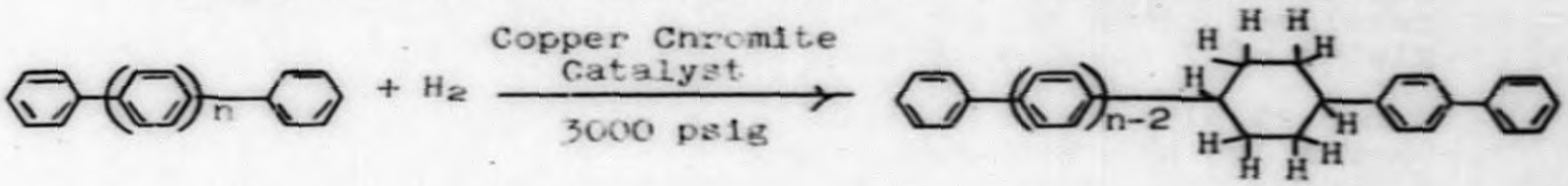
The chemical methods that have been investigated for use in reclamation of high boiler are catalytic hydrocracking and partial hydrogenation. A chemical reclamation involves a change in the polyphenyl molecule and yields products which show differences in chemical and physical properties compared to the original polyphenyls.

The equations for the reactions are shown below

Catalytic Hydrocracking of Core II High Boiler:



Catalytic Partial Hydrogenation of Core II High Boiler:



This method, of necessity, may therefore require more extensive evaluation of products and process variables in a pilot plant study than a physical reclamation method.

Results of the chemical reconstitution methods are discussed below.

A. CATALYTIC HYDROCRACKING STUDIES

1. Introduction

Research during this calendar year has been directed toward optimizing the hydrocracking process to improve the economics of the process. In our previous work (Ref. 11) it was demonstrated (1) that a polyphenyl system can be hydrocracked to lower molecular weight polyphenyls, (2) that product from hydrocracking has some coolant properties which are improved compared to starting feed materials, and (3) that the two-stage hydrogenation-hydrocracking process is technically feasible.

To complete the laboratory evaluation of this method to reclaim HB, the following studies were made: (1) hydrocracking of high boiler to check previous results (ref. 12) in view of the high coke yields obtained in those runs, (2) hydrocracking of 15.8 and 51.5% partially reduced high boiler to determine if yields can be increased by a variation of the hydrogen content of the high boiler; results of this work will be compared with those obtained by hydrocracking 7.4% partially reduced high boiler (reported earlier in ref. 13), and (3) hydrocracking of a model polyphenyl, $m,m,m\text{-}\phi_5$, to determine the reactions involved when the polyphenyl system is treated under catalytic hydrocracking conditions.

2. Catalytic Hydrocracking of OMRE Core II High Boiler

The object of this phase of the work was to increase the product yields and decrease the coke yields since in previous studies (ref. 12) low product yields and high coke yields were obtained. Since the early studies were made, conditions and the catalyst system have become more accurately defined. For this reason, the results from the present work make hydrocracking a more technically feasible process than was shown in the early work.

Experimental data: The results of the hydrocracking of high boiler are shown in Table 12. These new data show that coke yields are low and varied from 2.7 to 7.6 wt-% based on feed material. For a six-hour run (206) the coke yield was 0.9 wt-%/hour or 2.7 wt-%/hr based on the catalyst. This is a marked decrease over previous runs, in which coke yields of 7 to 22 wt-% were reported (ref. 12).

Table 12 also shows that high boiler recovery yields (product) of 61-83% are obtained and conversions are of the order of 20 to 40%. Biphenyl and terphenyl yields are low (1.9 to 6%) but alkylbiphenyl and -terphenyls are produced in greater concentration (by a factor of 2 to 5).

Nuclear magnetic resonance studies of product from runs 204 and 206 show a variety of aromatic and aliphatic chemical environments, but no specific assignments could be made to the very broad resonance patterns exhibited by the samples. The relative number of protons shown for these two samples is as follows:

Sample	Relative Number of Protons: Inner Protons of Fused Aromatic System	Other Aromatic	Aliphatic (total)
Run No. 204 (34456A-1)	1.0	21.8	7.14
Run No. 206 (34475A-1)	1.0	16.7	1.68

Core II high boiler showed little or no aliphatic character. The hydrocracked high boiler samples show a relatively large number of aliphatic protons indicating the presence of alkylpolyphenyls.

Table 12

CATALYTIC HYDROCRACKING OF CORE II HIGH BOILER

Pressure: 1000 psig
H_2/HC (moles): 9 to 24
Liters H_2/g total feed: 1.5 to 3.4

Feed: 50 wt-% HB in p-xylene
Catalyst: Girdler G-13 copper chromite
Run Duration: 180-360 minutes

Run No.	199	198	204[a]	201	205	206	202	200	203
Space Velocity, hr^{-1}	2.1	2.1	2.0	2.2	2.0	2.1	3.6	5.2	5.2
Temperature, °C	475	495	495	525	525	525	525	525	525
<u>Yields, wt-% Total Feed</u>									
Total Recovery	81	66	89	81	97	88	81	86	82
Coke on Catalyst	4.0	6.1	2.7	7.2	7.6	5.4	6.9	4.3	7.4
Gas, C_1, C_2	0.9	1.6	-	1.6	-	-	2.4	1.1	1.7
<u>Yields, wt-% HB Feed</u>									
Product	83	64	83	61	75	79	73	79	68
Hydrocarbons boiling $>\phi_2$ and $<$ triphenylene, $R\phi_2$, $R\phi_3$[b]	8.5	9.4	13	9.7	18	5.5	8.7	12	11
ϕ_2, ϕ_3	2.4	no incr	no incr	2.7	1.9	3.6	6	no incr	1.8
Conversion	21	38	18	47	44	17	36	22	38
Selectivity for $R\phi_2$, $R\phi_3$	40	24	70	21	40	32	24	54	29
Selectivity for ϕ_2, ϕ_3	12	-	-	5.8	4.3	21	17	-	4.7

---

[a] 1500 psig

[b] Exclusive of terphenyls, these hydrocarbons were not identified

As is shown with the model hydrocracking studies on m,m,m-quinquephenyl, a hydrogenation-cracking reaction accounts for the large concentration of alkylpolyphenyls produced in the hydrocracking process. The hydrogenolysis reaction does not appear as important as the hydrogenation-cracking reaction.

A decrease in space velocity from 5.2 to 2.1 at 525°C does not appear to increase the conversion significantly and hence the product yields are constant for these runs.

Temperature has a marked effect on the product molecular weight and viscosity as shown by comparing run 204 with run 201 (Table 13). The hydrocracking temperature for run 204 was 495°C; that for run 201 was 525°C. In general, all runs show a molecular weight decrease (from 550 to 350) and viscosity decrease (10.7 to 1.7 cp) when compared to starting high boiler. A typical chromatogram of product from one run (205) is shown in Figure 2. For qualitative comparison, a chromatogram of high boiler is also shown (Figure 3). The chromatogram of high boiler shows no biphenyl, a 12% terphenyl concentration, and a high concentration of components eluting after p-terphenyl (peak No. 3). The chromatograms of most hydrocracked products (runs 198-206) show two changes: (1) the appearance of biphenyl and hydrocarbons eluting between biphenyl and triphenylene, and (2) a decrease in the concentration of components eluting after p-terphenyl. This results in a lower average molecular weight and lower viscosity as shown in Table 13. The six-hour runs (204 and 206) show no adverse effect on the coke yield, product properties, and conversion when compared to the shorter runs. The molecular weight decrease, viscosity decrease, and thermal stability increase could justify consideration of a hydrocracking process to reclaim coolant. The extent to which a hydrocracked product containing alkylpolyphenyls is resistant to reactor radiation and fouling will be important in assessing the use of a hydrocracking process for reclamation. The final worth of a hydrocracking process, however, will be governed by economic factors. For an economical process, consistent product yields of 70 to 80% are necessary in addition to a low coke reaction. Our calculations (Table 41) show that an annual incremental profit of $371,000 is realized from an 80% yield process, and $222,000 from a 70% yield process. Since these values could be in error by ± 30% (these calculations are based on laboratory work and do not include pilot plant data on this process), the hydrocracking process becomes economically questionable even for an 80% yield process.

3. Catalytic Hydrocracking of Partially Reduced High Boiler

a. Introduction

During this calendar year, research in this area has been devoted to studying the hydrocracking of 15.8% and 51.5% partially reduced high boiler (PRHB) for comparison with studies made on 7.4% partially reduced high boiler (ref. 13).

Table 13

YIELDS AND PROPERTIES OF HYDROCRACKED CORE II HIGH BOILER

Run No.	HB[a]	199	198	204	201	205	206	202	200	203
Yield, Wt-%	-	83	64	83	61	75	79	73	79	68
No Avg Mol Wt	550	384	343	403	306	313	320	296	-	323
C/H Ratio	1.40	1.24	1.23	1.29	1.30	1.29	1.35	1.30	1.32	1.30
Viscosity at 265°C,cp	10.7	-	-	3.9	1.35[b]	1.36[b]	1.60	1.70	-	1.70
Thermal Decomposition Temperature, °C[c]	360	-	-	405	414	-	-	-	-	-
Color and State	blk solid	blk vis tar	blk vis tar	blk solid	dk-br oil	br vis tar	blk vis tar	blk vis tar	blk vis tar	blk vis tar

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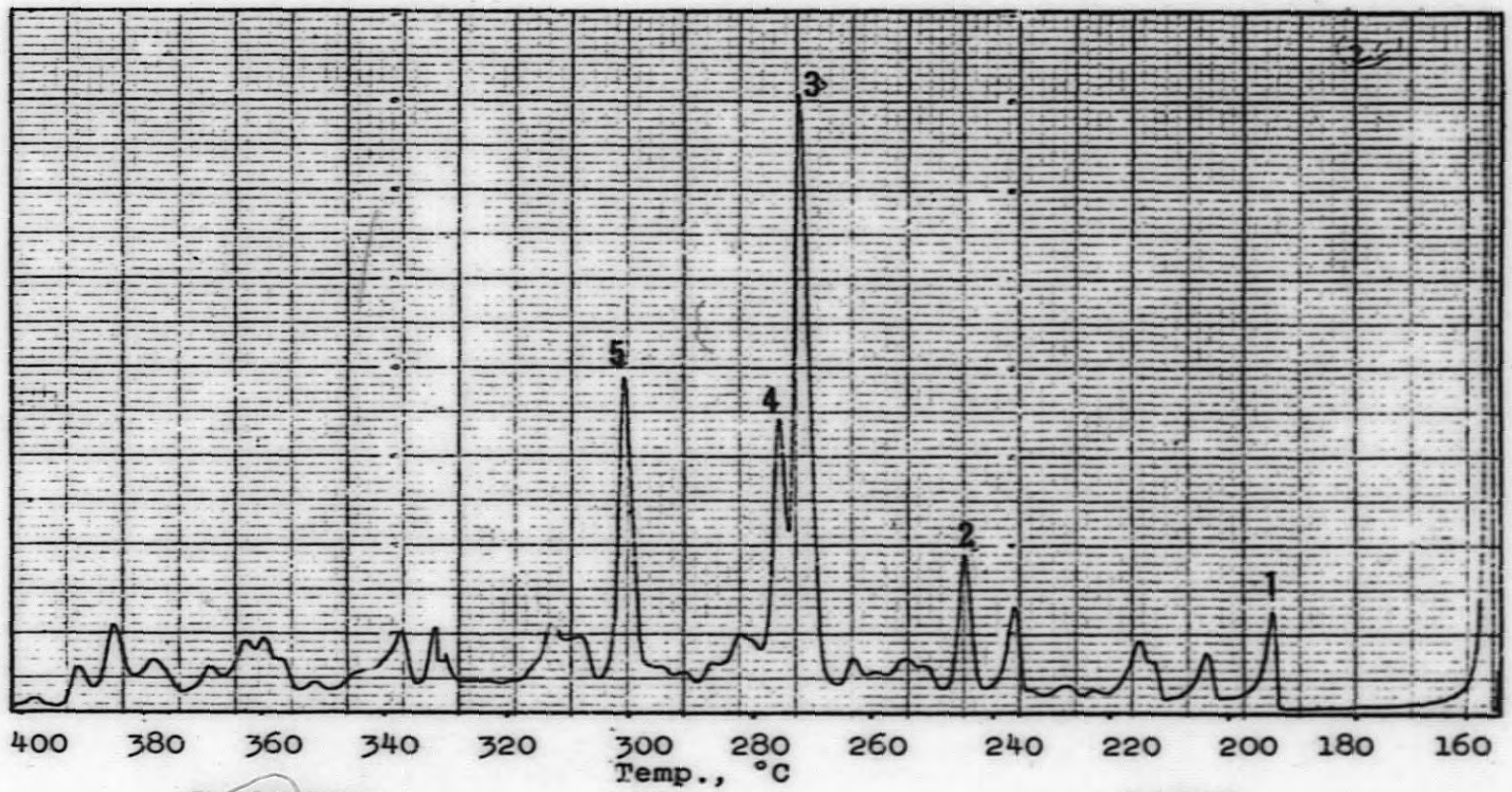
[a] For comparison

[b] Measured at 227°C using the Cannon-Fenske viscometer. These values are in centistokes

[c] See page 6 for definition



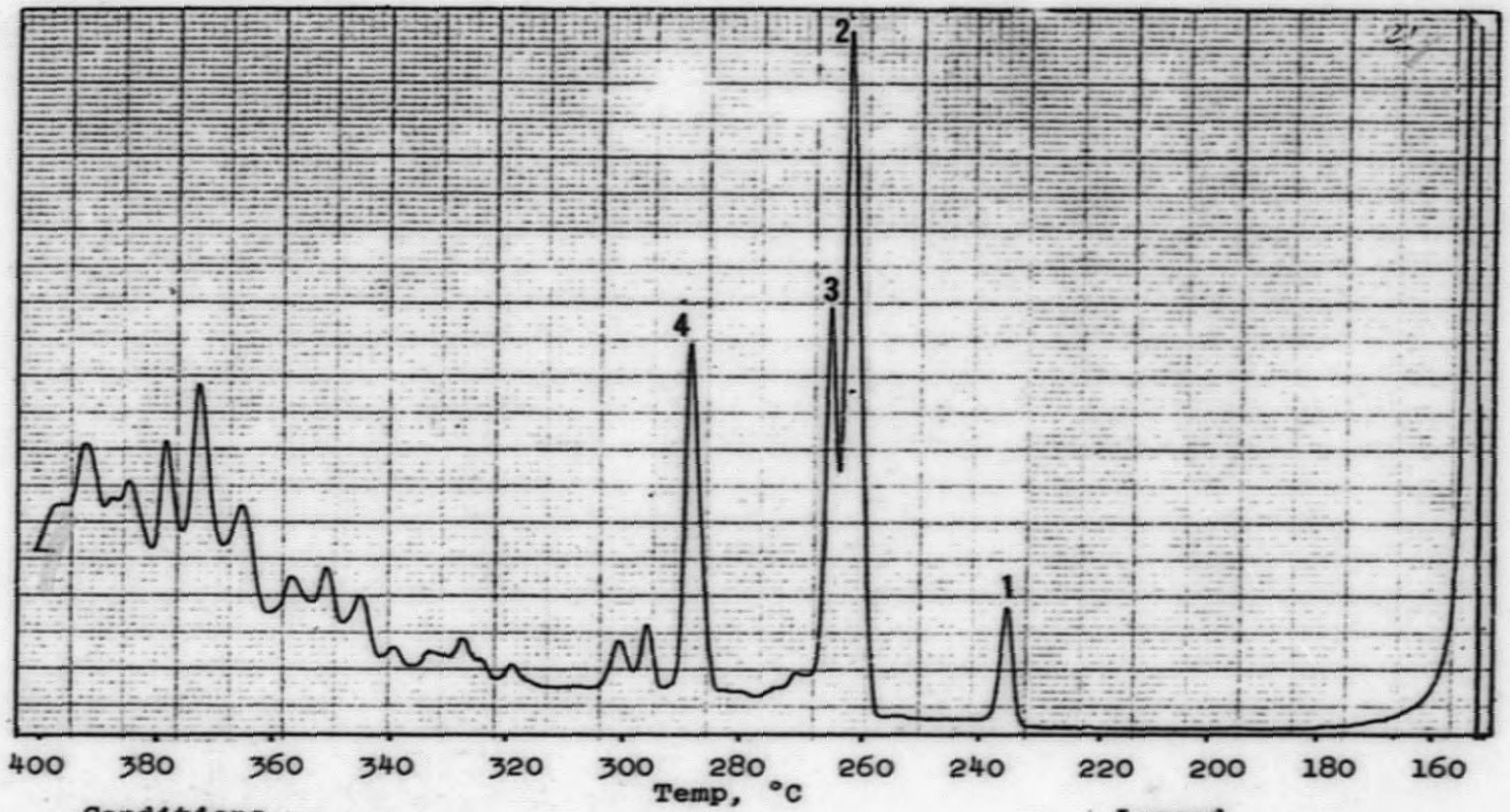
Conditions

Solvent: Tetrahydrofuran
Sample Size: 8 µl
Column: 6 ft, 10% SE-30 on Chromosorb P
30-60 mesh
Column Temp.: 150-400°C
Carrier Gas: Helium 60 psi

Legend

Peak 1 = Biphenyl
" 2 = o-Terphenyl
" 3 = m-Terphenyl
" 4 = p-Terphenyl
" 5 = Triphenylene

Figure 2. VPC of Core II Hydrocracked High Boiler (Run 205, Sample 34457A-1, Temperature-Programmed)



Conditions

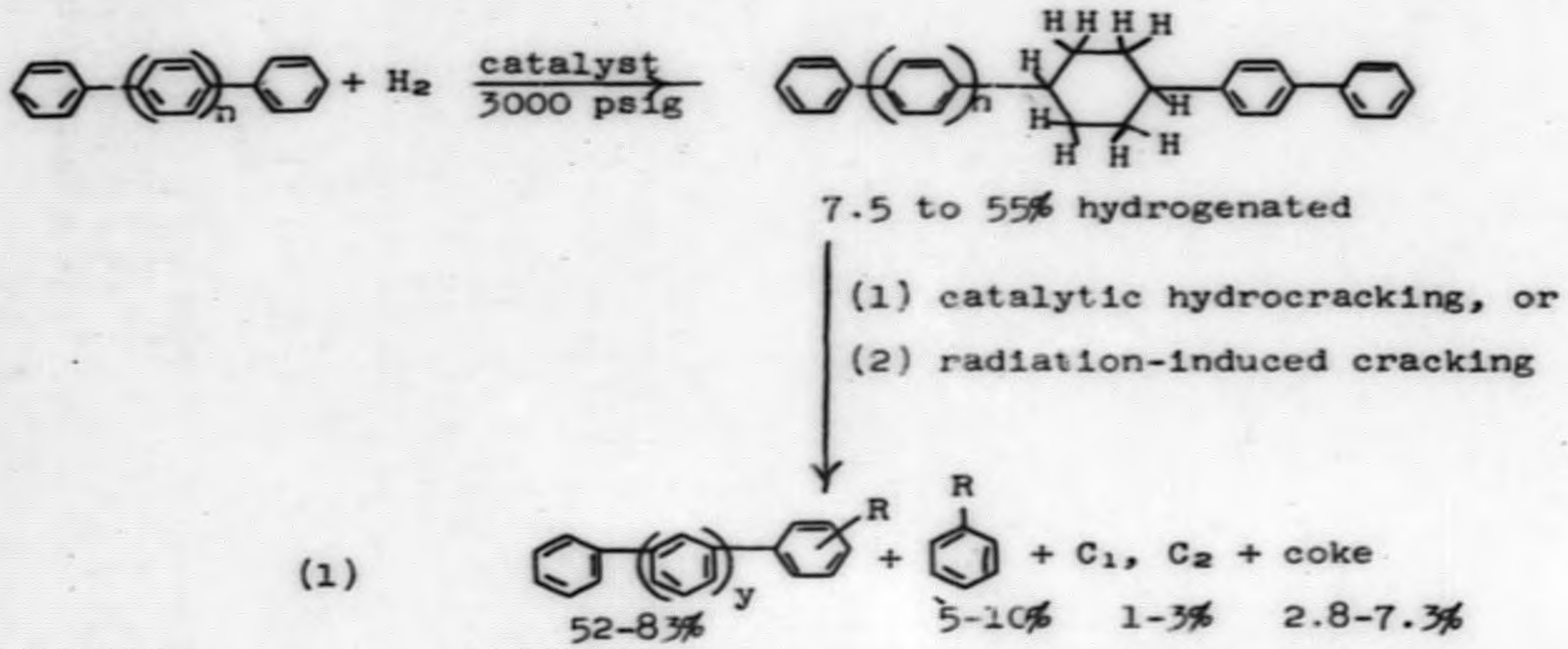
Solvent: Tetrahydrofuran
Sample Size: 26 µl
Column: 6 ft, 10% SE-30 on Chromosorb P
30-60 mesh
Column Temp.: 150-400°C
Carrier Gas: Helium 60 psi

Legend

Peak 1 = *o*-Terphenyl
" 2 = *m*-Terphenyl
" 3 = *p*-Terphenyl
" 4 = Triphenylene

Figure 3. VPC of Core II High Boiler (Temperature-Programmed)

This method of reclaiming high boiler is a two-stage process: (1) partial reduction of high boiler followed by (2) hydrocracking of the partially reduced high boiler. The equations for the two reactions are shown below.



R = alkyl or H

y ≅ 0,1,2,3

Yield depends on the hydrogen content

(2) Lower polymer yield after exposure to electron irradiation. Solutions in Santowax OMP gave lower polymer yield than Santowax OMP.

Results of the irradiated partially reduced high boiler are discussed on pages 65-67.

High boiler was reduced at 225°C and 3500 psig in an autoclave to the extent of 7.4 and 15.8% using Girdler G-13 copper chromite catalyst and to 51.5% using Girdler G-49 catalyst. The partially reduced products from the three hydrogenations were then hydrocracked using the best catalyst resulting from reclaimed high boiler hydrocracking studies (ref. 11).

Process variables of temperature, pressure and space velocity were studied in an effort to optimize the hydrocracking process using these partially reduced high boiler feeds and Girdler G-13 copper chromite as the hydrocracking catalyst. In addition to these process studies, three catalysts (results for which were incomplete for the 3rd Annual Report (ref. 13)) were also tested. These results are also discussed below.

b. Results and Discussion

(1) Hydrocracked 7.4% Partially Reduced High Boiler

These results were reported in the Third Annual Report (ref. 13). However, a comparison with the 15.8 and 51.5% partially reduced high boiler feeds is made on pages 41-43.

(2) Hydrocracked 15.8% PRHB

The data for the hydrocracking runs using copper chromite catalyst are listed in Table 14. They represent the relationship of temperature, pressure, and space velocity to product yield, coke, conversion, and product properties.

The product yields, in general, vary from 60 to 80%. These are lower than those reported for hydrocracking of 7.8% partially reduced high boiler with the same catalyst and reaction conditions, but molecular weight decreases are greater with the present feed (15.8% partially reduced high boiler). Biphenyl and terphenyls are not produced in any appreciable quantity. Alkylbiphenyl and alkylterphenyls are produced in 13 to 37% yields. Conversions range from 20 to 50%, but fall mostly in the 40% region.

Low coke yields (3.9 to 8.3%) were obtained over the range of conditions studied. This is significant since the process can be operated over a broad range without excessive coke buildup. At low space velocity, the highest coke yield obtained was 8.3% (run 171). Figure 4 shows the coke yield as a function of pressure. High pressure has the effect of preventing excessive coke deposition on the catalyst. Table 14 and Figure 5 show that increasing the reaction temperature did not cause an increase in coke formation as might be expected. In fact, coke yield appears to decrease with increasing temperature. Under these conditions, more points in the 500°C area are needed.

High temperatures (525 and 550°C) increase conversion, but as shown in Figure 6, the effect of temperature on the product yield is not particularly obvious. More runs were made at the higher temperatures at this space velocity and pressure so that it is difficult to predict whether the yield obtained from the 500°C run represents a trend. It was expected that the yield would decrease as the temperature increased because coke, gas, and light end yields are expected to increase. This was not the case, however, although high temperatures do have a marked effect on product properties. This is illustrated in Figure 7 which shows that product from the high temperature runs has a considerably lower viscosity than product from the low reaction temperature runs.

Table 14

HYDROCRACKING OF 15.8% REDUCED HIGH BOILER[a]

0-13 Copper Chromite Catalyst
Pressure: 1500 psig
Run Time: 60-330 min.

Feed: 50 wt-% PRHB in p-xylene
H_2/HC (mole): 10-20
Liters H_2/g total feed: 1 - 2.7

Run No.	HB[b]	PRHB[b]	178	181	171	180	179	170	172	169	182	184	173	183	185	186	187	174	175
Temperature, °C			490	490	495	495	495	495	495	495	520	520	525	550	548	549	549	549	495
LHSV, hr^{-1}			2.2	2.2	2.2	2.2	3.6	2.2	3.6	5.1	3.6	3.6	4.8	3.6	3.6	3.6	3.6	3.9	4.0
Yields, wt-% Feed Charged																			
Total Recovery			71	75	81	70	77	89	86	84	75	82	83	88	81	86	87	86	82
Coke on Catalyst			7.8	6.5	6.3	4.9	5.1	5.0	7.6	5.0	3.6	4.3	5.0	5.6	-	2.7	2.7	7.3	-
Gas, C_1-C_3			1.6	1.5	1.6	1.4	1.1	1.9	1.4	2.0	2.6	1.9	1.6	2.2	-	1.3	-	2.5	2.3
Yields, wt-% PRHB Feed																			
Product			92	75	61	83	75	61	69	67	55	66	61	69	59	63	68	68	70
$R\phi_2$, $R\phi_3$[f]			16	-	37	20	-	18	25	13	17	19	20	34	-	18	15	17	29
ϕH, $R\phi$			-	-	3.2	-	-	4	4.7	-	-	-	2.9	-	-	2.7	5.4	-	-
Conversion			13	-	44	20	-	40	31	38	45	36	30	35	-	40	38	50	34
Selectivity for ϕ_2, ϕ_3			31	-	-	5.8	-	-	-	-	-	-	4.9	-	-	-	-	7.8	-
Selectivity for $R\phi_2$, $R\phi_3$			-	-	84	90	-	45	79	35	36	52	67	90	-	-	42	33	86
Product Properties																			
C/H Ratio	1.40	1.14	1.20	-	1.12	1.11	-	1.12	1.12	1.24	1.14	-	1.09	1.18	-	1.18	1.20	1.24	1.22
No Avg Mol Wt	550	518	299	-	271	312	-	337	263	285	324	-	254	270	-	295	320	253	306
Viscosity at 265°C, cp	10.7	8.0	-	-	1.35[c,d]	0.64[d]	-	-	-	-	-	-	-	1.12[d]	-	0.89[d]	1.23[d]	1.18[c,d]	-
Decomposition Temp, °C[e]	360	~370	-	-	-	-	-	443	393	394	-	-	393	363	-	393	-	397	388
Color and State	blk solid	blk solid	dk-br visc. oil	blk tacky solid	br oil cryst	dk-br tacky solid	blk tacky tar	gr-br visc. oil	br oil-cryst	blk visc oil	dk-br visc. oil	blk visc. oil	gr-br oil cryst	y-br visc. oil	gr-br oil-cryst	dk-br visc. oil	dk-br visc. oil	gr-br oil-cryst	gr-br oil

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[a] Core II High Boiler reduced with copper chromite catalyst at 230°C, ~4000 psig in an autoclave to the extent of 15.8%

[b] High boiler and 15.8% partially reduced high boiler both placed here for comparison

[c] Viscosity at 200°C

[d] In centistokes, multiplication of this value by the density at the test temperature gives the value in centipoise

[e] See page 6 for definition

[f] Not identified

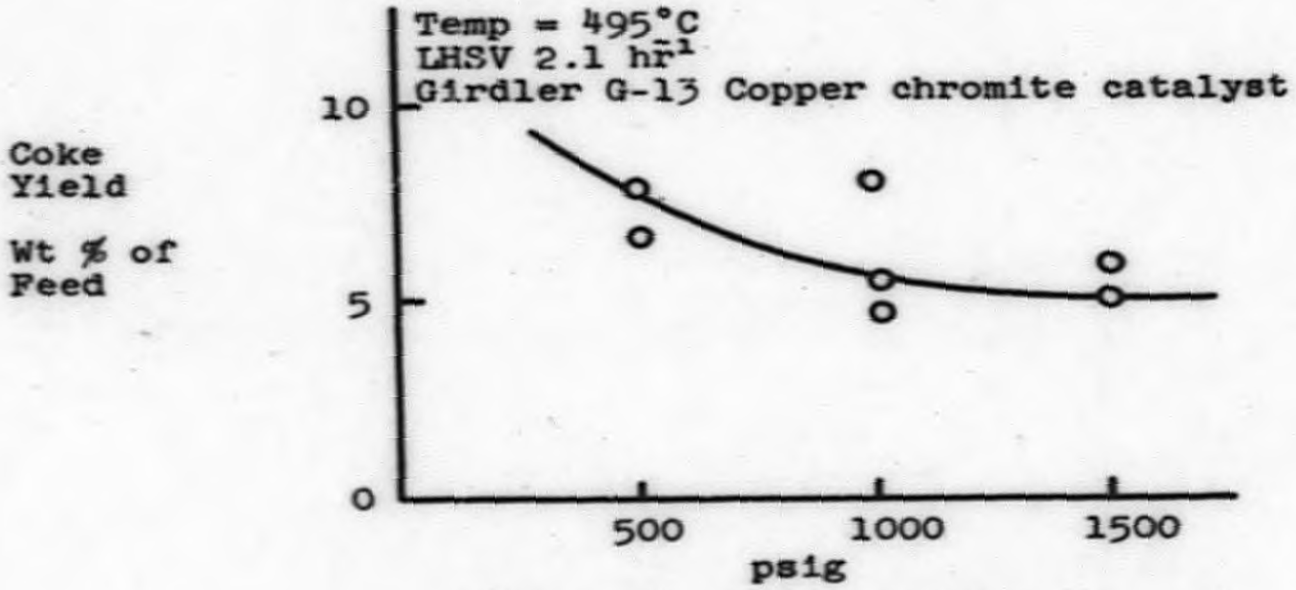

Figure 4. Hydrocracking of Partially Reduced High Boiler

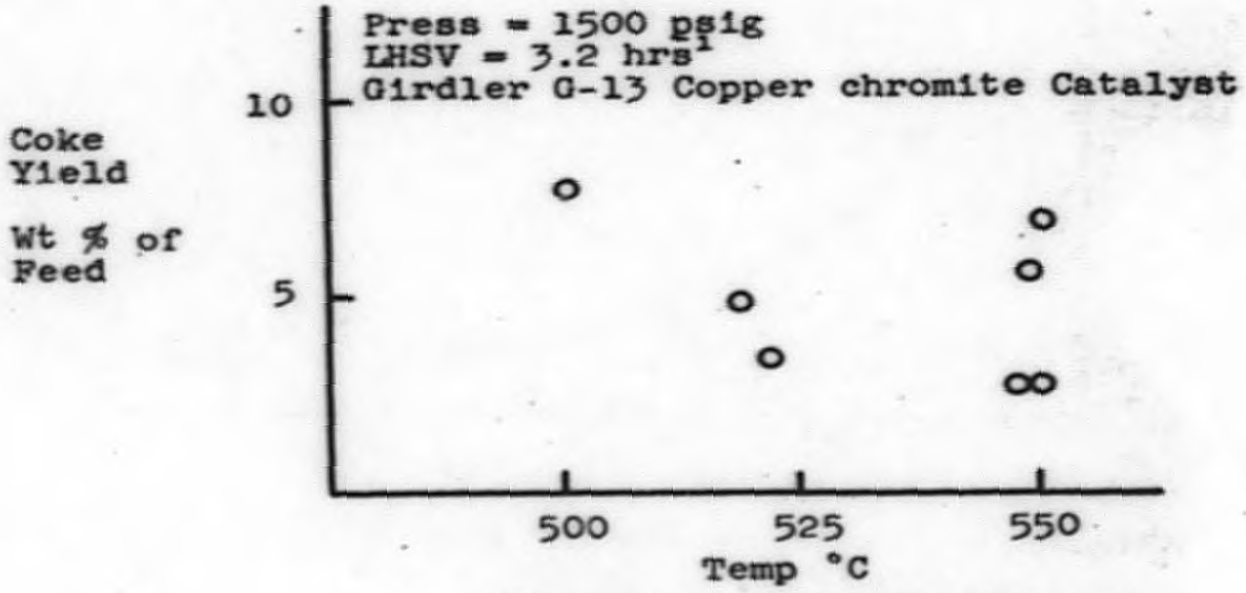

Figure 5. Hydrocracking of Partially Reduced High Boiler

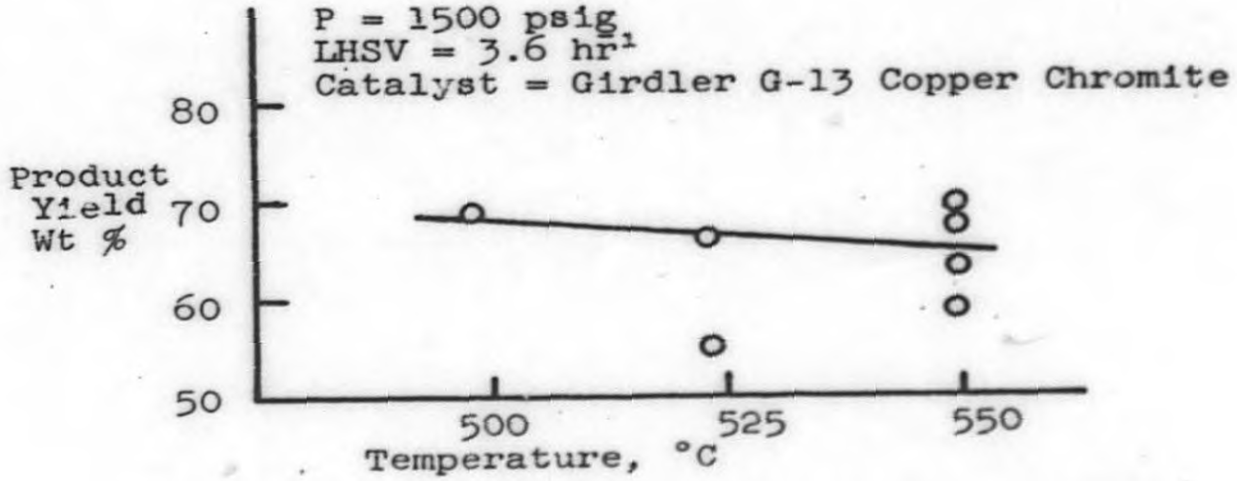

Figure 6. Hydrocracking of Partially Reduced High Boiler Yield vs Temperature

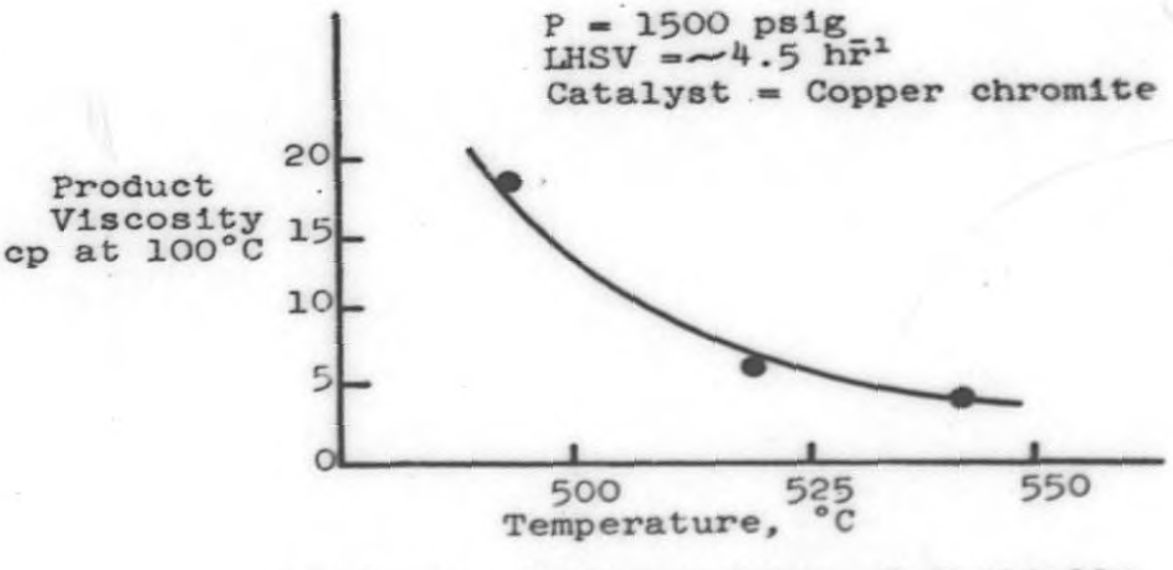

Figure 7. Hydrocracking of Partially Reduced High Boiler Viscosity vs Temperature

Increased pressure reduces the coke yield of the hydrocracking reaction. This is important since the cost of the process is dependent, among other things, on the catalyst cycle time before regeneration and on the catalyst life. Table 14 and Figure 8 show that increasing pressure also appears to decrease the product yield. However, no effect on product properties is noted.

The liquid hourly space velocity at constant temperature and pressure affects the product yield and product properties. The effect on product yield is shown in Figure 9. Low space velocity ($2.2\ hr^{-1}$) runs gave lower product yield, but products from these runs usually have lower viscosity than product from high space velocity runs. The high space velocity ($4.8\ hr^{-1}$) runs require a temperature of 550°C to yield product exhibiting good coolant properties.

The properties of hydrocracked products differ markedly from the starting partially reduced high boiler. This is also shown in Table 14. Molecular weights were decreased from 518 to about 300. The viscosity is changed by a factor of 8 to 10 (8.0 cp compared to 0.64-1.3 cp). The thermal decomposition temperature is increased by about 25°C from 370°C to 395°C. This shows that hydrocracked products, although containing alkylpolyphenyls, are equal to or better than high boiler or partially reduced high boiler in thermal stability.

A six-hour run was made to compare product and coke yields with those of shorter runs. The data for this run (no. 186) are shown in Table 14. The product yield, conversion, coke yield, and product properties are similar to those from shorter run times (run 183). This illustrates that catalyst activity was maintained during this period. To verify that no loss of catalytic activity occurred, run 187 was made using the same catalyst as was used in run 186. The results are essentially the same as those obtained with run 186. This further showed that the catalyst system was not appreciably deactivated by coke deposition or catalyst deterioration. The coke yield over the seven-hour period was only 2.7%. This is 0.4 wt-% per hour, which is well within limits for a low coke hydrocracking process.

The results of the hydrocracking process studies show that the process can operate over a broad range of temperatures, pressures, and space velocities. The temperature, pressure, and space velocity are critical variables as far as product yields, coke, and product properties are concerned. Pressure is less important in regulating the product properties. With Girdler G-13 copper chromite catalyst and 15% partially reduced high boiler as feed, the hydrocracking as a once-through operation can be defined within the limits shown below.

Temperature °C	Pressure psig	Liquid Hourly Space Velocity, hr^{-1}	Product Yields wt-%
495-550	500-1500	2.1 - 4.8	60 - 80

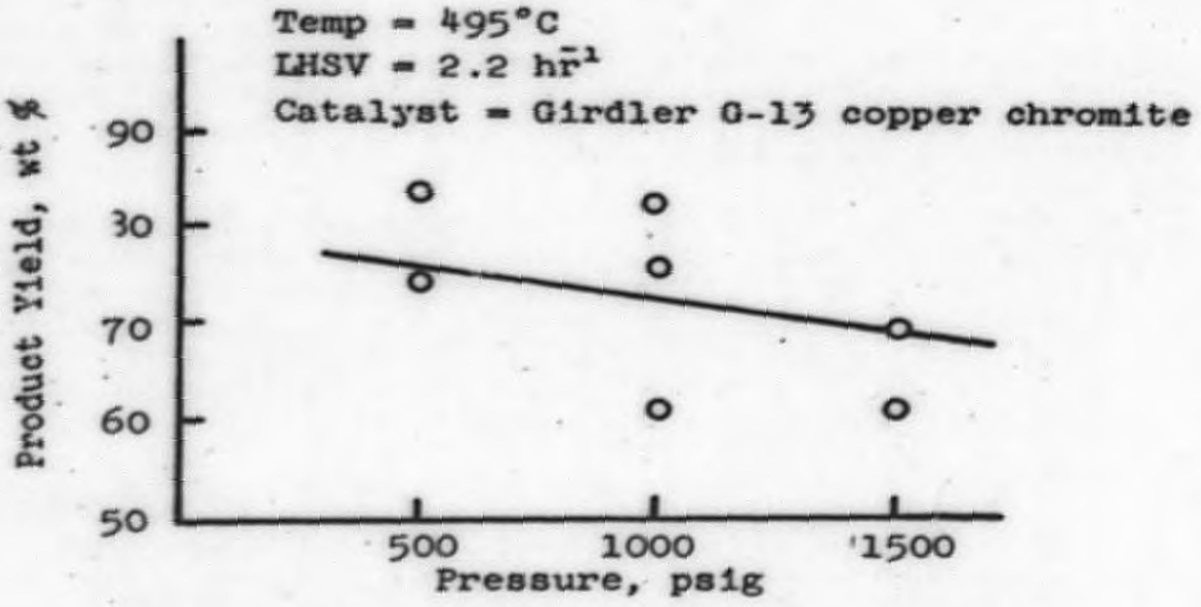

Figure 8. Hydrocracking of Partially Reduced High Boiler; Yield vs Pressure

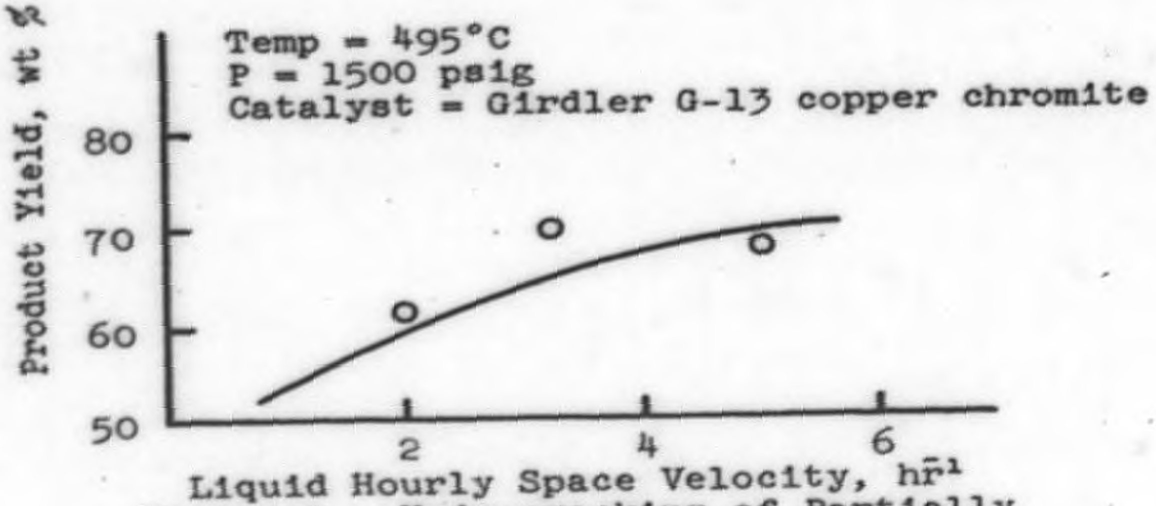

Figure 9. Hydrocracking of Partially Reduced High Boiler; Yield vs LHSV

The economics of this process are extremely dependent on yield. Cost evaluation of 60, 70 and 80% yield processes show the corresponding yearly profits to be -\$142,000, +\$110,000, and +\$259,000, compared to the case where high boiler is burned and replaced with terphenyl coolant. The corresponding returns on investment for the 70 and 80% yield processes are 3.8 and 9.3%. These calculations are based on a 300 Mw(e) reactor operating at a steady state 30% high boiler concentration, and producing high boiler at the rate of 1000 lb/hr.

In addition to the runs using Girdler G-13 copper chromite catalyst, three other catalysts were also studied. Results with the three catalysts tested are shown in Table 15. Nickel-chrome-alumina and molybdenum sulfide-alumina catalysts gave good results with reclaimed high boiler feed (ref. 11) and equally good results with partially reduced high boiler feed. Product yield was 70%, coke yield 3.9%, and gas yields only 1.9 to 3.7%. Biphenyl and terphenyl concentration was not increased, but alkylterphenyl type compounds were produced in 11-18% yield. Table 17 shows that these catalysts gave product with a much higher carbon-to-hydrogen ratio than the starting material. From the carbon-to-hydrogen ratio, molecular weight, and viscosity data, it is quite apparent that at least two reactions are occurring: (1) hydrocracking of the partially reduced polyphenyls, and (2) aromatization of the polyphenyl species before or after hydrocracking. This explains both the carbon-to-hydrogen increase from 1.14 to 1.30, the molecular weight decrease (550 to 300-350), and viscosity decrease (10.7 cp to 1-3 cp). These catalysts can be considered active hydrocracking catalysts for this feed system and under these conditions.

(3) Hydrocracked 51.5% PRHB

The products resulting from hydrocracking 7.4 and 15.8% PRHB have good coolant properties, but yields generally fail in the 60-70% region. Our previous cost evaluations (ref. 39) indicate that yields of 80% or greater must be obtained for an economic hydrocracking process. Therefore, to make high boiler less refractory toward hydrocracking and in an effort to increase yields, high boiler was hydrogenated to a 51.5% level and subjected to catalytic hydrocracking. These results are shown in Tables 16 and 17. In general, the yields are moderately good, ranging from 52 to 69%. There was no increase in biphenyl and terphenyl concentration, indicating that the predominant reaction occurring is cracking of the carbon-carbon bonds between the methylene groups. Runs made at space velocity 2 gave higher coke yields (~5%) than those runs made at space velocities 3.5 and 5.2 (~3% coke).

Considering the highly reduced nature of the high boiler, gas yields are low (1-3%). Conversion yields are in the order of 30 to 40% at space velocity 2. Lower conversions (26-28%) were obtained at higher space velocities of 3.5 and 5.2.

Table 15

HYDROCRACKING OF 15.8% REDUCED HIGH BOILER

Pressure: 1500 psig
Temp: 495 ± 10°C
LHSV: 3.8-4.6 v/v/hr
Run time: 120 min.

Feed: 50 wt-% PRHB in p-xylene
H_2/HC (mole): 9-11
Liters H_2/g total feed: 1.3-1.7

Run No.			164	165	166
Catalyst			$Ni\text{-}Cr\text{-}Al_2O_3$	$MoO_3\text{-}Al_2O_3$	$MoS_2\text{-}Al_2O_3$
<u>Yields, wt-% Feed Charged</u>					
Total Recovery			91	77	90
Coke on Catalyst			3.9	4.9	-
Gas, C_1-C_3			2.7	5.6	1.9
<u>Yields, wt-% PRHB Charged</u>					
Product			70	49	72
ϕ_3, ϕ_2			0.5	no incr.	0.7
Hydrocarbon Boiling above ϕ_2 and below triphenylene, $R\phi_2$, $R\phi_3$			18	15	11
ϕH, $R\phi$			7.4	1.0	8.3
Conversion			34	55	32
Selectivity for ϕ_2, ϕ_3			1.4	-	2
Selectivity for $R\phi_2$, $R\phi_3$			53	28	36
	HB[a]	PRHB			
C/H Ratio	1.40	1.14	1.35	1.30	1.30
No Avg Mol Wt	550	518	349	298	344
Viscosity at 265°C, cp	10.7	8.0	3.1	1.3	2.0
Decomposition Temp, °C[b]	360	370	395	396	371

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[a] High boiler and 15.8% partially reduced high boiler are placed here for comparison

[b] See page 6 for definition

Table 16

CATALYTIC HYDROCRACKING OF 51.5% PARTIALLY REDUCED HIGH BOILER[a]

Press: 1000 psig
H_2/HC(mole): 10-20
Liters H_2/g total feed: 1.5-2.7

Copper chromite catalyst
Feed: 50 wt % PRHB in p-xylene

Run No.	192	190	191	194	197	207	195	196
Duration of run, min.	180	121	330	90	90	300	90	120
Temp. °C	475	495	495	493	495	495	495	495
LHSV, hr^{-1}	2.1	2.1	1.9	2.2	2.1	2.1	3.5	5.2
Yields, wt % feed charged % total recovery	80	84	81	73	78	83	82	84
% coke on catalyst	-	5.1	4.4	6.2	7.3	4.1	2.8	3.7
% gas, C_1, C_2	1.4	2.1	0.7	3.1	-	-	1.7	1.4
Yields, Wt % PRHB charged	69	61	60	52	54	56	68	66
% $R\phi_2$, $R\phi_3$	26	23	27	20	17	30	24	23
% ϕH, $R\phi$	2.9	-	8.2	-	11	-	6.5	3.2
% Conversion	28	34	35	40	41	38	26	28
% Selectivity for $R\phi_2$, $R\phi_3$	93	91	76	49	41	79	93	84

[a] High Boiler reduced to the extent of 51.5% with Girdler G-49 nickel catalyst at 233°C, 2850-3800 psig.

[b] The alkyl biphenyls and -terphenyls have not been identified.

Table 17

YIELDS AND PROPERTIES OF 51.5% PARTIALLY REDUCED HIGH BOILER

Run No.	HB	PRHB	192	190	191	194	197	207	195	196
Yields, wt %	-	-	69	61	60	52	54	56	68	66
Carbon-to-hydrogen ratio	1.40	0.82	0.812	-	0.86	0.840	0.910	0.875	0.825	0.862
No Ave Mol weight	550	510	305	-	309	305	281	-	306	305
Viscosity at 100°C, cs	-	-	9.6	-	9.7	9.6	-	-	12.7	14.0
200°C, cs	10.7[a]	8.3[a]	1.57		1.57			1.30[a]	1.78	1.81
Decomposition Temp., °C[b]	360	366	394	-	395	-	399	-	-	-
Color and state	blk solid	blk solid	dk br oil	gr-br oil	gr-br oil	gr-br oil	or-br oil	gr oil	dk-br oil	gr-br oil

[a] at 265°C, in centipoise

[b] See page 6 for definition

Nuclear magnetic resonance studies of product from runs 191 and 196 show a variety of aromatic and aliphatic chemical environments, but no specific assignments could be made to the very broad resonance patterns exhibited by the samples. The relative number of protons shown for these samples are as follows:

	Relative Number of Protons		
Run No.	Inner Proton of Fused Aromatic System	Other Aromatic	Aliphatic (total)
191	1.0	11.0	26.4
196	1.0	10.3	27.3

The hydrocracked PRHB samples show an increase in the relative number of aromatic protons compared with starting PRHB indicating that aromatization has occurred. The relative number of aliphatic protons also appears to be slightly increased. The high boiler resonance spectrum does not show aliphatic proton. This strongly suggests that a high concentration of alkylpolyphenyls are present in hydrocracked PRHB samples and that these compounds arise from the cracking reaction. The large decrease in viscosity and molecular weight and the low C/H ratio also indicate the presence of alkylbiphenyl, alkylterphenyls, and other alkylpolyphenyls.

(4) Comparison of 7.4, 15.8, and 51.5% PRHB Hydrocracking Processes

A comparison of the effect of hydrocracking high boiler reduced at various levels is shown in Table 18. Even at the different levels of reduction, the hydrocracking process on PRHB gave essentially the same coke and gas yields. The product yields appear to decrease and conversion appears to increase with an increase in hydrogen content of the feed.

There is some variation in the product properties, but this variation can be attributed mostly to the properties of the starting PRHB in each case. For example, the carbon-to-hydrogen ratio of the feed material undergoes little change as a result of the hydrocracking reaction. The large decrease in viscosity and molecular weight, however, supports the contention that hydrocracking of the high molecular weight partially hydrogenated polyphenyl molecules to lower molecular weight polyphenyl and alkylpolyphenyl molecules has occurred to a significant extent.

The product properties, however, became better as the reduction level (hydrogen content) of the feed material increased. The 7.4% and 15.8% PRHB feeds were obtained by treating high boiler with copper chromite and hydrogen at 225°C and 2500-4000 psig in an autoclave.

Table 18

HYDROCRACKING OF PARTIALLY REDUCED HIGH BOILER WITH DIFFERENT HYDROGEN CONTENTS

Temp: 495°C	Feed: Partially Reduced HB in
Pressure: 1500 psig[a]	p-xylene (50 wt-%)
S.V.: 2.2 hr^{-1}	Copper Chromite Catalyst

% Reduction	7.4	15.8	51.5
Wt % Hydrogen	6.2	6.8	9.2
Yields, Wt-% Feed Charged			
Total Recovery	94	70-89	78-84
Coke	3.7	5.0-8.3	2.8-7.3
Gas	1.4	1.1-2.0	1.4-3.1
Yields, Wt-% PRHB			
Recovery (product)	72	61-83	52-69
$R\phi_2$, $R\phi_3$[e]	22	13-37	17-30
$R\phi$, ϕH	7.4	3.2-4.7	3.2-11
Conversion	33	20-44	26-41
Selectivity for $R\phi_2$, $R\phi_3$	67	35-90	49-93

Product Properties	PRHB	HPRHB[f]	PRHB	HPRHB	PRHB	HPRHB
No. Avg. Mol. Wt.	544	355	518	271-337	510	309
C/H Ratio	1.26	1.28	1.14	1.12-1.24	0.82	.812-.910
Viscosity at 265°C, cp	11.7	2.4	8.3	0.64-1.35	8.3	1.30-1.78[b]
PCFT Value, mg	5.1	3.9[c]	4.0	-	-	2.1[d]
Thermal Decomposition Temperature, °C	375	369	370	382-443	-	394-399
Color and State	blk solid	blk, vis. tar	blk solid	gr-br vis-oil	blk solid	gr-br oil

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[a] Pressure, 1000 psig for 51.5% PRHB runs

[b] Viscosity at 200°C in centistokes

[c] 15 wt-% in Santowax-OMP

[d] 25 wt-% in Santowax-OMP

[e] This analysis includes materials boiling between biphenyl and triphenylene. The alkylbiphenyl and -terphenyls have not been identified.

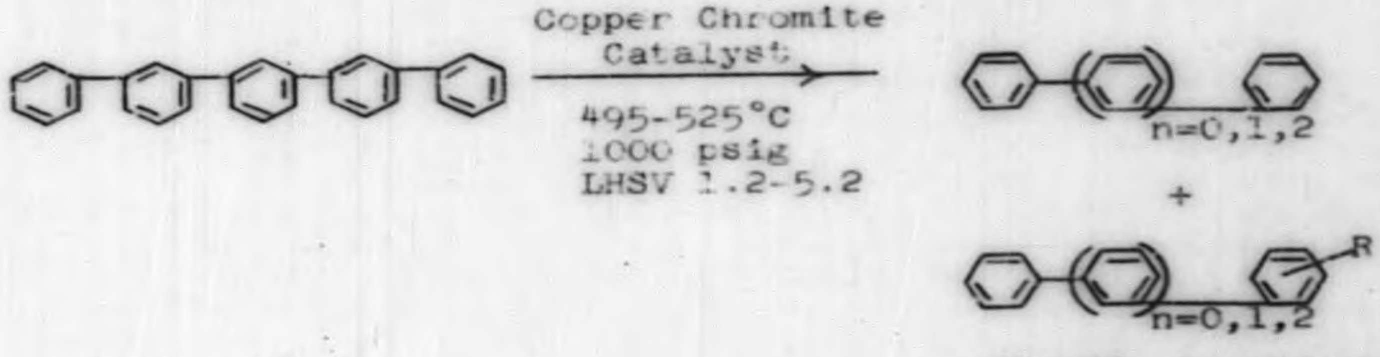
[f] Hydrocracked Partially Reduced High Boiler

The 51.5% PRHB feed was obtained by treating HB with nickel catalyst and hydrogen at 233°C and 2850-3800 psig, also in an autoclave. Reduction levels of greater than 20% could not be achieved with copper chromite catalyst so that it was necessary to use nickel for the 51.5% partially reduced high boiler. The use of a different catalyst for the hydrogenation had no apparent effect on the product properties resulting from the hydrocracking step. Hydrogen content of the feed appears to be the prevailing factor that affects the final properties. The increased hydrogen content provides a greater number of saturated carbon-hydrogen bonds which are cracked more readily than the aromatic carbon-hydrogen bonds. Hence, product from hydrocracked 51.5% PRHB is less viscous and contains more hydrogen than product from hydrocracked 7.4 or 15.8% PRHB. This is accomplished at the expense of obtaining lower yields. In all cases, the properties of the products are better than those of HB or PRHB. These results indicate that there is no particular advantage in hydrocracking high boiler reduced to 50% or greater over 7 or 15% PRHB since economic evaluations show that yields of 80% or better are needed for an economic hydrocracking process. The greatest yields were obtained from the 7.4 and 15.8% PRHB feeds.

4. Catalytic Hydrocracking of m,m,m-Quinquephenyl

The high yield of alkylbiphenyl and alkylterphenyls from catalytic hydrocracking of high boiler indicated that a hydrogenation-cracking reaction predominated over the hydrogenolysis reaction.

In an effort to determine (1) the extent of outer versus inner ring hydrogenolysis or ring cleavage, and (2) the extent of the competing reactions, hydrogenolysis of the carbon-carbon bond between aromatic rings and the hydrogenation-cracking (ring cleavage) reaction, a model polyphenyl, m,m,m-quinquephenyl, was subjected to hydrocracking. The conditions used were similar to those used for high boiler hydrocracking studies shown by the equation



56-93%, liquid product
C_1,C_2 + coke
1% 0.5-1.9%

25 components on chromatogram between ϕ_2 and m,m,m-ϕ_5

Results of the runs and some product properties are shown in Table 19. Conversions are high (83-96.5%) at the lower space velocities (1.3 to 2.4 hr^{-1}). There is little doubt concerning the effectiveness of this catalyst system. The product is an amber-colored liquid while the starting material is a white solid. The presence of appreciable quantities of biphenyl, terphenyls, and product boiling between biphenyl and m-terphenyl were noted at 495°C (S.V. = 1.2, run 208) and 526°C (S.V. = 2.1, run 212).

The low carbon-hydrogen ratios of the products (Table 19) strongly suggest the presence of alkylpolyphenyls. The chromatograms of the products reveal more than 25 components eluting between biphenyl and m,m,m-quinquephenyl.

Nuclear magnetic resonance studies of samples from runs 211 and 212 gave the following data:

Run No.	Aromatic Protons	Aliphatic Protons
Ethylbiphenyl*	7.3	2.5
211	1.0	1.04
212	4.3	1.0

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*Standard sample

Further interpretation of results on the hydrocracked sample from run 211 gave the following:

Group Type	%
Ethyl Aromatic	35
Methyl Aromatic	22
Aliphatic	43

These data confirm the presence of alkylpolyphenyls in hydrocracked m,m,m-Ø_5 samples, and provides additional evidence for a hydrogenation-cracking reaction. All of the alkylpolyphenyl yields, however, are greater than the polyphenyl yields. From these data it is difficult to determine the quantity of benzene produced because of mechanical losses and also because some benzene was formed from p-xylene hydrocracking. Since p-xylene is used as a diluent in the hydrocracking process, two runs using p-xylene alone were made to determine the amount of benzene and toluene produced.

The data for these runs are shown in Table 20. The quantity of benzene and toluene in the recovered liquid of the m,m,m-Ø_5 experiments was no more than that expected from p-xylene hydrocracking. This can be seen by comparing the product recovered using p-xylene feed (Table 20) with that of the liquid recovered using p-xylene-m,m,m-Ø_5

Table 19

HYDROCRACKING OF m,m,m-QUINQUEPHENYL

Press.: 1000 psig
H-/HC(mole): 10 to 20

Copper chromite catalyst
Feed: 25 wt-% m,m,m-ϕ_5 in p-xylene

		Run No.				
	m-ϕ_5	208	209	210	211	212
Temp., °C	-	495	495	495	472	526
LHSV, hr^{-1}	-	1.3	3.4	5.6	2.1	2.4
% Total Recovery	-	72.5	93.8	94	84	83
% Liquid Recovery (b.p. up to 140°C)	-	70	92.5	91.5	86	69
% Coke	-	1.9	0.75	0.47	1.5	0.79
% Gas, C_1, C_2	-	0.9	-	-	-	1.02
Yields, wt-% m,m,m-ϕ_5 feed						
Product Recovery (b.p. p-xylene)	-	56	85	91	70	70
Conversion	-	96.5	61.5	43.5	91.5	83
ϕ_2, m-ϕ_3, m,m-ϕ_4	-	25	11.3	9.3	6.82	25.4
Alkylpolyphenyls, Rϕ-Rϕ_4	-	27.5	35.5	25	54.5	27.4
Selectivity for ϕ_2, m-ϕ_3, m,m-ϕ_4	-	25.8	18.3	21.4	7.45	30.6
Selectivity for Alkylpolyphenyls Rϕ-Rϕ_4	-	28.5	57.5	57.4	59.5	33.2
Product Properties						
C/H Ratio	1.366	1.095	1.163	1.215	0.972	1.22
Viscosity at 100°C, cs	-	-	26.7	41.7	-	4.52
Viscosity at 200°C, cs	4.5	-	2.33	2.95	-	1.06
No Avg Mol Wt	382	237	273	363	296	232
Thermal Decomposition Temp , °C	467	409	380	412	473	423

Table 20

HYDROCRACKING OF p-XYLENE

P = 1000 psig
H_2/HC(mole) = 17-20

Copper Chromite Catalyst

Run No.	113	114
Temperature, °C	495	525
LHSV, hr^{-1}	1.98	1.80
Duration of run, min.	120	120
% Total Recovery	90	85
% Coke	0.5	0.3
% Gas	1.04	1.4
% p-Xylene Recovered	74	58
% Benzene	4.0	5.7
% Toluene	9.9	16
% Residue>p-xylene	0.41	1.5
% Selectivity for hydrogenolysis (total)	54.5	52.5
% Selectivity for ϕH	15.5	13.5
% Selectivity for ϕCH_3	28.0	61.5
% Conversion (to all products)	26	42

feed. However, from the data, an estimate of the degree of end ring versus inner ring reactions can be made assuming about a 10% mechanical loss. The low product recovery yields in runs 208, 211 and 212 (LHSV 1.3 to 2.4 hr^{-1}) indicate that 20 to 30% benzene should have been obtained, allowing for a 10% loss. Conversion data bear this out. Assuming complete reaction and equal change for both outer and inner ring reactions by hydrogenolysis, 10 g of m,m,m-ϕ_5 should give about 7.2 g of product (80% yield) boiling above benzene and 1.8 g of benzene (20% yield). Consecutive reactions could decrease the product yields (b.p. >80°C) and increase the benzene yields. Since the product recovery yields range from 56 to 70% in these runs, it would indicate that reaction between end rings occurs to about the same extent as the reaction between inner rings. The total benzene yield in the p-xylene diluent, however, does not equal 20% even if the quantity produced from p-xylene was considered to be derived from m,m,m-ϕ_5. It therefore appears that end ring hydrogenolysis does not occur to any great extent. If one considers the yield expected in the case of a hydrogenation-cracking reaction only, somewhat different product yields (b.p.>benzene) can be obtained. For end versus inner ring reactions, benzene yields would be zero and alkylpolyphenyl yields would be about 75% (assuming complete reaction). For all combinations for this type of reaction (simultaneous and consecutive reactions), benzene and toluene yields would be about 20% and alkylpolyphenyl yields would be about 58%. A loss of about 12% is expected from fragmentation reactions. In any case, the maximum product yield (b.p.>toluene) that could be expected for a hydrogenation-cracking reaction is 75%. Since the actual benzene and toluene yields were no greater than is expected from the p-xylene diluent used with the m,m,m-ϕ_5, it appears that a hydrogenation-cracking reaction occurs mostly at the inner aromatic rings with a minor amount of end-ring reaction (hydrogenolysis and hydrogenation-cracking).

Even if one assumes that the polyphenyls (ϕ_2, m-ϕ_3, m,m-ϕ_4) result from hydrogenolysis of the carbon-carbon bond between aromatic rings, the data still indicate that the hydrogenation-hydrocracking reaction predominates over the hydrogenolysis reaction. It should be noted that the runs made at low space velocity (run 208, LHSV, 1.3 hr^{-1}) or high temperature (run 212, 526°C) gave about equal concentrations of polyphenyls and alkylpolyphenyls. Under the milder conditions, however, the alkylpolyphenyl yields are increased over the polyphenyl yields by a factor of 3 to 10. The more stringent conditions used in the former runs may be leading to hydrodealkylation (ref. 14). This result tends to magnify the extent of the hydrogenolysis reaction compared to the hydrogenation-cracking reaction. In summary, the data indicate (1) that the inner rings are attacked preferentially to the outer rings, and (2) that the predominant reaction occurring is partial hydrogenation of a ring to give a transitory diene structure which is subsequently cracked to an alkylpolyphenyl, (3) hydrogenolysis of the bonds between the aromatic rings is a competing but minor reaction, and (4) the hydrogenolysis reaction occurs to a lesser degree under pressure than at atmospheric pressure (ref. 15). This means that a hydrocracking process using this catalyst system would produce a sizeable concentration of alkylpolyphenyls. A great deal of evaluation would be needed to prove the usefulness of such a product mixture as reactor coolant.

5. Capsule Irradiation of Hydrocracked RHB and PRHB

Several samples of hydrocracked high boiler have been irradiated in the Materials Testing Reactor. Molecular weights and polymer yields of the samples before and after irradiations were determined. The results are shown in Table 21. Except for sample No. MRC-5, there is little increase in the molecular weight in the samples exposed to irradiation. This is not consistent with the increase in polymer yield experienced upon irradiation.

Samples MRC-1 and -3 were obtained from the hydrocracking of reclaimed high boiler (the high molecular weight fractions removed by the solvent treatment method (ref. 11)). These samples contained 9.5 and 11% alkylpolyphenyls ($R\phi_2$, $R\phi_3$), respectively. Nuclear reactor irradiation of these samples gave relative polymer yields of 0.95 and 0.85. Solutions of these samples (30 wt-%) in Santowax OMP also gave similar polymer yields (0.89, 1.27, 0.94, 0.91 for MRC-2 and -4, respectively). The gas yields for the neat samples are high in all cases (2 to 8 x Santowax OMP value).

Samples MRC-5, -7 and -9 were obtained from hydrocracking 15.0% partially reduced high boiler. These samples contained 25, 20, and 25% alkylpolyphenyls ($R\phi_2$, $R\phi_3$), respectively. The relative polymer yield values for MRC-5 and -7 are 1.40 and 2.37. Santowax OMP solutions (30 wt-%) of these products gave low polymer yield values (0.81, 0.74, 0.84, 0.77, 0.72, 0.72) similar to those obtained with the hydrocracked RHB-Santowax OMP samples. From these limited data, no general conclusions can be drawn, but a few comments can be made.

(a) The results indicate that a limited concentration of alkylpolyphenyls may be tolerated in coolant intended for reactor use (neat samples with 10% $R\phi_2$, $R\phi_3$ gave lower polymer yields than neat samples with 25% $R\phi_2$, $R\phi_3$).

(b) When the hydrocracked samples are diluted in Santowax OMP, samples with the largest concentration of alkylpolyphenyl gave slightly lower polymer yields. The polymer yields in these cases were lower than those obtained with Santowax OMP. The alkylpolyphenyls are either cracking to lower molecular weight species and/or they are inhibiting the terphenyl degradation by formation of allylic free radicals. Thus, a small concentration of the alkylpolyphenyl may increase the coolant life.

Table 21

CAPSULE IRRADIATION OF HYDROCRACKED HIGH BOILER

(Materials Testing Reactor, Temp. 245°C, Dose 4.3×10^9 rads)

Sample No.	Description	Before Irradiation No. Avg. Mol. Wt.	Before Irradiation Polymer Yield wt-%	After Irradiation No. Avg. Mol. Wt.	After Irradiation Polymer Yield Wt-%	Relative Polymer Yield	Relative Gas Yield
MRC-1	HC sample (Run 138)	288	48.7	320	71.1	0.95	2.5
-2	HC sample (Run 138)[b]	-	11.4	-	32.5	0.89	0.38
-2	HC sample (Run 138)	-	11.4	-	40.4	1.27	1.65
-3	HC sample (Run 145)	243	36.9	288	57	0.85	4.6
-4	HC sample (Run 145)[b]	-	7.8	-	27.9	0.94	0.90
-4	HC sample (Run 145)[b]	-	7.8	-	27.9	0.94	0.69
-5	HC sample (Run 172)	263	37.1	343	70	1.40	7.7[a]
-6	HC sample (Run 172)[b]	-	5.7	-	24.9	0.81	0.96
-6	HC sample (Run 172)[b]	-	5.7	-	23.2	0.74	0.79
-7	HC sample (Run 173)	254	37.1	245	93.3	2.37	8.7
-8	HC sample (Run 173)[b]	-	5.5	-	25.3	0.84	lost
-8	HC sample (Run 173)[b]	-	5.5	-	23.8	0.77	4.1
-9	HC sample (Run 175)[b]	-	14.6	-	31.5	0.72	0.85
-9	HC sample (Run 175)[b]	-	14.6	-	31.7	0.72	0.55
-14	Santowax-OMP	230	0	252	23.6	1.00	1.00

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[a] High dose

[b] 30 wt-% in Santowax-OMP

a. Evaluation of Hydrocracked HB and PRHB

Products from the hydrocracking processes have been evaluated to determine their use as reactor coolant. Except for data on irradiation stability, the important properties are listed in the tables of properties of hydrocracked HB and PRHB. The evaluation data on hydrocracked high boiler are shown in Table 22 in summary form since this process is the most economical of the hydrocracking processes. Included in this table are the data on reactor irradiation of the hydrocracked samples.

The molecular weight decrease, viscosity decrease, and thermal stability increase could justify consideration of a hydrocracking process to reclaim coolant. The radiolytic polymer yields are also encouraging. The extent to which a hydrocracked product is resistant to fouling will be important in evaluating the use of a hydrocracking process for reclamation. As with any reclamation process, the final worth of the process will be governed by economic factors. The cost calculations indicate that the solvent treatment process is more economical than hydrocracking, even if 80% product yields are realized from the hydrocracking process. Since the values could be in error by ± 30%, the hydrocracking process becomes questionable even for yields greater than 80%.

Some advantages of the catalytic hydrocracking process are:

a. Lower molecular weight species are produced.

b. A greater yield of reclaimed product is possible.

c. High molecular weight species and inorganic particulate matter greatly reduced in concentration resulting in a marked decrease in the PCFT value.

d. Reduces terphenyl make-up costs by replacement of HB with polyphenyls and alkylpolyphenyls.

Some disadvantages of this process are:

a. Products will require more extensive evaluation because alkylpolyphenyl species are present.

b. The process will require a more extensive pilot plant study than a physical reclamation process.

c. Cost evaluations show that it is not as economical as the physical reclamation processes - solvent treatment or wiped-film distillation.

d. Possible production of saturated hydrocarbons in the hydrocracking process. These might cause extensive coking on heated surfaces.

e. Erosion of catalyst may introduce inorganic species and coke.

Table 22

YIELDS AND PROPERTIES OF HYDROCRACKED CORE II HIGH BOILER

	High Boiler	Hydrocracked HB
Yields, wt-%	-	61-83
No avg mol wt	550	296-403
Viscosity at 265°C, cp	10.7	1.7-3.9
Thermal Decomposition, Temp, °C	360	405-414
C/H Ratio	1.40	1.32-1.29
PCFT Value, mg	-	3.3[a]
Radiolytic Polymer Yield[c] MTR Irradiation at 245°C, 4.3 x 10^9 rads	1.03[a]	0.72-0.95[a,b]
Radiolytic Gas Yield	0.55[a]	0.55-4.1

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[a] 30 wt-% in Santowax OMP

[b] These are hydrocracked reclaimed HB samples - high molecular weight fraction removed before cracking. These values are given to illustrate those expected from hydrocracked high boiler

[c] Relative to Santowax OMP

B. PARTIAL REDUCTION OF POLYPHENYLS

1. Introduction

Partial reduction of high boiler is also a method under consideration as a reclamation process. This method has the advantage over other methods because it is a one-step process, and the product can be obtained in quantitative yield.

In our Third Annual Report (ref. 16), some model studies with m-terphenyl, hydrogenated to the extent of 28-37% using both copper chromite and nickel catalysts, were reported. This work was done to determine the reason for the large viscosity decrease exhibited by high boiler partially hydrogenated in the presence of copper chromite compared to the viscosity of HB partially hydrogenated in the presence of nickel catalyst. From the model study results (composition and viscosity data), it was concluded at that time that the viscosity decrease was due principally to promotion of central ring hydrogenation of the polyphenyl by the copper chromite catalyst. The nickel was reported to promote random reduction.

This work was of interest because, in addition to lowering the viscosity, selective central ring hydrogenation would provide a "built-in" weak link in the polyphenyl molecule, and cracking to lower molecular weight compounds might proceed either external to or in the nuclear reactor.

To determine if the terphenyl isomers show similar reduction paths when treated under similar conditions and to relate this work with partially reduced high boiler, o-terphenyl and p-terphenyl were studied in addition to m-terphenyl. The results of this work are given below.

2. Partial Catalytic Hydrogenation of the Terphenyl Isomers to Determine the Reaction Paths

Table 23 summarizes the partial hydrogenation experiments carried out on the three terphenyl isomers using Girdler G-49 nickel, Harshaw 0500-P nickel, and G-13 copper chromite catalysts. The data on m-terphenyl were previously reported (ref. 16) as were the data using the Harshaw catalyst (ref. 17), but are included here for overall comparison. The per cent reduction achieved in each case was calculated from the carbon-hydrogen analytical data. Vapor phase chromatography was then employed to determine the weight per cent of each component in a given reduced sample. The components were then identified by trapping them in capillaries as they were eluted from the chromatographic column and analyzing by infrared and ultraviolet spectrophotometry. Comparison of the ultraviolet and infrared spectra of the eluted component with that of three standards, 1,3-diphenylcyclohexane, 1,4-dicyclohexylbenzene, and 1-methyl-4-(4-xenyl)cyclohexane, was also made to identify components. In some cases, carbon-hydrogen elemental analyses of the eluted components were performed to help in the identification.

Table 23

PARTIAL HYDROGENATION OF o-, m-, AND p-TERPHENYL WITH GIRDLER G-13 COPPER CHROMITE, G-49 NICKEL AND HARSHAW 0500P NICKEL CATALYSTS

Compound	o-Terphenyl		m-Terphenyl								p-Terphenyl				
Catalyst	G-13	G-49	G-13			G-49		0500P			G-13		G-49	0500P	
Sample No.	30425	30416	6203-1, 2	25699	1377A	6204	30403	6207	6208	4745-1	4727	30428	30417	6206	6205
Reduction Conditions															
Temp, °C, max.	280	195	263	260	275	270	225	250	260	270	295	290	275	260	255
Pressure, psig, max.	2500	2000	1500	2500	2200	1350	1200	1450	1380	1400	2000	2500	2500	1380	1300
Time, Hrs.	10	0.2	1.75	2.2	2.75	0.03	0.2	0.3	0.05	0.3	5	11	0.2	0.7	0.5
Product Analysis															
% C	90.6	90.7	92.2	91.9	90.3	-	91.3	90.5	91.8	91.5	-	90.7	89.9	92.6	91.6
% H	9.1	9.2	7.5	8.0	9.6	-	8.6	6.9	7.8	8.6	-	9.1	10.2	7.3	8.4
% Hydrogenation															
Cal'd. from C/H	44.1	45.7	20.6	28	51.5	-	37	11.8	25.0	36.8	-	44.4	60.4	17.7	33.1
Cal'd. from VPC*	38.2	43.8	18.3	26	47.7	33.3	39	15	23.3	40.5	33.3	44.4	64.3	12.3	21.9

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* Vapor phase chromatographic analysis

5.5

As an additional check on the per cent reduction calculated using carbon-hydrogen data, the per cent reduction was computed on the basis of the weight distribution of the components in the sample. The per cent reduction obtained in this way usually agreed with the carbon-hydrogen value within experimental error. Tables 24, 25 and 26 summarize the vapor phase chromatographic data. Figures 22 through 36 (Appendix I) show the vapor phase chromatograms of each reduced isomer with legends indicating operating conditions and structures assigned to each peak.

a. Results using Copper Chromite Catalyst

From the data in Tables 24, 25 and 26, it seems apparent that the degree of central ring selective reduction effected with copper chromite catalyst is in the order ortho>meta>para. In the case of the o-terphenyl reduced to a level of 44% with G-13 copper chromite, 68.5% of 1,2-diphenylcyclohexane (middle ring reduced product) appears in the product with 2.4% 1-phenyl-2-cyclohexylbenzene (outer ring reduced product), the only other possible product with a single ring reduced.

In the case of m-terphenyl, the ratio of inner ring to outer ring reduced product is about 3:2 at 20% reduction, 2:1 at 28% reduction, and less than 2:1 at 51% reduction. This isomer therefore shows a decreased tendency toward central ring attack with copper chromite when compared with o-terphenyl. Reduction of the p-terphenyl isomer to a level of 33.3% gives a statistical product distribution and therefore the reduction path is random.

With o-terphenyl, only one reduced sample is available for study. However, this sample happens to be nearly 50% reduced and even at this relatively high level, the preponderance of the center ring reduced isomer is striking.

Three reduced m-terphenyl samples are available for comparison. In Sample No. 6203-1,2 (reduced to a level of 17.7%), 33.8% of 1,3-diphenylcyclohexane (middle ring reduced) occurs together with 21.3% of 1-phenyl-3-cyclohexylbenzene (outer ring reduced). For Sample 25699 (28% reduced) these components are present in percentages of 53.4% and 24.3%, respectively, while in Sample 1377A (51.5% reduced), the percentages are 56.6% and 0%, respectively. Therefore, as reduction of m-terphenyl proceeds in the presence of this catalyst, the ratio of middle ring reduced isomer to end ring reduced isomer increases, becoming greater than 2:1.

In addition, in Samples 6203-1,2 and 25699, no isomer with both end rings reduced appears and only the middle ring reduced and single end ring reduced isomers are present together with unreacted m-terphenyl. This is strong evidence that the reduction of m-terphenyl in the presence of copper chromite at low levels proceeds selectively toward the center ring.

It is also interesting to note that in Sample 1377A, the most highly reduced of the three samples, 1,3-dicyclohexylbenzene (both <u>end</u> ring

Table 24

COMPOSITION OF PARTIALLY HYDROGENATED o-TERPHENYL

Sample No.	30425	30416
Catalyst	Copper Chromite (G-13)	Nickel (G-49)
% Hydrogenation	44.1	45.7
<u>Components, Area-%</u>		
o-Tercyclohexyl	0.4	14.4
1,2-Dicyclohexylbenzene	2.5	2.7
1-Cyclohexyl-2-phenylcyclohexane	18.9	15.6
1-Phenyl-2-cyclohexylbenzene	2.4	10.8
Unassigned	4.4	5.5
1,2-Diphenylcyclohexane	68.5	40.8
o-Terphenyl	2.8	10.2

Table 25

COMPOSITION OF PARTIALLY HYDROGENATED m-TERPHENYL

Catalyst	G-13			G-49		0500P		
Sample No.	6203-1,2	25699	1377A	6204	30403	6207	6208	4745-1
% Hydrogenation	20.6	28	51.5	-	37	11.8	25.0	36.8
<u>Component, area-%</u>								
m-Tercyclohexyl	-	-	-	13.8	17.0	0.7	1.6	17.0
1,3-Dicyclohexylbenzene	-	-	35.0	4.4	7.0	2.8	5.6	
1-Phenyl-3-cyclohexylbenzene	21.3	24.3	-	29.8	30.2	20.9	29.2	46.8
1,3-Diphenylcyclohexane	33.8	53.4	56.6	8.3	22.0	6.8	8.0	30.4
1-Phenyl-3-cyclohexylcyclohexane	-	-	8.3	5.9	-	4.7	8.4	-
m-Terphenyl	43.0	21.2	-	37.5	21.4	63.0	45.6	13.1

reduced) appears and comprises 35% of the sample. The concentration of the central ring reduced product is virtually unchanged from its value in Sample 25699, indicating little attack on this compound. At the same time, the single end ring reduced isomer is absent, having been reduced to the dicyclohexylbenzene isomer. Therefore, it appears that under these reduction conditions, the catalyst selectively adsorbs m-terphenyl while it is present and reduces the central ring. Then, as the concentration of terphenyl nears zero, adsorption of the single end ring reduced isomer (cyclohexylbiphenyl) is preferred (over the benzene derivatives) and attack on this isomer is limited to end ring reduction.

Preferential adsorption of the polynuclear aromatic species in the m-terphenyl work appears to follow the order m-terphenyl > 1-phenyl-3-cyclohexylbenzene > 1,3-diphenylcyclohexane.

Figure 10 depicts the change in concentration of meta-terphenyl and two of the partially reduced compounds with change in per cent hydrogenation. The initial reduction of terphenyl and the biphenyl derivative is illustrated.

Para-terphenyl, reduced to the same level as the ortho compound (44.4%), shows only 4.8% 1,4-diphenylcyclohexane and 59.0% 1-phenyl-4-cyclohexylbenzene (outer ring reduced), but 25% of 1-phenyl-4-cyclohexylcyclohexane (outer and inner ring reduced). With the p-isomer, two possible conclusions may be drawn. If it is assumed that all the 1-phenyl-4-cyclohexylcyclohexane (outer and inner ring reduced product, 25.2%) arises from 1,4-diphenylcyclohexane (middle ring reduced product, 4.8%), then the ratio of the products with the outer ring reduced to those of inner ring reduced is about 2:1. This ratio would indicate that the reduction goes in a statistical manner with no outer or inner selectivity. On the other hand, it may also be possible that 1-phenyl-4-cyclohexylcyclohexane (outer and inner ring reduced product) arises from hydrogenation of 1-phenyl-4-cyclohexylbenzene (outer ring reduced, 59%). In this event, very little of the central ring reduction product (1,4-diphenylcyclohexane) is ever present and the reduction proceeds with selectivity toward the outer ring.

In sample 4724 (33.3% reduced), with no necessity for making similar assumptions, the reduction appears to go in a random fashion.

The conclusions to be drawn from the data, therefore, are that the reduction of p-terphenyl with copper chromite proceeds either by a random or outer ring path but not by selective attack on the central ring.

Similar to the m-terphenyl isomer, as the reduction level increases, the p-terphenyl concentration decreases, single and two-ring reduced product concentration decreases, but no p-tercyclohexyl appears in the product mixture. This indicates that the terphenyl molecule is more readily hydrogenated than the biphenyl or benzene intermediates.

Table 26

COMPOSITION OF PARTIALLY HYDROGENATED p-TERPHENYL

Catalyst	G-13		G-49	0500P	
Sample No.	4724	30428	30417	6206	6205
% Hydrogenation	33.3	44.4	60.4	17.7	33.1
Components, area-%					
p-Tercyclohexyl	-	-	22.8	-	-
1,4-Dicyclohexylbenzene	-	9.6	47.5	-	-
1-Phenyl-4-cyclohexyl-cyclohexane	11	25.2	-	-	-
1,4-Diphenylcyclohexane	24	4.8	3.3	-	-
1-Phenyl-4-cyclohexyl-benzene	54	59.0	26.4	36.8	65.8
p-Terphenyl	10	-	-	63.2	21.0

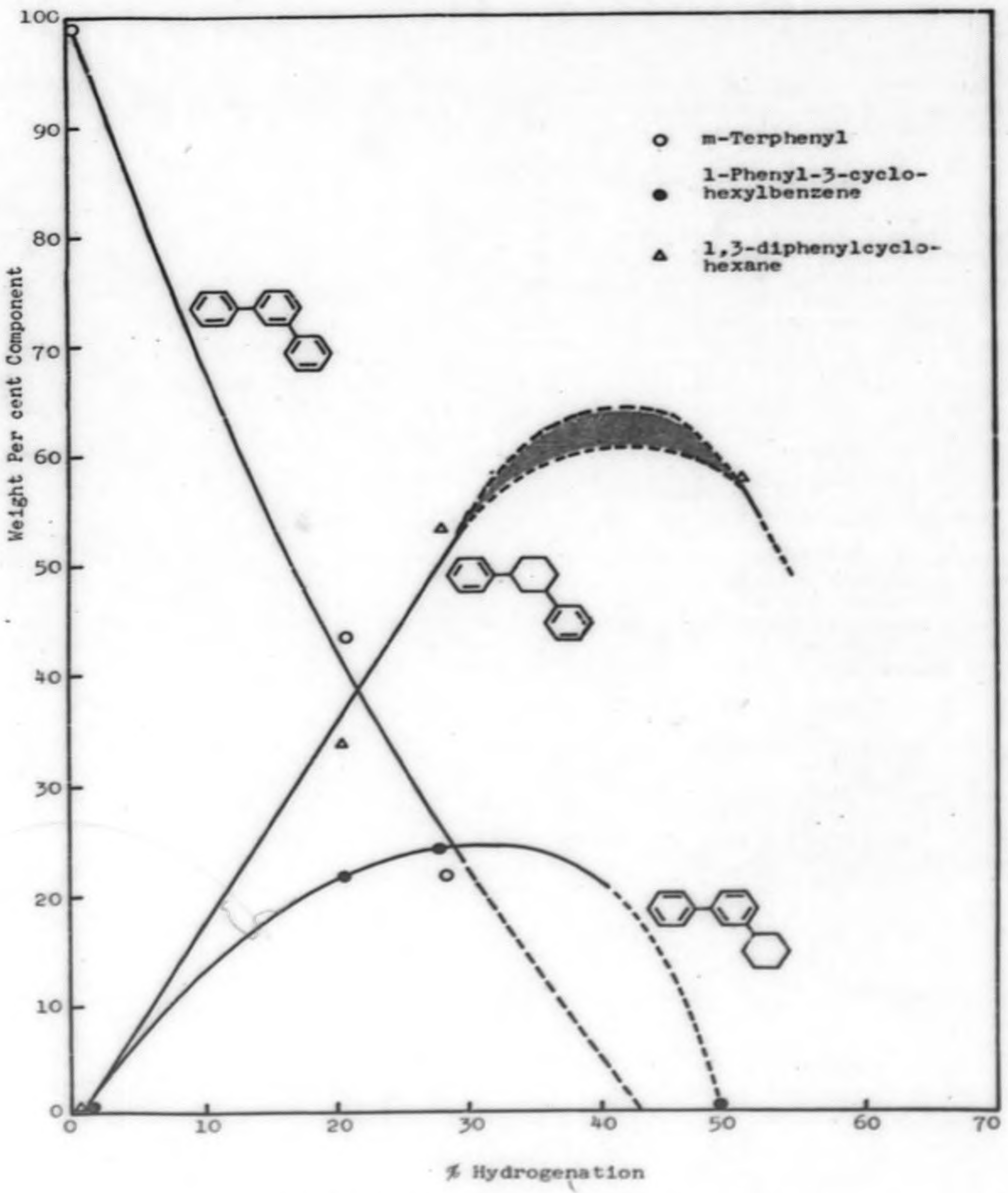

Figure 10. Wt % Component vs % Hydrogenation

From the data, it is difficult to determine whether the biphenyl intermediates are reduced in preference to the benzene derivatives as in the case of m-terphenyl.

b. Results using Nickel Catalyst

Reduction of the terphenyl isomers with nickel catalyst gave products that showed marked differences in composition compared to the copper chromite work. Only in the o-terphenyl reduction with nickel does the central ring reduced component predominate. This compound, 1,2-diphenylcyclohexane, comprises 40.8% of this reduced sample with other partially reduced components varying from 3 to 16 weight per cent. The nickel catalyst with m-terphenyl gives a preponderance of the outer ring reduced isomers for reduction levels of 11 and 25%, but as the m-terphenyl concentration approaches zero and the reduction level increases, the product composition becomes statistical. Product distribution obtained when p-terphenyl is reduced in the presence of Girdler nickel to a 60% level is preponderantly in favor of outer ring reduction. In fact, 74% of the sample is accounted for by two compounds, 1,4-dicyclohexylbenzene (2 outer rings reduced) and 1-phenyl-4-cyclohexylbenzene (outer ring reduced).

With Harshaw nickel catalyst, Sample No. 6205 and 6206, the results are even more dramatic. At 33% reduction, 65.8% of the sample has been converted to 1-phenyl-4-cyclohexylbenzene (outer ring reduced) with only minor quantities (1-3%) of each of the other reduced components present. Therefore, the order of selectivity for outer ring attack is para>meta>ortho for nickel catalyst.

c. Summary

Table 27 sums up the results of these studies in terms of the relative tendencies of each isomer to undergo outer, central or random ring reduction with nickel and copper chromite catalysts, under the conditions described. The copper chromite results are similar to those reported (ref. 18) using platinum oxide catalyst at room temperature and 74 psig.

Table 27

HYDROGENATION PATH OF o-, m-, AND p-TERPHENYL FOR ONE-RING SATURATION

	Catalyst	
Isomer	Copper Chromite	Nickel
Ortho-terphenyl	Center ring	Center ring
Meta-terphenyl	Center ring	Outer ring
Para-terphenyl	Random or outer ring	Outer ring

The reaction path for the initial saturation of one-ring of each isomer may be explained by a consideration of steric and electronic factors. The exceptionally strong tendency for the center ring of o-terphenyl to be reduced first may be explained by the restriction of rotational freedom at the carbon-carbon bonds between phenyl groups. This may cause the center ring to be selectively adsorbed on the catalyst. In the case of the meta isomer, the rotational restriction decreases so that the selective reduction of the center ring is less pronounced than with o-terphenyl. The rings of the p-terphenyl isomer have essentially complete rotational freedom and selectivity for center ring attack disappears. In addition, a stronger contribution of polar excited states (resonance) is expected with p-terphenyl than with o- or m-terphenyl. The p-isomer can more readily achieve 3-ring resonance, leaving charge centers on the terminal rings. The m-isomer can only achieve 2-ring resonance leaving charge centers on the center ring and outer ring. The o-isomer could achieve 3-ring resonance but the steric requirements for this may not be satisfied and therefore 2-ring resonance would be most probable. Ultraviolet absorption studies of polyphenyl isomers by G. Forrest Woods (ref. 19) show that o-isomers exhibit an absorption shift which is attributed to a hindered biphenyl absorption. No absorption due to 3-ring resonance was found. In all cases, however, there will be a certain amount amount of attack on adjacent rings which are not favored. The result with nickel can be explained in the same way, except that the reaction rates will be increased considerably. There is a definite stepwise attack on a single ring probably followed by desorption and readsorption.

d. Relationship of Viscosity to the Composition of Partially Hydrogenated Terphenyl Isomers

The product distributions obtained in these partially reduced terphenyl isomers bring about interesting changes in the viscosities. It was noted previously (ref. 16) that the viscosity of m-terphenyl partially reduced in the presence of copper chromite was considerably lower over a wide temperature range than the viscosity of the nickel reduced product (see Figure 11). The same phenomenon is observed with the o-terphenyl reduction products as shown in Figure 12. In both the ortho- and meta- cases with copper chromite catalyst, the compound predominating is the diphenylcyclohexane derivative (central ring reduced product). With nickel catalyst, the concentration of this compound in the hydrogenated ortho- and meta- samples is decreased by 28 and 32 per cent, respectively. Correspondingly, there are increases in the concentration of totally reduced terphenyl (3 rings reduced) from 0.4 to 14.4% in the ortho isomer and 0 to 17.0% in the meta isomer.

The totally hydrogenated isomers have viscosities greater than those of the partially hydrogenated isomers. Therefore, the presence of tercyclohexyls tends to increase the viscosities of the reduced samples.

Figure 13 gives the viscosity-temperature relationship for the p-terphenyl hydrogenated mixture. The viscosity of the p-terphenyl

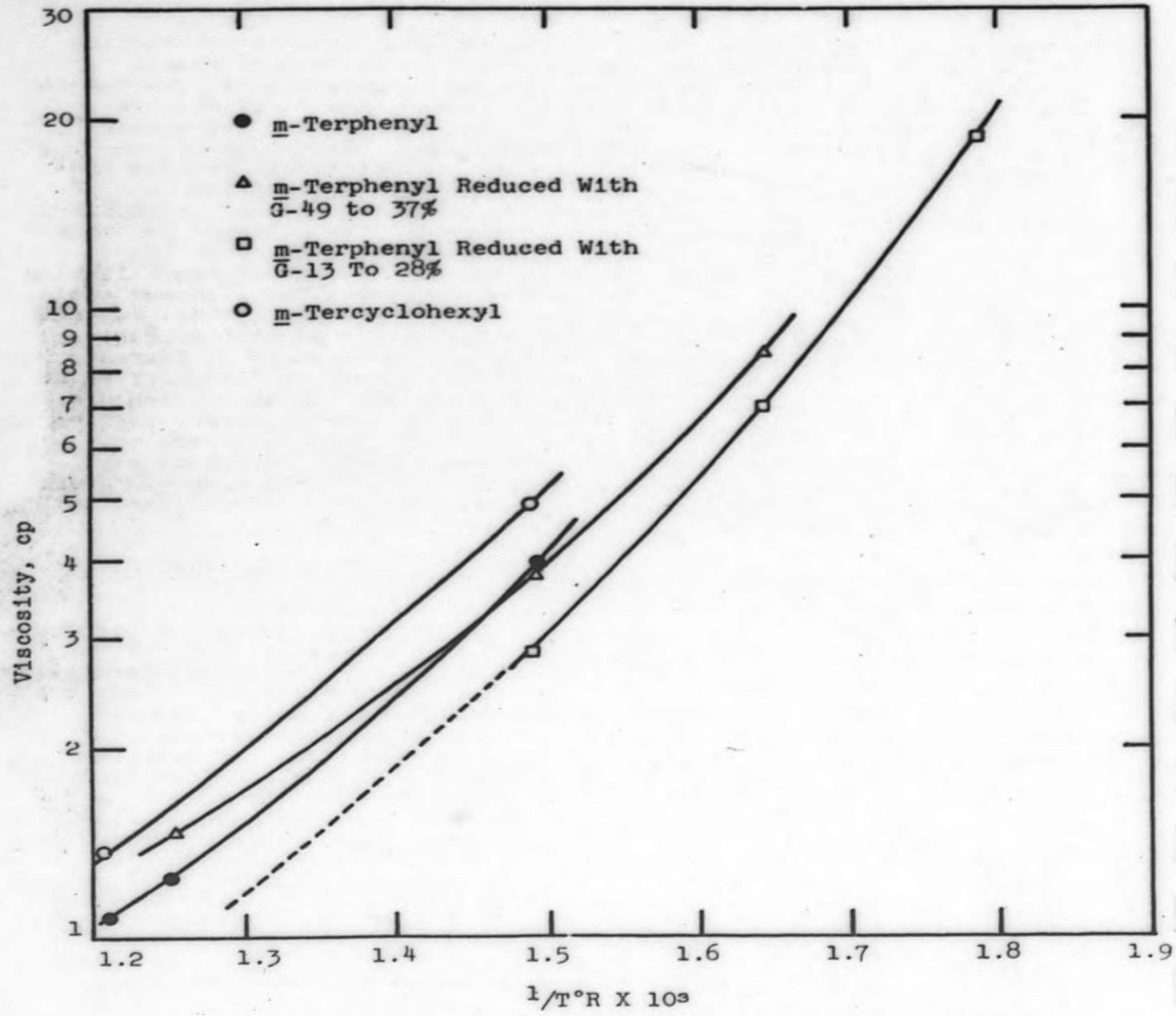

Figure 11. Logarithm Viscosity Versus $^1/T°R$ For m-Terphenyl And Various Reduction Products

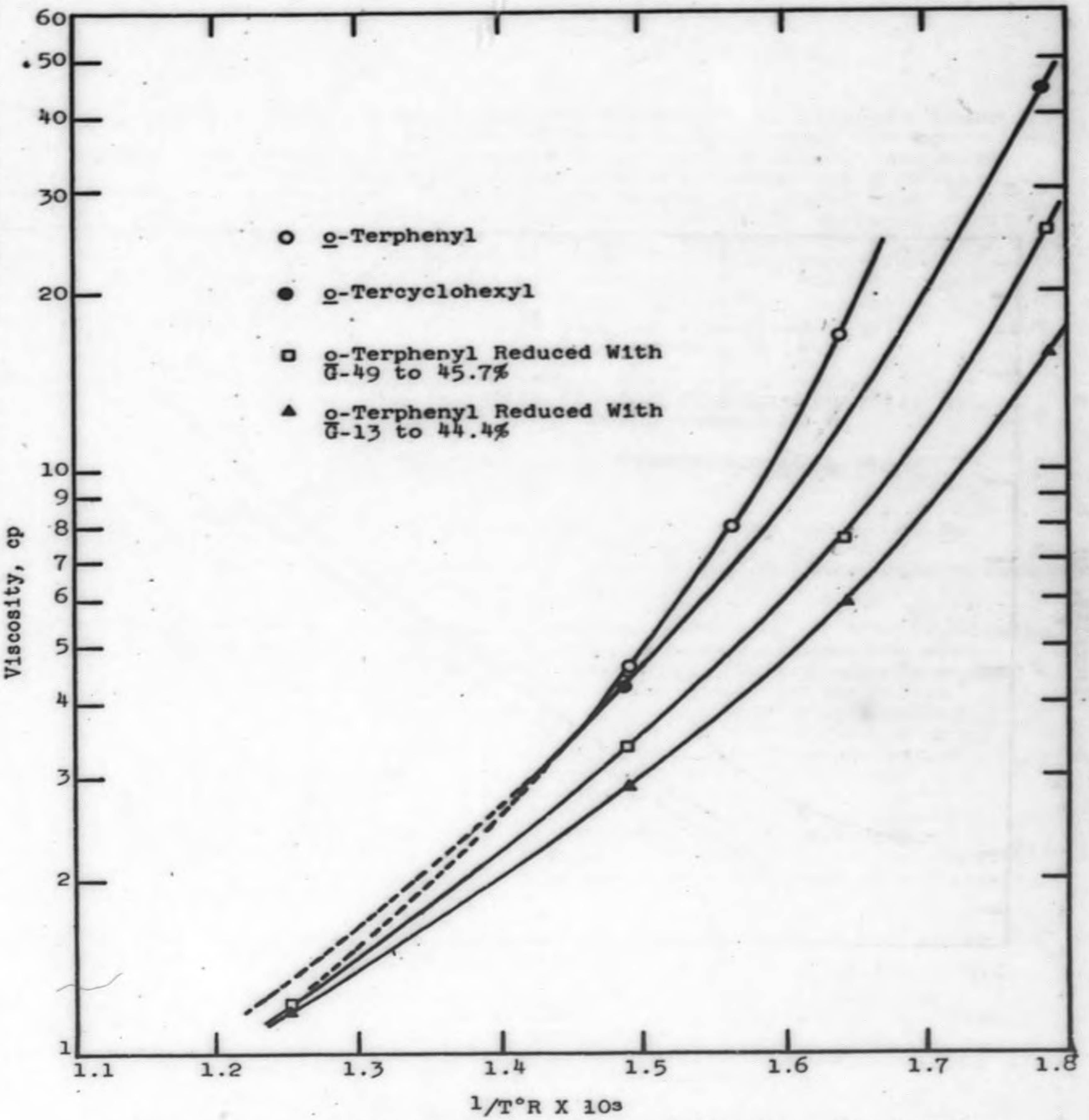

Figure 12. Logarithm Viscosity Versus 1/T°R For o-Terphenyl And Various Reduction Products

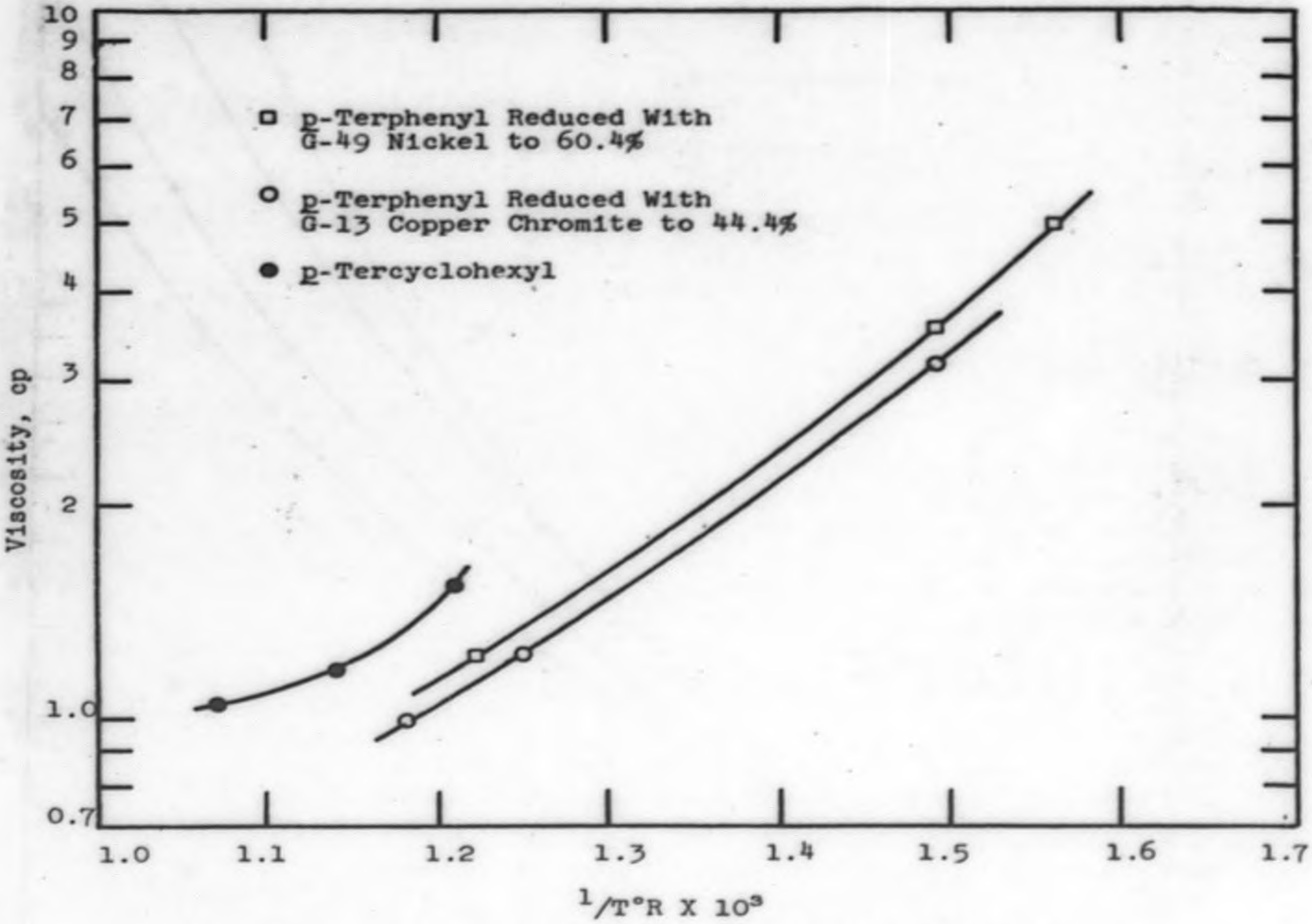

Figure 13. Logarithm Viscosity Versus $^1/T°R$ For p-Terphenyl And Various Reduction Products

product arising from the copper chromite reduction is slightly lower than that for the nickel reduction. The small difference can be explained on the basis of the composition of each mixture. Assuming that the viscosity of 1-phenyl-4-cyclohexylcyclohexane and p-tercyclohexyl are nearly equivalent, then a large excess of single ring reduced product from copper is expected to lead to a viscosity decrease similar to that experienced with o- and m-terphenyl. However, the large concentration of 1,4-dicyclohexylbenzene (47%, two outer rings reduced) in the nickel mixture probably has the same effect of one-ring reduced product, and the viscosities of the copper and nickel products tend to approach each other.

The resultant viscosity of a given mixture will therefore depend on the relative amounts of components with a single (not necessarily central) ring reduced to components with two or three adjoining rings reduced.

e. Electron and MTR Irradiation of Partially Reduced High Boiler

Several partially reduced samples of high boiler were subjected to electron irradiation at 400°C using the Van de Graaff electron accelerator at our Dayton Laboratories. Raw data for the electron irradiations were given in our Third Annual Report (ref. 20).

To determine whether or not radiation-induced cracking of the irradiated partially reduced HB samples occurred, some irradiated samples were subjected to gas phase chromatographic analysis. This analysis showed that radiation-induced cracking of the reduced rings to materials boiling in the terphenyl range occurred with the PRHB neat samples reduced to levels of 11 to 65%. No difference in the number of components was noted on the chromatograms of irradiated samples which were reduced by copper chromite or nickel catalysts (14184 and 14185, respectively) to about the same level.

The chromatograms of the irradiated PRHB-Santowax OMP samples (30 wt-% PRHB in OMP), however, did not show an increase in the number of components after exposure to irradiation. The PRHB may be acting as an inhibitor in this system.

Relative radiolytic polymer and gas yields were calculated for these samples. The results are given in Table 28.

The relative polymer yields of the PRHB solutions in Santowax OMP vary between 0.17 to 0.57. A trend seems to be exhibited by the PRHB samples: the relative polymer yield decreases as the per cent hydrogenation increases. The gas yields were increased 4 to 16-fold over m-terphenyl.

Table 28

ELECTRON IRRADIATION OF PARTIALLY REDUCED HIGH BOILER
(400°C, 2 Mev electrons, 20 watt-hr/g)

Sample No.	% Hydrogenation	Before Irradiation		After Irradiation		Relative Gas Yield	Relative Polymer Yield
		Molec. wt.	Polymer Yield	Molec. wt	Polymer Yield		
m-Terphenyl	0	230	0	506	16.9) 17.2) 21.1)	1.00	1.00
Core I HB[a]	0	550	34.7	350	38.6	2.6	0.19
14184[a]	11	386,496	91	-	90.5	8.2	0
14184A[b]	-	-	25.3	-	31.9	8.6	0.39
30168D[a,c]	-	520	29.1	-	36.2	3.2	0.34
14188[c]	12	~ 500	87	502	90.5	28	0.20
14188A	-	-	25.2	-	30.2	7.7	0.30
14185[c]	19	489	87	487	90.6	15	0.21
14185A	-	-	20.6	-	30	2.8	0.57
14181[c]	29	-	87	458	86.3	12	0
14181A	-	-	19.7	-	23.6	15.5[d]	0.23
14182[c]	55	418	86	414	69.3	16.5	<0
14182A	-	-	18.9	-	21.9	4.2	0.17
14178[c]	65	-	86	-	75	22.5	<0
14178A	-	-	21.8	-	21.8	14.7	0
30168D[a,e]	15.8	550	32.4	-	56.7	4.1	1.05

---

[a] Reduced in the presence of copper chromite catalyst.

[c] Reduced in the presence of nickel catalyst

[b] Suffix "A" indicates 30 wt % soln. of previous sample in Santowax-OMP

[d] Leak developed during irradiation giving high gas value

[e] Core II HB reduced to level of 15.8%, irradiated to dose of 4.4×10^8 rads in the Materials Testing Reactor. 30 wt % in Santowax-OMP.

In addition to the vapor phase chromatograms, these data indicate that radiation-induced cracking has occurred to a significant extent in the highly reduced samples (55 and 65% PRHB). No increase in polymer was obtained when these neat samples were exposed to irradiation. In fact, in these two samples, a decrease in polymer yield resulted in contrast to HB and the PRHB samples containing less hydrogen. All samples appear to have undergone radiation-induced cracking including the Core I HB sample.

In addition, the low radiolytic relative polymer yield of the PRHB-Santowax OMP systems indicate that PRHB behaves as an inhibitor in the PRHB-Santowax OMP system. This inhibitor effect may have resulted from hydrogenated rings of the polyphenyl system which act as hydrogen donors suppressing terphenyl dimerization and polymerization. The partially reduced polyphenyl molecule may itself be stabilized by formation of benzylic-type free radicals.

f. Thermal Stability of Partially Reduced High Boiler

Samples of partially reduced high boiler were evaluated for thermal stability in the high temperature isoteniscope.

Table 29 lists a few thermal stability determinations.

Table 29

THERMAL STABILITY OF PARTIALLY REDUCED HIGH BOILER

Sample No.	Per Cent Reduction	Catalyst	Thermal Decomp. Temp., °C*
Core II HB	0	-	375
25231A-1	8.9	copper chromite	330
28040C	11.6	copper chromite	371
30184A( )	15.8	copper chromite	330-370
30168D	51.5	nickel	366

---

* Temperature at which decomposition rate is 1 mole per cent/hour

From the data in Table 29 it appears that the thermal decomposition temperatures of partially reduced samples are slightly lower than that of starting high boiler. However, these differences are probably not significantly greater than the precision of the method used. Therefore, partial hydrogenation does not materially change the thermal stability of high boiler as measured in the isoteniscope.

3. Experimental: Terphenyl Reductions

All reductions were performed in a 300 ml Aminco rocking autoclave. In a typical experiment, 25 grams of the terphenyl (Eastman reagent) was charged to the autoclave together with 2.5 grams of catalyst. No solvent was employed in any of the reductions. The bomb was then closed, flushed thoroughly with nitrogen, followed by hydrogen and then pressurized to a few hundred pounds below the desired reduction pressure. The bomb was then heated without shaking to the desired reaction temperature. Shaking was then started and the degree of reduction followed by the pressure drop in the system. When the calculated pressure drop had been achieved, the shaker and heaters were turned off and the bomb was allowed to cool to room temperature before opening. When the bomb was opened, the contents were melted on a steam plate (if solid) and rinsed out with benzene. The benzene solution was filtered to remove catalyst and then the benzene was removed in a rotary evaporator. Subsequent analyses of the product were then performed.

IV. PRODUCT EVALUATION

A. POLYMER YIELD DETERMINATION

The microdistillation tube for use in determining polymer yield of irradiated and unirradiated reclaimed coolant samples is shown in Figure 14. The empty distilling tube is weighed accurately on an analytical balance and then is loaded with about one gram of sample and reweighed. The receiver is also accurately weighed. The tube, cap, and receiver are then assembled, connected to a vacuum manifold and evacuated to 0.1 mm Hg at room temperature. The distilling tube is then lowered gradually into one of the wells in a specially machined heated aluminum block which is maintained at 200°C. The tube is finally immersed in the well to a depth of 9" (up to the take-off side arm). Dow-Corning silicone fluid is used as heat transfer medium around the tube. Distillation of the sample is then carried out for two hours at 200°C and 0.05-0.1 mm Hg. The block is designed to accommodate four samples at a time. At the end of a run, the system is brought to atmospheric pressure, and the tube wiped clean of silicon oil (acetone wash first) and silicon vacuum grease. The distilling tube and receiver are then reweighed separately to obtain polymer and distillate weights. The following (Table 30) gives typical data showing material balance obtained and reproducibility of runs.

B. PYROLYTIC CAPSULE FOULING DATA

Although some PCFT data are given elsewhere in this report (particularly in the solvent distribution section), Table 31 lists all PCFT values obtained in this laboratory on Core I, II, and IIIA high boiler and spent coolant samples, as well as data obtained on those samples which have been reclaimed by hydrocracking, partial reduction, solvent distribution, and wiped film distillation. Some of these data have been previously reported, but it is felt that a summation in a single report would be helpful.

Table 30

POLYMER YIELD DATA ON TYPICAL COOLANT SAMPLES

Sample No.	Sample Size	% Distillate	% Polymer (Polymer Yield)	% Loss
MRC-2-174	1.1996	69.0	30.9	0.05
"	1.2095	66.7	33.9	0.65
MRC-9-184	1.0264	67.3	33.2	0.5
"	0.9926	68.8	31.1	0.1
MRC-6-177	1.0409	76.7	23.2	0.1
"	0.9166	86.6	23.2	0.15
MRC-12-181	0.5667	67.0	31.2	1.8
"	0.9502	65.7	34.05	0.25
MRC-9-185	0.7960	69.0	30.1	0.9
"	1.1459	65.8	33.4	0.8
MRC-8-183	0.8631	76.2	23.5	0.3
"	0.8100	75.6	24.1	0.3

Table 51

PYROLYTIC CAPSULE FOULING DATA ON OMRE SPENT COOLANTS, HIGH BOILERS, BEFORE AND AFTER RECLAMATION

Sample No.	Sample	Conc. in Santowax, wt %	PCPT Value, mg Film
-	Santowax-OMP	-	2.9, 2.5, 3.0
-	Core I Spent Coolant (SC)	Neat	64.5 (ave. of 4)
25679	Core I Reclaimed Spent Coolant (RSC)	Neat	0.9, 1.4
-	Core II SC	Neat	52.3
34459A	Core II RSC	Neat	0.5
30449	Core II RSC	Neat	8.2, 7.0
30433C	RSC (From 5% Core II HB in OMP)	Neat	9.6
30421D	RSC (From 5% " " " ")	Neat	14
30421	RSC (From 10% " " " ")	Neat	4
30423B	RSC (From 20% " " " ")	Neat	1
30422D	RSC (From 30% " " " ")	Neat	4
30420B	RSC (From 30% " " " ")	Neat	6
30422B	RSC (From 40% " " " ")	Neat	4
30420	RSC (From 40% " " " ")	Neat	1
30419	RSC (From 50% " " " ")	Neat	5
30433E	RSC (From 50% " " " ")	Neat	10.3
30424	High Mol. Wt. Fraction (HMWF) from Core II SC	12.5	16
30424	HMWF from Core II SC	25	31.3
33439A	Core II RSC from Run No. 1 - Centrifuge	Neat	5.9
33440A	Core II RSC from Run No. 2 - Centrifuge	Neat	19.6
-	Core II HB	5	21.1
-	Core II HB	25	36.1, 20.1
-	Core II HB	30	50.4, 35.6
-	Core II HB	50	61
	Core II HB	95	145
33418[a]	Filtered Core II HB	Neat	6.1, 11.9
33418[a]	Filtered Core II HB	25	10.5, 7.1
32159-2[b]	Distilled HB (DHB)- Cut No. 2-Distillate	37.5	4.0
32159-2R[b]	DHB- Cut No. 2 - Residue	37.5	38.5
32159-5[b]	DHB- Cut No. 5 - Distillate	25	6.2
32159-5R[b]	DHB- Cut No. 5 - Residue	37.5	47.5
34458A	Core II Reclaimed High Boiler (RHB)	Neat	4.5
33450A	Core II RHB	Neat	1.1, 6.5
-	Core II RHB	Neat	8.0
33450B	Core II HMWF	25	79.6
33450B	Core II HMWF	50	142.5
33450C	Core II HMWF plus Celite	50	252.1
25949A-1[c]	Hydrocracked RHB (HCRHB) (Runs Nos. 136 and 139)	22	3.3
25919A-1[c]	HCRHB (Run No. 111)	22	2.9
25922A-1[c]	HCRHB (Run No. 114)	15	3.9
28040C[d]	Partially reduced Core II HB (PRHB)	Neat	5.1
28040C[d]	PRHB	25	4.3
30168D[e]	PRHB	25	4.0
28134A-1[e]	Hydrocracked PRHB (HCPRHB)	5.2	5.6
31709A-1[e]	HCPRHB (Run No. 179)	7.4	6.6
31613A-1[e]	HCPRHB (Run No. 182)	11	5.4
31725A-1[e]	HCPRHB (Run No. 187)	12.5	5.7
28134A-1[e]	HCPRHB (Run No. 165)	20	8.6
28134A-1[e]	HCPRHB (Run No. 169)	20	4.0
31723A-1[e]	HCPRHB (Run No. 183)	25	5.5
31739A-1[f]	HCPRHB (Run No. 194)	15	2.1
-	Core III A HB	Neat	8.7, 13.6
34462	Core III A RHB	Neat	1.8

Legend

a - Benzene solution of HB filtered through Celite. Benzene then removed by distillation.

b - Distillate or residue from wiped film distillation.

c - High boiler first reclaimed by solvent distribution followed by hydrocracking.

d - PRHB is Core II HB reduced to extent of 8.9% with copper chromite catalyst; Celite filter aid used in recovery process.

e - HB reduced to extent of 15.8% with copper chromite; Celite filter aid used in recovery process.

f - HB reduced to extent of 51.5% with nickel catalyst at 233°C, 2850-3800 PSIG; Celite filter aid used in recovery process

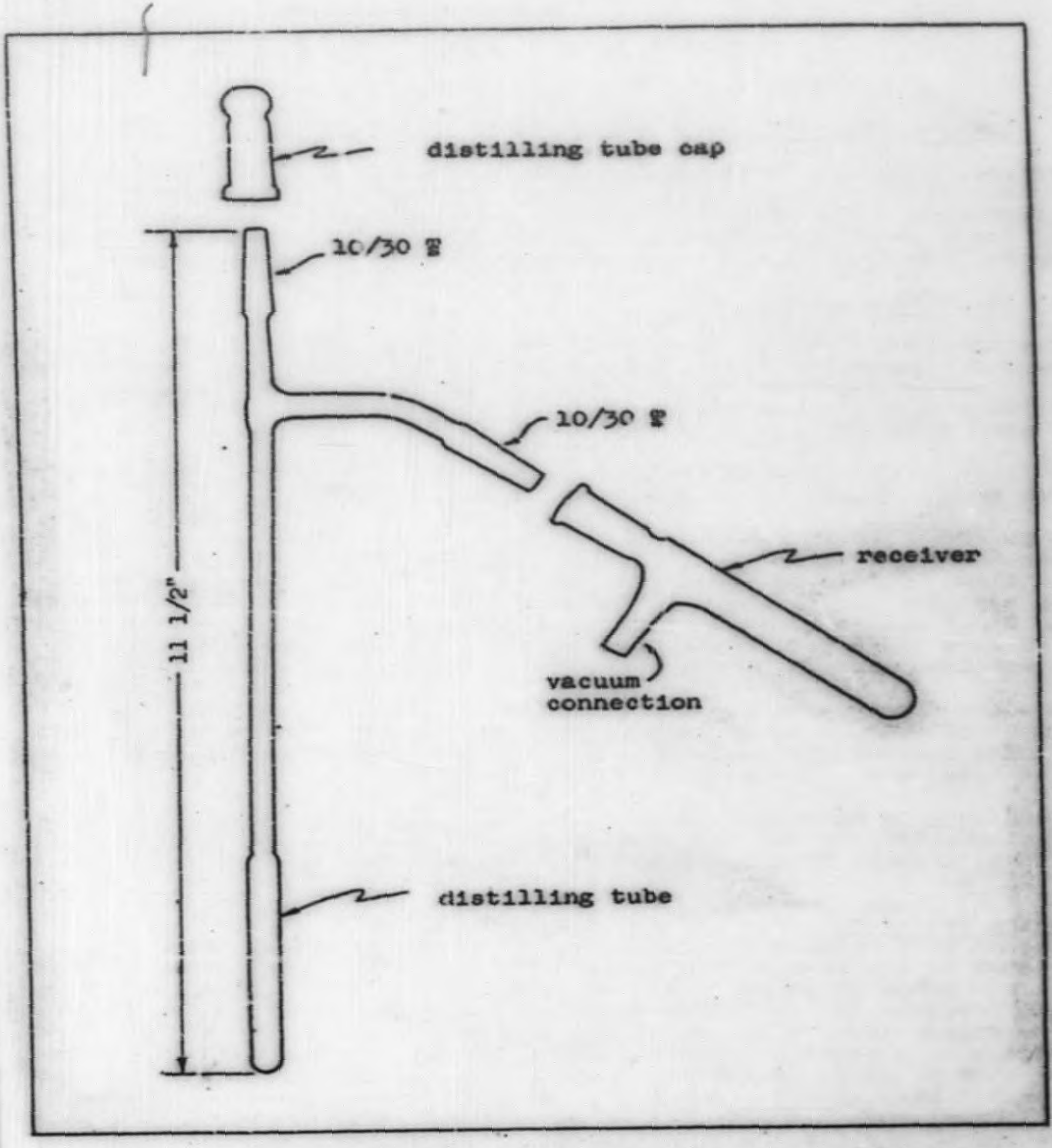

Figure 14. Microdistillation apparatus for polymer (residue) determination.

C. CAPSULE IRRADIATION OF RECLAIMED COOLANT SAMPLES

Several reclaimed coolant samples were irradiated in the Materials Testing Reactor under the supervision of the California Research Corporation. The relative radiolytic polymer yields were determined and these results are discussed in the appropriate sections of this report. The raw data for the irradiations are given in Table 32.

D. ASH DETERMINATION

In connection with the Standards and Advisory Committee of the Organic Reactor Program, an ashing method (micro) was developed* to determine parts per million ash in coolant, and reclaimed coolant samples. Standard runs with Santowax and added metal oxides, as well as Core II HB with added metal oxides, are given in Table 33.

Two runs on Santowax OMP using a macro (150 gram sample) technique were made. Values of 10 and 14 ppm were obtained.

In general, the recovery for the 1000°C ignition was in good agreement with the 750°C ignition, indicating no loss of metal during the 1000°C ignition. This also indicated that the 750°C ignition temperature was adequate for complete ignition of the organic material. This is the final ignition temperature that was used in subsequent ash analyses. Runs with added ferrocene showed low recovery because the ferrocene volatilized during the evaporation and ignition process.

Emission spectrographic runs were made on the ash obtained from a number of samples to determine level of individual elements present in CMRE coolant and reclaimed coolants and to compare total ppm metals with total ash. These are given in Table 34.

There is good agreement between the total ash value and total ppm metal obtained by the emission spectra. This indicates that little, if any, organic material remains in the ash and resists oxidation at 750°C.

Ashing Procedure: An empty 8 ml platinum crucible which had been cleaned with potassium pyrosulfate and dried in a desiccator was weighed to the nearest microgram. The crucible was then charged with about 4 grams of sample and reweighed to the nearest microgram. The open crucible was then placed on the platform of the combustion tube (see Figure 15). With the preheater furnace (A. H. Thomas, No. 5676-A) and electric heating tapes on, and a stream of oxygen flowing through the tube at 10-12 liters per minute, the crucible was heated cautiously with a Bunsen burner. After all the liquid sample had evaporated (and oxidized), a Bunsen burner was placed under the combustion tube and the burner flame was increased to full for ten minutes. The crucible was then removed from the combustion tube and carefully flamed over the Bunsen burner to remove last traces of easily oxidized material. The crucible was then laid on its side on a platinum triangle

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*Developed at our Dayton Laboratories under the supervision of Dr. William Scribner.

Table 32

CAPSULE IRRADIATION OF RECLAIMED COOLANT SAMPLES
(Materials Testing Reactor, Hole HB-5, Shuttle tube)

Sample No.	Description	Dose[a] 10^9 rads	Temp °C + 5	Gas Evolution Press. in capsule, psi	Gas Evolution Volume ml/g, STP
MRC-1	HC[d] sample, run 138	4.3	247	133	7.3
-2	HC[d] sample, run 138[b]	4.3	244	33	1.1
-2	HC[d] sample, run 138[b]	4.3	176	91	4.8
-3	HC[d] sample, run 145	4.3	254	228	13.3
-4	HC[d] sample, run 145[b]	4.1	252	56	2.6
-4	HC[d] sample, run 145[b]	7.0	245	48	2.0
-5	HC[d] sample, run 172	4.3	247	371	22.3
-6	HC[d] sample, run 172[c]	4.3	246	60	2.8
-6	HC[d] sample, run 172[c]	4.3	254	52	2.3
-7	HC[d] sample, run 173	4.3	249	403	25.2
-8	HC[d] sample, run 173[b]	4.3	243	gas lost	
-8	HC[d] sample, run 173[b]	4.3	252	207	12.1
-9	HC[d] sample, run 175[b]	4.3	246	56	2.6
-9	HC[d] sample, run 175[b]	4.3	253	41	1.6
-10	15.8% Partially reduced HB[b]	4.4	249	203	11.8
-11	Core II HB[b]	4.3	247	41	1.6
-12	Core II RSC[d]	4.3	249	71	3.5
-12	Core II RSC[d]	4.3	252	66	3.2
-13	RSC (from 5% HB in Santowax-OMP)	4.3	238	50	2.2
-13	RSC (from 5% HB in Santowax-OMP)	4.5	248	139	7.8

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[a] Probable accuracy ± 25%

[b] Samples 30 wt% in Santowax-OMP

[c] 20 wt% in Santowax-OMP

[d] HC = hydrocracked; RSC = reclaimed spent coolant; RHB = reclaimed high boiler

[e] Mixture of samples 25699 (m-ϕ_3 reduced with Copper chromite) and 30403 (m-ϕ_3 reduced with nickel) and numbered 35928

S.S.

Table 32 (cont'd.)

CAPSULE IRRADIATION OF RECLAIMED COOLANT SAMPLES
(Materials Testing Reactor, Hole HB-5, Shuttle tube)

Sample No.	Description	Dose[a] 10^9 rads	Temp °C ± 5	Gas Evolution Press. in capsule, psi	Gas Evolution Volume ml/g, STP
MRC-14	Core II RHB[d]	7.3	246	no gas sample	
-15	Core II RHB[b]	4.4	246	43	1.8
-18	Partially reduced[e] m-ϕ_3	4.3	249	101	54
-18	Partially reduced[e] m-ϕ_3	4.4	246	104	55
-16	Santowax-OMP	4.4	260	62	2.9
-16	Santowax-OMP	4.3	256	62	2.9
CRC-170	Santowax-OMP	4.3	246	41	1.6
-171	Santowax-OMP	4.3	222	Penetrator clog	
-172	Santowax-OMP	5.3	←	not irradiated	→
-173	Santowax-OMP	4.3	249	Penetrator clog	

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[a] Probable accuracy ± 25%

[b] Samples 30 wt% in Santowax-OMP

[c] 20 wt% in Santowax-OMP

[d] HC = hydrocracked; RSC = reclaimed spent coolant; RHB = reclaimed high boiler

[e] Mixture of samples 25699 (m-ϕ_3 reduced with Copper chromite) and 30403 (m-ϕ_3 reduced with nickel) and numbered 35928

Table 33

MICRO ASH DETERMINATIONS

Sample No.	Sample	ppm Ash Recovered 750°C	ppm Ash Recovered 1000°C	ppm Ash Expected	% Recovered 750°C	% Recovered 1000°C
0 A 1	Santowax Only	22[d]	22[d]	-	-	-
0 A 2	Duplicate	27[d]	32[d]	-	-	-
1 A 1	Santowax + Ferrocene (~354 ppm Fe_2O_3)	80	88	380	21	23
1 A 2	Duplicate (~283 ppm Fe_2O_3)	92	117	309	30	38
2 A 1	Santowax + Fe_2O_3 (~344 ppm Fe_2O_3)	341	358	370	92	97
2 A 2	Duplicate (~42 ppm Fe_2O_3)	54	63	68	79	93
3 A 1	Santowax + Metal Oxides[a] (~3211 ppm oxides[c])	2863	2930	3237	88	91
3 A 2	Duplicate (~50 ppm oxides[c])	72	82	76	95	108
4 A 1	Santowax + Metal Oxides[a] (~4312 ppm oxides[c])	3970	-	4338	92	-
4 A 2	Duplicate (~45 ppm oxides[c])	58	-	71	82	-
0 B 1	Core II HB Only	418	425	-	-	-
1 B 1	Core II HB + Ferrocene (~622 ppm Fe_2O_3)	378	387	>1000	b	b
2 B 1	Core II HB + Fe_2O_3 (~36 ppm Fe_2O_3)	410	419	b	b	b
3 B 1	Core II HB + Metal Oxides (~41 ppm oxides[c])	428	436	b	b	b
28050A	Core I Spent Coolant	-	79			
30409A	Core II Spent Coolant	-	42			
30449	Core II Reclaimed Spent Coolant	21	-			
25679A	Core II Reclaimed Spent Coolant	-	32			
25679B	Core II Reclaimed Spent Coolant (after PCPT)	-	12			
33440C	Core II Reclaimed High Boiler	12	-			

[a] Ferrocene also added

[b] Not calculated due to uncertainty of blank

[c] Oxides of Fe, Ca, Mg, Mn, Si, Al, and Cu

[d] The average of these four results (26 ppm) was added to the ≈ ppm oxides to determine the ppm ash expected.

Table 34

EMISSION SPECTROGRAPHIC ANALYSIS OF COOLANT ASH

Sample No.	0 A 1	3 A 2	0-B-1	3 B 1	33440C	28050A	30409A	30449	25679A	25679B
Sample	Santowax-OMP[a]	Santowax plus 33 ppm metal oxides	Core II HB	Core II HB plus 28 ppm metal oxides	Core II RHB	Core I SC	Core II SC	Core II RSC	Core II RSC	Core II RSC (after FCPT)
<u>Element, ppm</u>										
Iron	2-6	5-13	100-300	80-250	2-5	15-45	5-15	2-5	<0.9	0.4-1.3
Calcium	-	7-21	8-24	6-18	-	-	-	-	-	-
Magnesium	2-5	1-4	3-8	2-5	2-4	<2	<2	2-4	<0.9	<1
Manganese	-	2-5	<3	2-5	-	<2	<2	-	-	-
Silicon	5-15	3-8	8-24	10-30	5-14	2-6	2-5	4-13	4-11	2-7
Aluminum	2-5	1-4	2-6	12-36	2-4	<2	<3	2-4	0.5-1.5	0.7-2
Copper	<2	11-34	8-24	4-12	<2	<2	<2	<2	0.9	<1
Nickel	<2	<2	<3	<2	<2	-	-	<2	-	-
Total, ppm	11-35	30-91	129-392	116-348	11-32	17-59	7-29	10-30	4.5-15.2	3.1-12.3
Ash, ppm (range)	22-32	72-82	418-425	428-436	12	79	42	21	32	12
Ignition Temp.°C	1000	1000	1000	1000	750	1000	1000	750	1000	1000

[a] 10-14 ppm obtained using a macro method (150g).

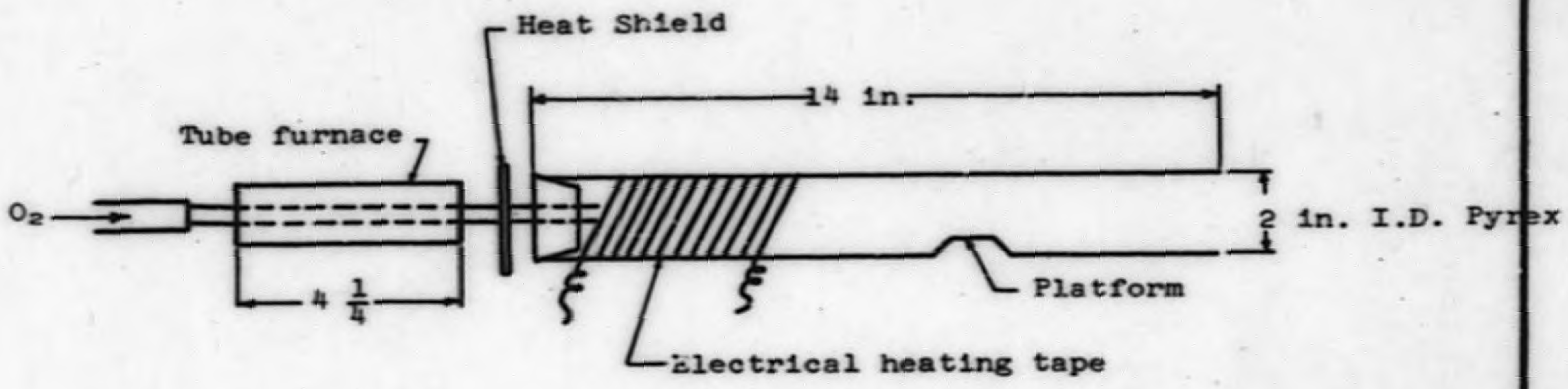


Figure 15. Ashing Apparatus

and the residue ignited with a Meker burner at 750°C for 1-1.5 hours or in a Lindberg muffle furnace at 1000°C for one hour. The crucible was then cooled in a desiccator and reweighed to the nearest microgram. Ash, expressed in ppm, was thus calculated as follows:

$$\frac{(\text{mg of ash})(1 \times 10^6)}{\text{g(sample)}} = \text{ppm ash}$$

V. FUNDAMENTAL COOLANT STUDIES

A. INTRODUCTION

Research in this area was undertaken to provide information for use in conjunction with the reclamation studies and to obtain fundamental information with regard to terphenyl degradation and film formation. The scope of work in this area included the following:

1. Synthesis of alkylpolyphenyls.
2. Determination of thermal and radiolytic stability of alkylpolyphenyls.
3. Synthesis and study of the thermal behavior of 1,3-diphenylcyclohexadiene-1,3.
4. Thermal decomposition rate of biphenyl.

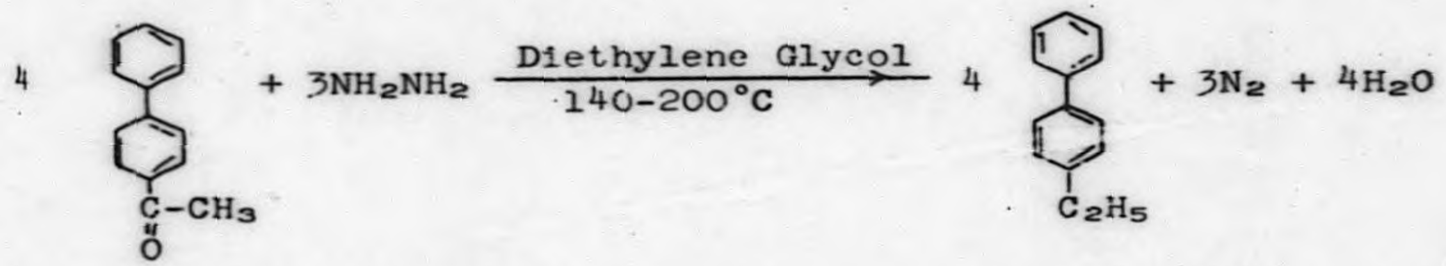
B. SYNTHESIS

In order to obtain pure biphenyl and terphenyl derivatives for thermal and radiolytic evaluation, a synthesis program to provide these compounds was undertaken. It has been shown (ref. 21) that high boiler contains small quantities of alkylpolyphenyls and the present work shows that hydrocracked reclaimed high boiler contains large proportions of alkylpolyphenyls. Since very little data exist on the thermal and radiolytic stability of pure alkylpolyphenyls, a program to obtain these data is of fundamental importance in evaluating hydrocracked high boiler for reuse as reactor coolant. In addition, polyphenyl dienes may be precursors to fouling films on reactor fuel plates so that two dienes were also synthesized for thermal and radiolytic study. All of these pure (96-100%) materials were made in varying amounts ranging from 5-100 grams.

1. Synthetic Routes

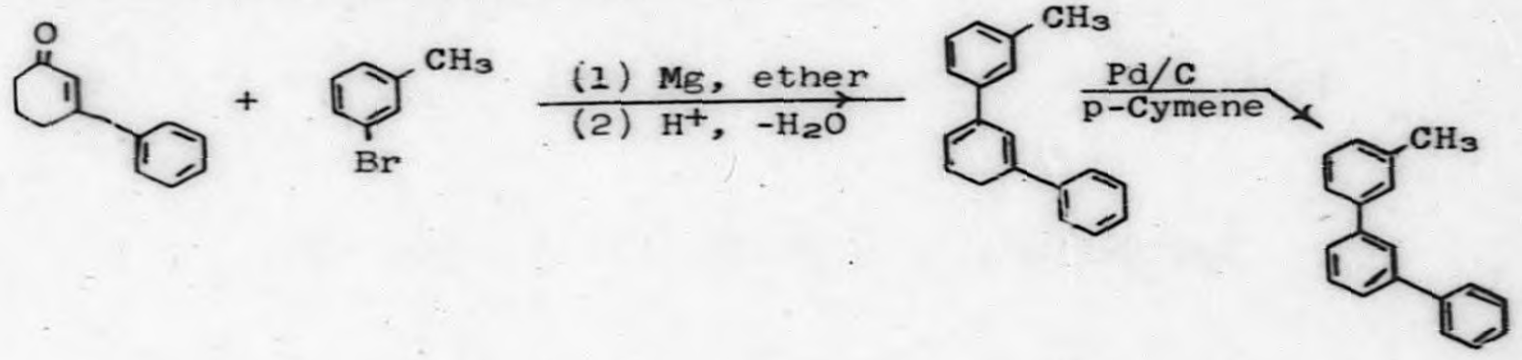
The compounds prepared and the synthetic route employed for each are shown below. The amount and purity are also given. Experimental details are given in Appendix II.

a. 4-Ethyl Biphenyl (ref. 22)



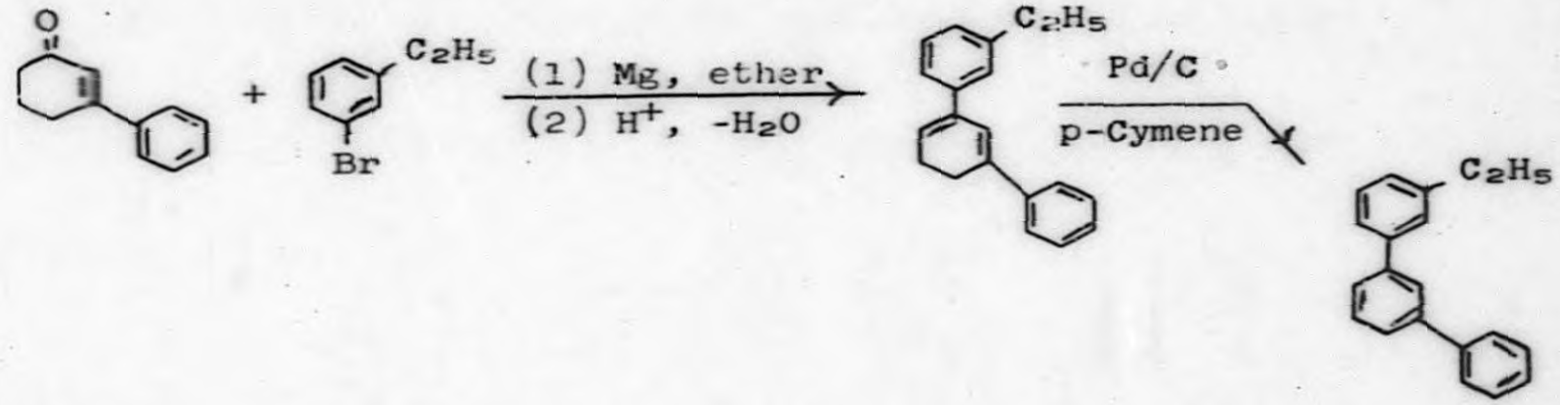
Total amount synthesized: 110 grams Purity: >99%

b. 3-Methyl-m-terphenyl (ref. 23,24,25)



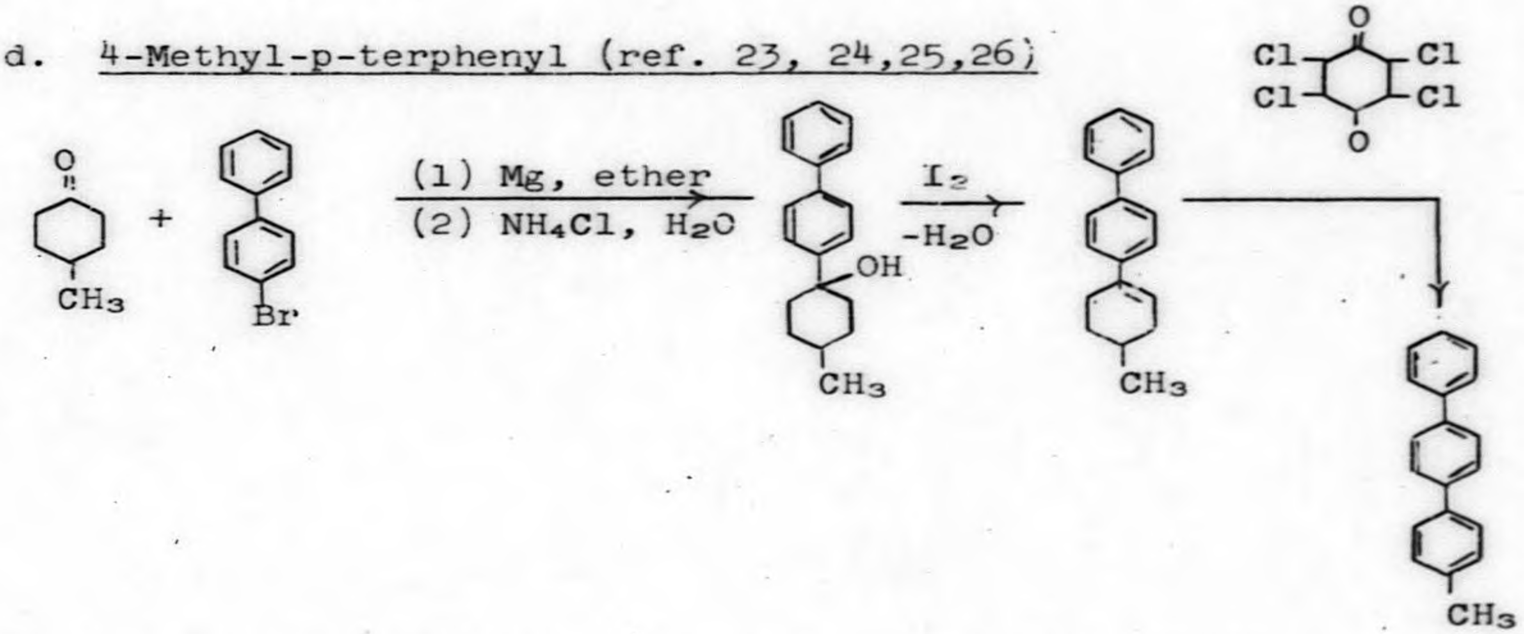
Total amount synthesized: 80 grams Purity: 96-98%

c. 3-Ethyl-m-terphenyl (ref. 23,24,25)



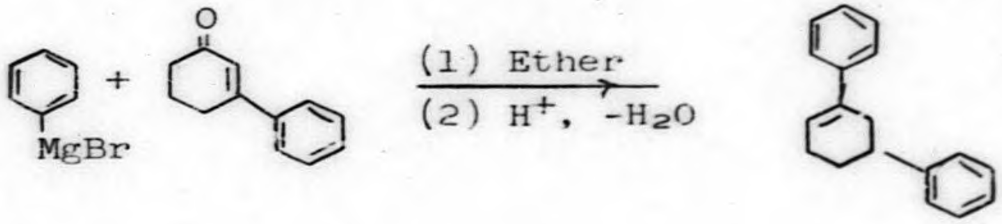
Total amount synthesized: 5 grams Purity: 96%

d. 4-Methyl-p-terphenyl (ref. 23, 24,25,26)



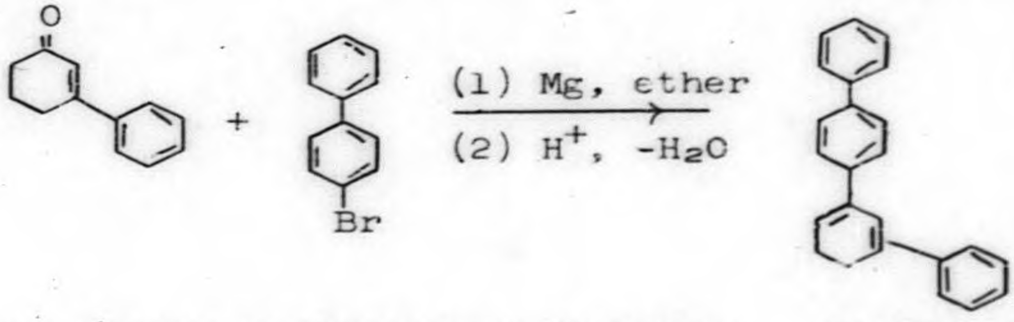
Total amount synthesized: 50 grams Purity: >99%

e. 1,3-Diphenylcyclohexadiene-1,3 (ref. 27)



Total amount synthesized: 85 grams Purity: 95%

f. 1-(4-Xenyl)-3-phenylcyclohexadiene-1,3 (ref. 27,28)



Total amount synthesized: 70 grams Purity: >90%

C. THERMAL STABILITY OF SOME POLYPHENYL DERIVATIVES

Five compounds were evaluated for thermal stability in the high temperature isoteniscope. Table 35 lists decomposition temperatures.

Table 35

THERMAL DECOMPOSITION TEMPERATURES OF POLYPHENYL DERIVATIVES

Compound	Thermal Decomposition, Temp., °C*
4-Ethylbiphenyl	451
3-Methyl-m-terphenyl	466
3-Ethyl-m-terphenyl	416
4-Methyl-p-terphenyl	457
1,3-Diphenylcyclohexadiene-1,3	388
p-terphenyl	478

---

* Temperature at which decomposition rate is 1 mole per cent per hour

D. RADIOLYTIC STABILITY OF SOME POLYPHENYL DERIVATIVES

Several samples were subjected to electron irradiation using the Van de Graaff electron accelerator at our Dayton Laboratories. Table 36 summarizes data obtained in these radiolytic experiments.

Table 36

ELECTRON RADIOLYSIS OF BIPHENYL AND TERPHENYL DERIVATIVES (400°C, 20 Mev electrons, 20 watt/hr/g)

Sample	Blank % Residue	Decomposition[a]			
		Gas	Volatile	Residue	Total
4-Ethylbiphenyl	0.10	3.28 (68.34)[b]	0.13 0.04	15.40 22.35	18.81 (90.73)[b]
3-Methyl-m-terphenyl	0.14	1.65 2.53	0.85 0.66	10.41 11.42	12.91 14.61
4-Methyl-p-terphenyl	0.20	0.92 0.97	0.13 0.10	11.68 10.66	12.73 11.73
1,3-Diphenylcyclohexadiene-1,3	0.00	4.92 3.71	4.05 2.49	8.64 10.77	17.61 16.93
m-Terphenyl	0.00	0.76	0.30	20.19	21.25

---

[a] Duplicate determinations are given

[b] A leak developed in the system during irradiation resulting in invalid values.

Table 37 summarizes the electron irradiation data expressed in relative gas and polymer yields.

Relative gas yield is defined as the ratio of gas produced on irradiation of the compound to that produced on irradiation of m-terphenyl under the same conditions. Relative polymer yield is defined as the ratio of the polymer produced on irradiation of the compound to that obtained on irradiation of m-terphenyl.

The polymer yields are obtained by distillation at 200°C/0.05-0.10 mm Hg for 2 hours.

Table 37

RELATIVE GAS AND POLYMER YIELDS OBTAINED WITH THE
Van de Graaff ACCELERATOR
(400°C, 2 Mev electrons, 20 watt-hr/gram)

Sample	Relative Gas Yield	Relative Polymer Yield
m-Terphenyl	1.00	1.00
3-Methyl-m-terphenyl	2.75	0.53
4-Methyl-p-terphenyl	1.25	0.54
4-Ethylbiphenyl	4.31	0.76
1,3-Diphenylcyclohexadiene-1,3	5.68	0.48

E. THERMAL BEHAVIOR OF 1,3-DIPHENYLCYCLOHEXADIENE-1,3

A study of the thermal behavior of this diene to determine the extent of the aromatization and/or the polymerization reaction was initiated. It is believed that this study could provide information on the role of dienes in film formation (fouling) and terphenyl polymerization. Initially, the diene was subjected to thermal treatment between 200 and 400°C for up to 90 hours to determine the quantity of hydrogen (via aromatization) and/or polymer produced. Results of the analyses are incomplete, but up to 300°C, no gas was evolved. Traces of methane, ethane, and hydrogen were found after treatment for 7 hours at 350°C. In all cases (except run No. 1, Table 38), the samples turned from a yellow-colored material to pale yellow or white. The diene from run 1 turned dark yellow.

Table 38

THERMAL TREATMENT OF 1,3-DIPHENYLCYCLOHEXADIENE-1,3
(Static Tests in Pyrex Tubes)
4.3×10^{-3} moles diene

Run No.	Sample No.	Temp °C	Time hr	Moles Gas Evolved	Gas Composition
1	36399A	200	92.41	1.2×10^{-4}	O_2
2	B	250	90.75	3×10^{-5}	O_2
3	C	250	45.83	9×10^{-5}	O_2
4	D	250	45.83	-	-
5	E	300	45.83	-	-
6	F	300	45.83	-	-
7	G	350	7.00	3×10^{-5}	CH_4 C_2H_6 H_2, O_2
8	H	400	7.00	gas leak	-

Gas chromatographic analysis of Sample No. 36399E gave the following: (6 ft 10% XE-60 on diatoport at 215°C, 60 psi)

Component	Retention Time	Area, %
1	7.5	7.5
2	8.0	3.4
3	8.7	22.8
4	9.7	6.8
m-terphenyl	14.0	59.6

The smaller number of components present on the chromatogram indicates that pyrolysis of the diene is not extensive. Infrared and ultraviolet spectra of the eluted peak No. 3 indicated biphenyl. No diene was found and the other components were not identified. The quantity of m-terphenyl produced in the chromatographic procedure is not known. A chromatogram of the diene at 260°C on an Apiezon column shows approximately 61% m-terphenyl indicating that aromatization occurred during the chromatographic procedure. The indications are, however, that aromatization of Sample No. 36399A occurred during thermal treatment. Polymer yield has not been determined, as yet.

E. THERMAL DECOMPOSITION OF BIPHENYL-RATE STUDIES

This study was undertaken to determine whether or not the rate constants for the thermal decomposition of various polyphenyls are the same regardless of the number of aromatic rings in the polyphenyl system. After determining the thermal decomposition rates of pure compounds such as biphenyl, o-, m- and p-terphenyl, p,m-quaterphenyl, and m,m,m-quinquephenyl and mixtures such as biphenyl and terphenyl, terphenyl and high boiler also were to be studied. It is believed that a study of this nature would aid in coolant management in reclamation processes or in coolant processing.

The program was initiated with a study of the thermal decomposition of biphenyl at temperatures between 350 to 510°C. The results of this work are discussed below.

1. Results

The experimentally determined values for biphenyl remaining (unreacted) after pyrolysis as a function of time are shown in Figures 16 and 17. The decomposition appears to follow a first-order rate expression over the temperature range investigated. A first-order decomposition at constant volume and temperature is given by

$$dx = K(a-x) \qquad (1)$$

where x = amount ϕ_2 reacting at time t

a = initial concentration

$(a-x)$ = conc. ϕ_2 remaining = C at time t

$$C_1 \frac{dx}{(a-x)} = k\ t_o\ dt \qquad (2)$$

Integration gives

$$-\ln(a-x) = kt + C \qquad (3)$$

if $t = o, x = o$, then $C = -\ln a$

which leads to

$$kt = -\ln C \qquad (4)$$

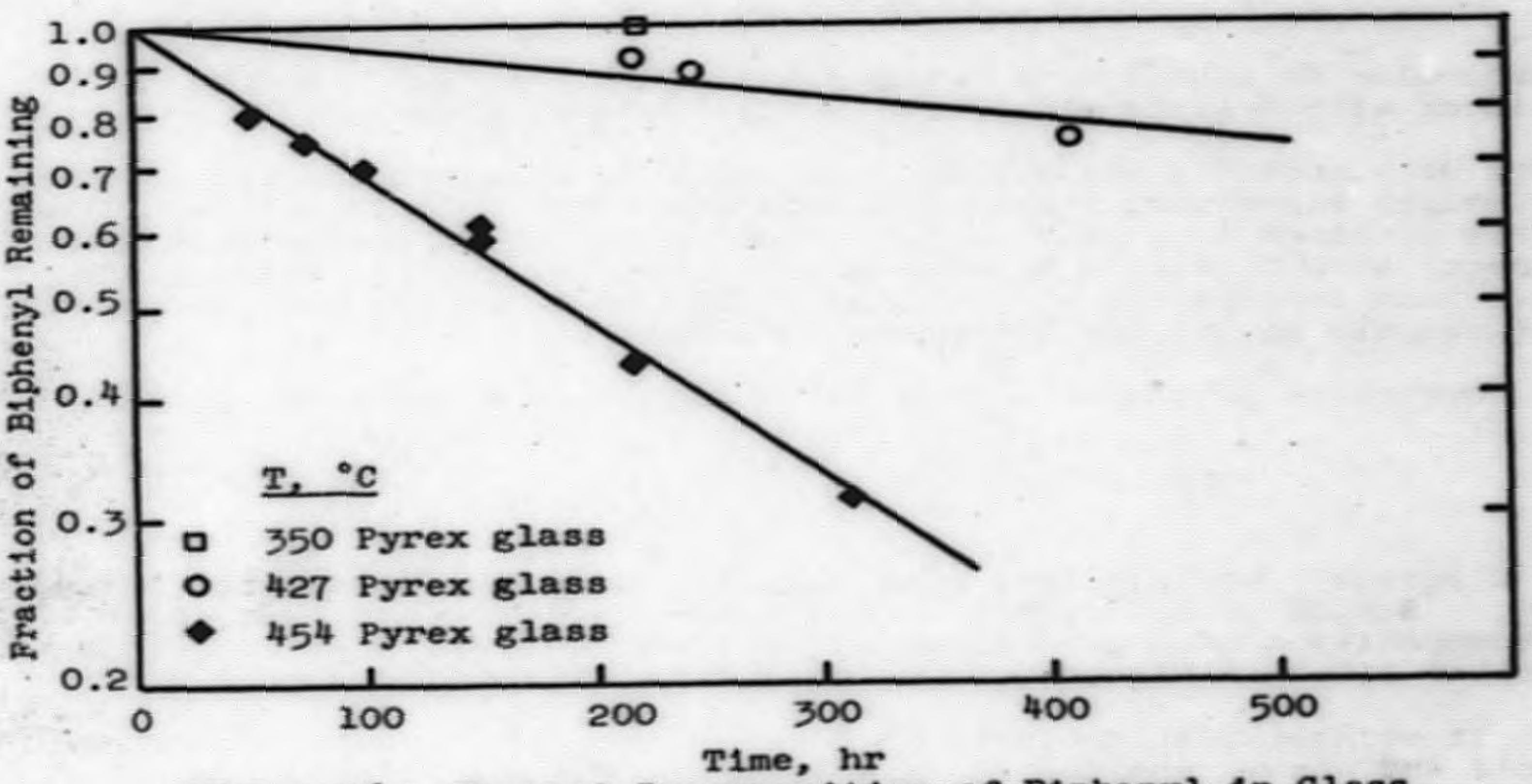
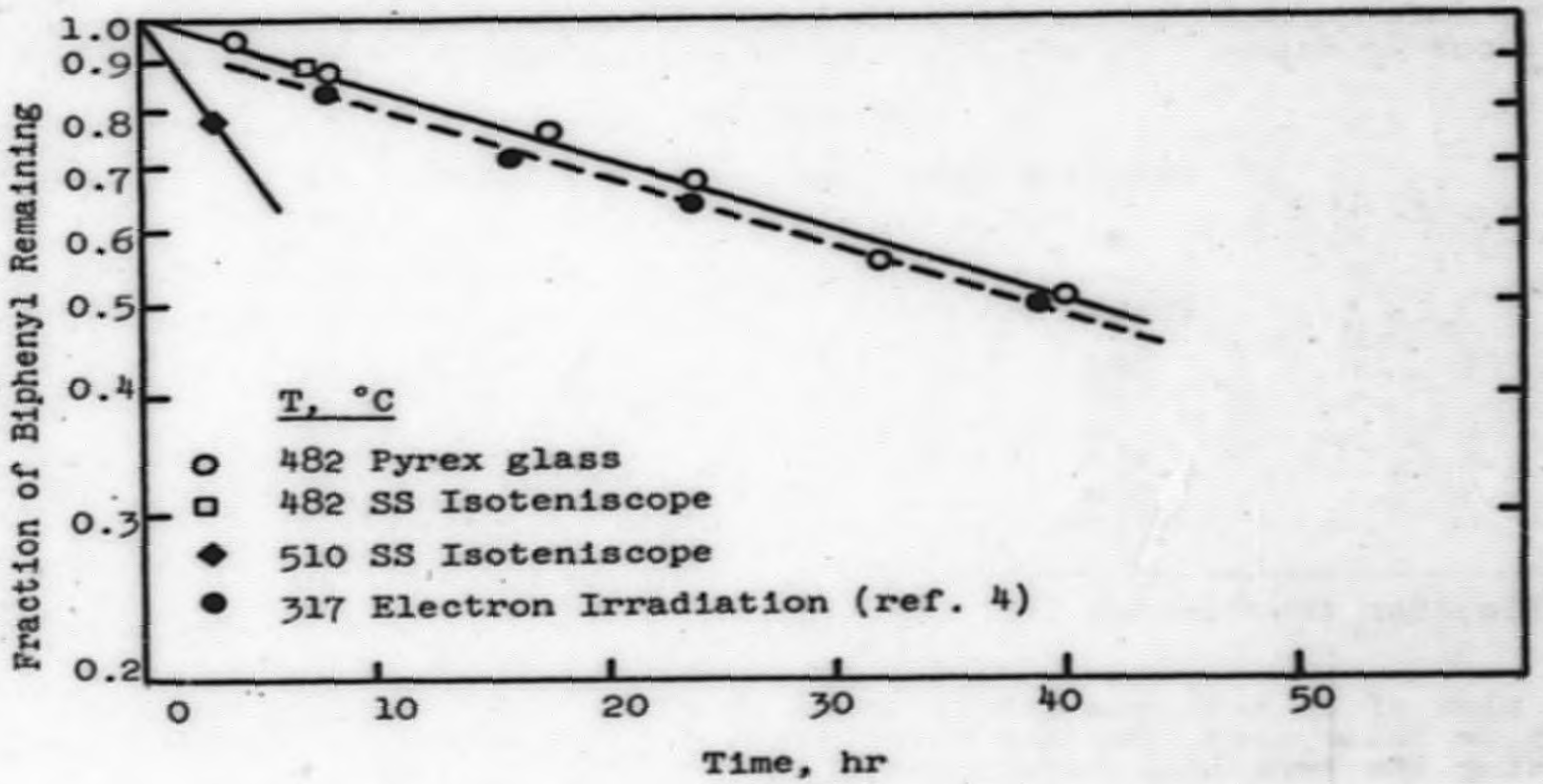


Figure. 16. Thermal Decomposition of Biphenyl in Glass.



3b

Figure 17. Thermal Decomposition of Biphenyl

According to equation (4), the plots in ln C versus t should be linear with a slope of -k, for a first-order decomposition.

The data shown in Figures 16 and 17 show a reasonable fit to straight lines and, therefore, indicate first-order kinetics. The data obtained at higher temperatures in the isoteniscope (60% free space) also show good agreement with that obtained in Pyrex glass. Electron irradiation at 317°C (ref. 29) is shown for comparison and is roughly equivalent to thermal decomposition at 482°C.

To determine whether the data fit a second-order rate expression,

$$\frac{1}{C} = kt + \frac{1}{C_o}$$

1/C versus t was plotted. The results are shown in Figures 18 and 19. A plot of 1/C versus t should be linear for a second-order decomposition of a pure compound, and would be represented by the dotted lines in Figures 18 and 19.

It is evident that the data in Figures 18 and 19 show a considerable and consistent upward swing as shown by the solid curved line, especially at higher conversions and therefore do not fit second-order kinetics.

The rate constants, k, shown in Table 39 were evaluated from the slopes in Figures 16 and 17, where k = -slope for each temperature.

Table 39

REACTION RATE CONSTANTS OF BIPHENYL

Temp, °C	Reaction Rate Constant, k sec^{-1}
350	$< 4 \times 10^{-9}$
427	1.5×10^{-7}
454	1.0×10^{-6}
482	4.7×10^{-6}
510	2.3×10^{-5}
317[a]	$\sim 5 \times 10^{-5}$

---

[a] Electron irradiation (ref. 29)

A plot of ln k versus 1/T is shown in Figure 20. Results reported by de Halas (ref. 30) and Rosen (ref. 31) are shown for comparison. Using the Arrhenius relationship

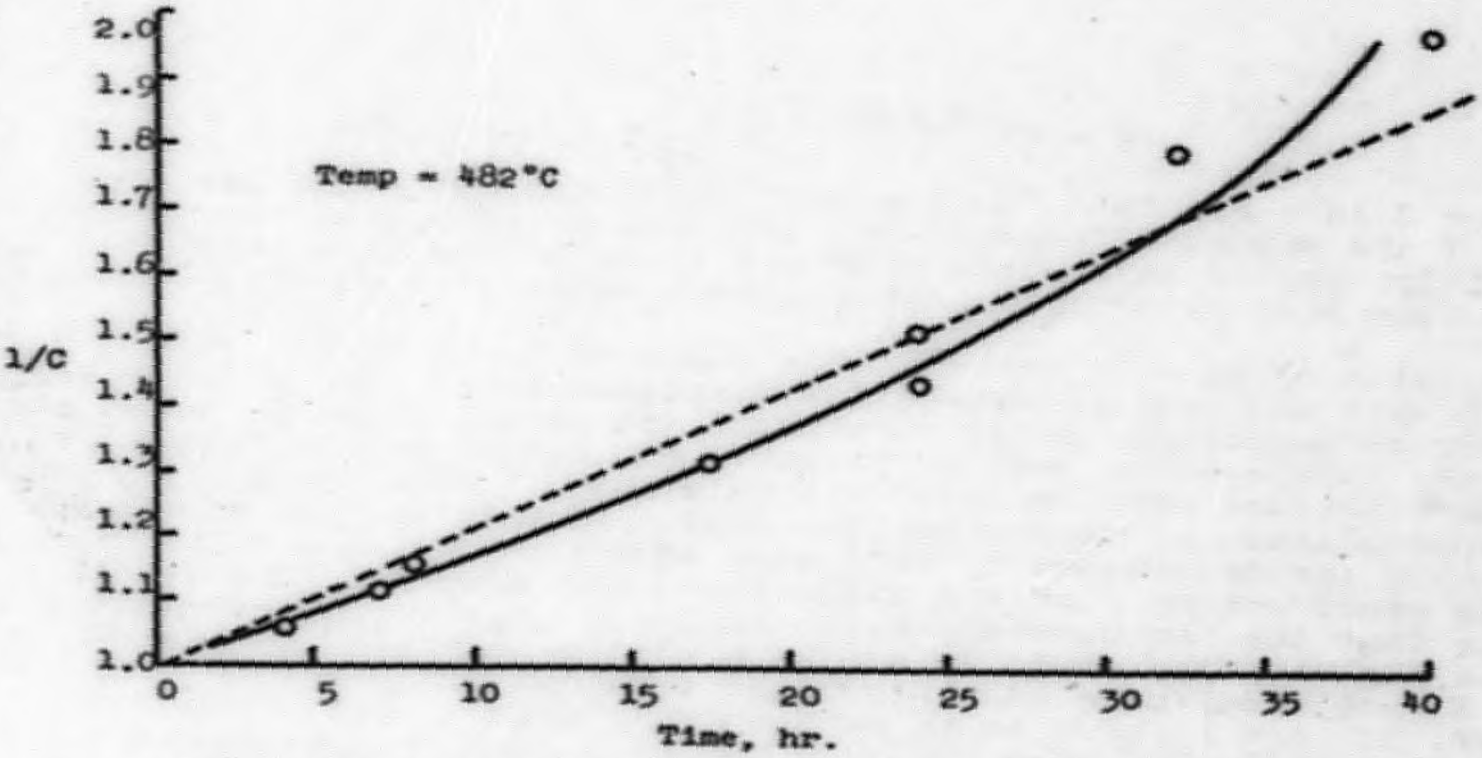


Figure 18. Thermal Decomposition of Biphenyl at 482°C Deviation from Second Order Kinetics

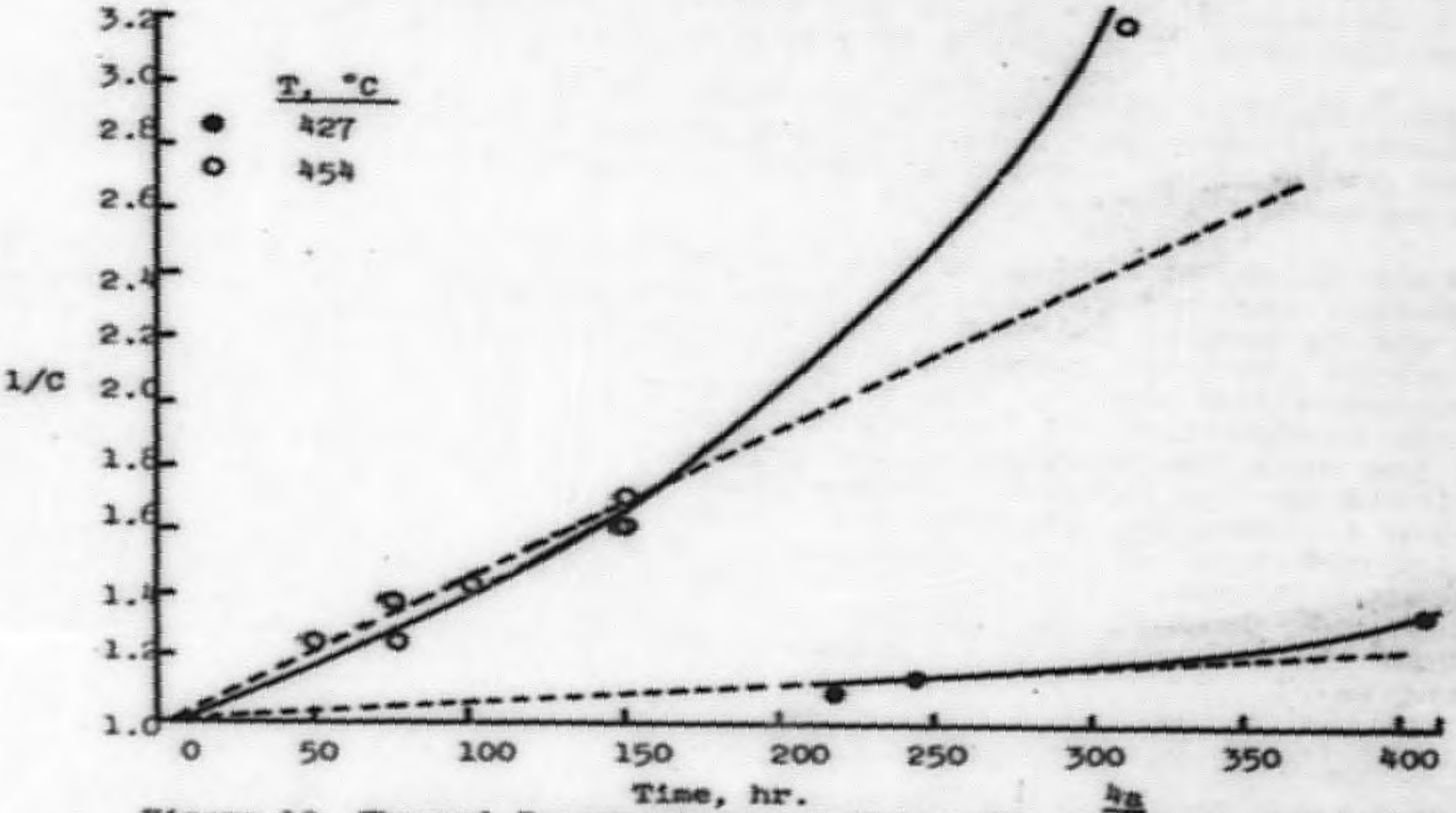


Figure 19. Thermal Decomposition of Biphenyl. 4a Deviation from Second Order Kinetics.

$$k = Ze^{-E_a/RT} \quad \text{or} \quad \ln k = -E_a/RT + Z$$

where Z is a constant, E_a the activation energy, R the gas constant, and T the absolute temperature, the activation energy for the decomposition can be determined from the slope of the line in Figure 20. The line best fitting the data gives a value of $E_a = 67 \pm 2$ kcal/mole.

The value of $E_a = 74{,}000$ cal/mole reported by de Halas (ref. 30) agrees well with the present data. The displacement of the de Halas line to lower decomposition rates is expected since all components removed in the single-plate reduced pressure distillation of products (tar determination) were included with biphenyl. This results in values characteristic of polymerization only. When products through terphenyls (as determined by VPC) were added to our values for biphenyl, only about one-half of the discrepancy was removed. This would indicate that the tar determination used by de Halas must have removed some higher polyphenyls in addition to terphenyls. The other value of $E_a = 92$ kcal/mole was calculated from data reported by Rosen (ref. 31) and appears to be considerably high. Some variation in decomposition rate with pressure has been note in isoteniscope runs in the present work, but no consistent correlation could be made. The points given for decomposition in the liquid and vapor phase were obtained in the isoteniscope in previous work (ref. 32) and correspond to a decomposition rate of one mole per cent per hour determined from the rate of pressure increase due to gas evolution.

A quantitative gas sampling was made in one run at 454°C. Trace amounts of hydrogen, methane, and ethane were detected, with less than one mole of gas being formed for every ten moles of biphenyl decomposed.

Figure 21 shows a plot of the terphenyls produced as a function of the biphenyl reacted for all the temperatures used. The relative amounts of the terphenyl isomers produced appear to be independent of temperature over the range studied. The fact that the o-terphenyl isomer concentration remains low is expected in view of the steric requirements needed for its formation. The known isomerization of o-terphenyl to the more thermodynamically stable m- and p-isomers may also contribute to the lower concentrations found. The fraction of polyphenyls above terphenyls, assumed to be comprised of some quaterphenyls, quinquephenyls and sexiphenyls, is also shown in Figure 20 for a few decompositions. The residue values determined by treatment of the pyrolyzed product at 200°C/0.1-0.05 mm Hg for 2 hours are also shown. These values appear to increase linearly in the same way as the terphenyls.

2. Biphenyl Decomposition Procedure

A quantity of purified (99.9+%) biphenyl is filtered (0.45 micron) and charged to a previously cleaned Pyrex glass tube to allow about

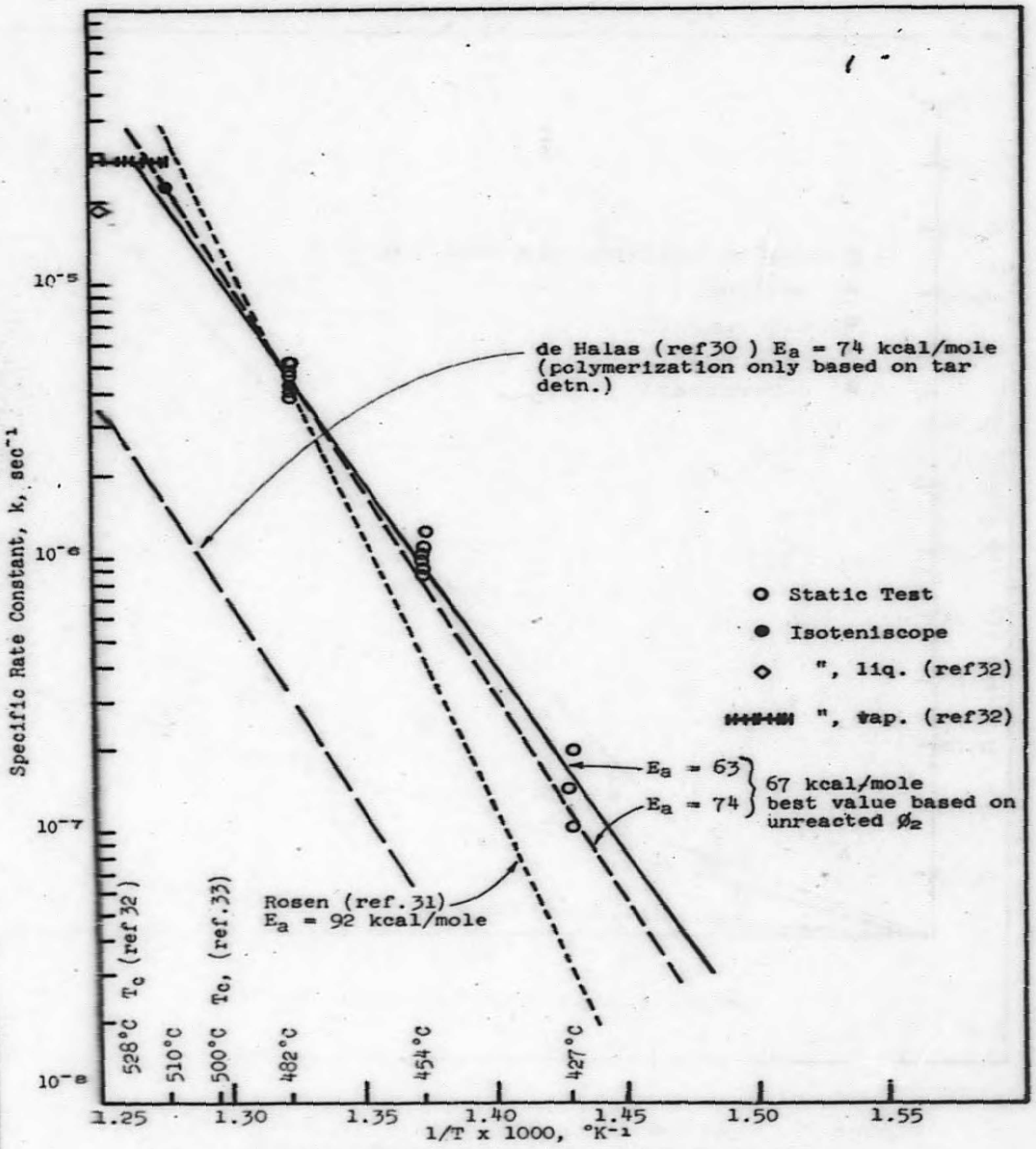


Figure 20. Arrhenius Plot for Thermal Decomposition of Biphenyl

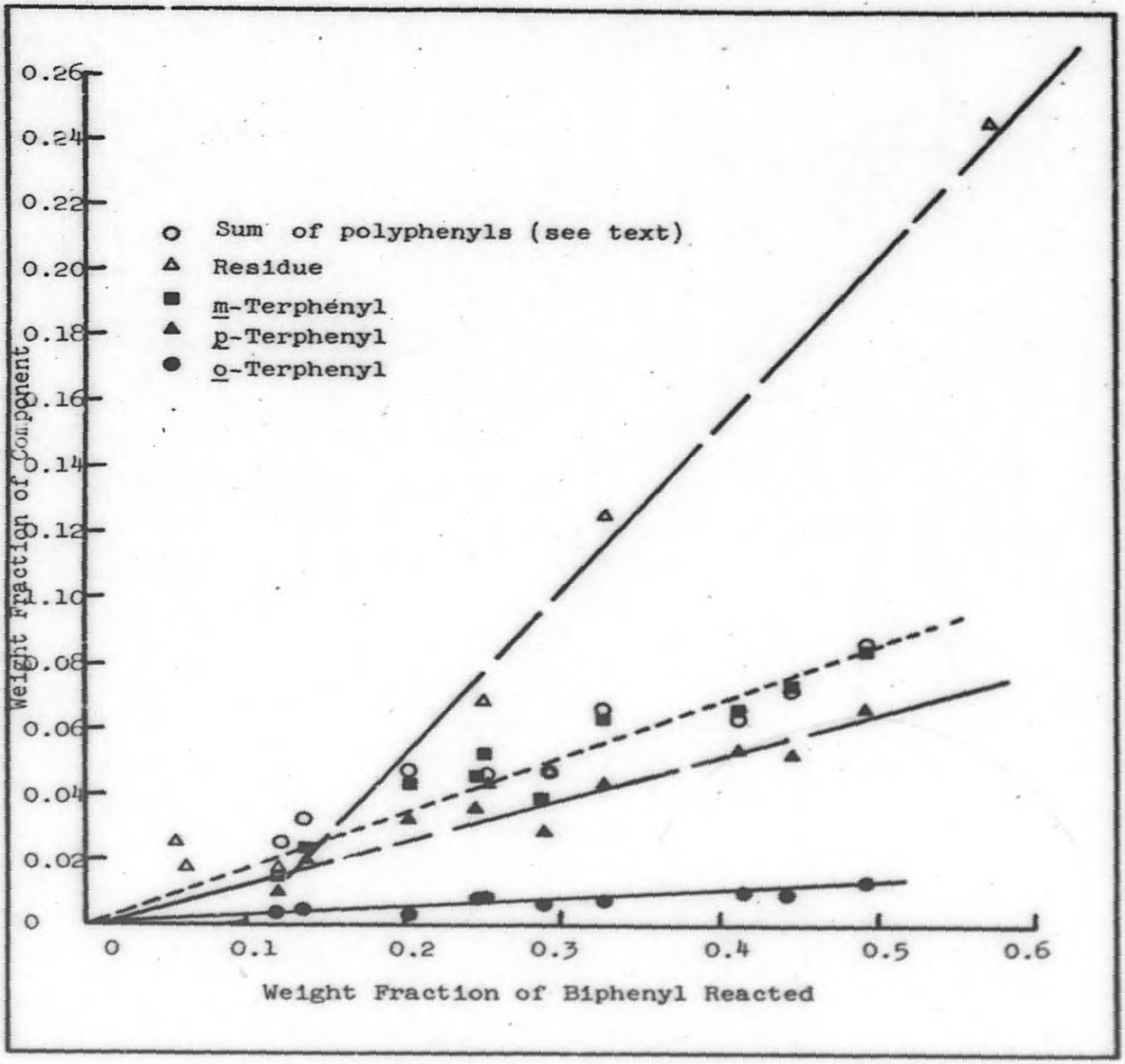


Figure 21. Decomposition Products of Biphenyl (T = 427-510°C) as a Function of Biphenyl Reacted

60% free space. The sample is melted, degassed, and the tube sealed under vacuum. The sealed tube is placed in a stainless steel cartridge (for protection) and preheated at ~250°C for fifteen minutes. It is then transferred to a hole in a heated and insulated aluminum block maintained at the desired run temperature (± 1°C). After heating for the desired time, the tube is removed and air quenched. The tube is cooled in liquid air prior to opening for analyses. Quantitative gas sampling is also possible. Several samples of biphenyl have also been decomposed in a high-pressure stainless steel isoteniscope (ref. 29).

Analysis for remaining biphenyl is made by vapor phase chromatography. Terphenyls and some higher polyphenyls are also determined.

VI. ECONOMIC EVALUATION OF VARIOUS RECLAMATION PROCESSES

The utility of a reclamation process which is technically feasible will ultimately be determined by economic factors. In order to obtain a general idea of the relative economic potential of various reclamation processes, cost calculations of these processes were made.

Preliminary economic evaluation of various reclamation processes were reported in the Third Annual Report (ref. 39, p. 83). Since then, the various reclamation processes have been re-evaluated by our process engineering group to check out the previous estimates. In addition, some refinements and the following cost estimates were made.

(1) Economic evaluation of the solvent distribution method for reclaiming spent coolant containing 5, 10, 15 and 22 wt-% high boiler.

(2) Economic evaluation of the partial reduction-hydrocracking reclamation process using product yields of 60, 70, and 80%.

The calculations are based on a 300 Mwe reactor operating at a steady state high boiler concentration of 30% and producing high boiler at the rate of 1000 lb/hr. For the spent coolant reclamation costs, steady state high boiler concentrations of 5, 10, 15, and 22%, with the corresponding high boiler production rates of 2000, 1700, 1400, and 1000 lb/hr, were also used. In making the original calculations (ref. 40) for solvent treatment reclamation of spent coolant containing various quantities of high boiler, the same operating costs were used. However, these operating costs will differ mainly in the heat requirements necessary to process the different quantities of coolant and will be significantly higher in the spent coolant containing 5% high boiler compared to all other cases. To allow for this, the heat requirements were calculated for each case, and the solvent distribution processes were re-evaluated using this additional cost requirement. In the base case, spent coolant is distilled to remove reusable terphenyl coolant, the high boiler residue is burned and replaced with fresh terphenyl coolant. The difference in cost of this operation (recovery of terphenyl and addition of new terphenyl) and the cost of a reclamation process (reducing the make-up terphenyl) is the incremental annual profit.

The results of the evaluations are shown in Tables 40, 41 and 42.

The economic trend in this and the previous evaluation (ref. 39) is the same, but the fixed capital and operating costs are greater in the present evaluation. The profits are lower because operating costs have been increased. Physical methods are more economical than chemical methods, except for partial reduction of high boiler (process 16) where a profit of $723,000/year is shown over the base case (process 1).

The wiped-film distillation process, in which yields of 25% are obtained, shows an incremental profit of $322,000, return on fixed capital of 23.1%, and payout time of 4.2 years. This is a yield that was obtained in an actual pilot plant experiment and although better profits are shown for the two processes which follow, yields have not been confirmed by experiment.

Table 41 shows that the base case with spent coolant containing 5% high boiler (processes 5 and 5a) have high fixed capital and operating costs, and it is questionable whether or not a reactor can operate economically at this high boiler concentration (no reclamation). Reclamation in these two cases is economical, but economy is increased twofold by reclamation of spent coolant containing 10% high boiler. The capital and operating costs become increasingly higher at low level high boiler concentrations because at these levels the terphenyl decomposition rate is high. Therefore, large amounts of coolant must be processed to maintain steady state high boiler concentrations of 5-10%.

Therefore, reclamation using the solvent treatment method becomes more profitable at the 15% high boiler level and above.

The same trends would most likely apply to any process that operates at reduced high boiler concentrations (15% or less).

Except for processes 3 and 4, the reclamation processes shown are supported by experimental evidence and are technically feasible.

The solvent distribution process on spent coolant containing 20% or greater high boiler is the most profitable of those shown (processes 8 and 9). Processes 6 and 7 show equally good profits, but the operating and fixed capital costs are high. The per cent return on investment (25-30%) in these two cases can be considered marginal because of the high investment and operating costs. The next best process is wiped-film distillation of high boiler using the

Table 40

ECONOMIC EVALUATION OF PHYSICAL RECLAMATION PROCESSES
(300 MWe Reactor, Steady State 30% HB Concentration)

Physical Methods	Fixed Capital $	Operating Cost and make-up ϕ_3 17 cents/lb $	Incremental Profit Over Base Case $	% Return on Fixed Capital	Operating cost/lb Reclaimed Coolant cent/lb	Operating and Make-up Cost/lb Reclaimed Coolant cent/lb	Payout Time, year
Distillation Process							
1. Primary distillation (1000 lb/hr disposal) Base Case[a]	950,000	2,055,000	-	-	2.77	10.1	-
2. Primary distillation and wiped-film distillation (750 lb/hr disposal rate)	1,350,000	1,733,000	322,000	23.8	3.48	7.64	4.20
3. Primary distillation and wiped-film distillation (500 lb/hr disposal rate)	1,354,000	1,529,000	526,000	38.8	3.16	6.15	2.60
4. Primary distillation and forced circulation distillation (500 lb/hr disposal rate)	854,000	1,365,000	690,000	81	2.10	5.5	1.24

---

[a] Applies to processes 2, 3, and 4

Table 41

ECONOMIC EVALUATION OF PHYSICAL RECLAMATION PROCESSES
(300 MW(e) Reactor, Steady State HB Concentration Specified in Process Description)

	Base Case								
Physical Methods	Fixed Capital $	Operating Cost and Make-up @ 17 cents/lb $	Fixed Capital $	Operating Cost and Make-up @ 17 cents/lb $	Incremental Profit Over Base Case $	% Return on Fixed Capital	Operating Cost/lb Reclaimed Coolant cent/lb	Operating and Make-up Cost/lb Reclaimed Coolant, cent/lb.	Payout Time, year
5. Solvent distribution on spent coolant (5% HB content, 606 lb/hr disposal rate)			8,550,000	4,049,000	858,000	10	0.914	1.118	10
Base Case[a]	5,250,000	4,907,000	-	-	-	-	0.58	1.48	-
5a. Concentrating 5 wt-% HB in SC to 30 wt-% then solvent distribution on concentrated SC (606 lb/hr disposal rate)	-	-	5,990,000	4,226,000	687,000	11.5	0.96	1.22	9
Base Case	5,250,000	4,907,000	-	-	-	-	0.58	1.48	-
6. Solvent distribution on spent coolant (10% HB content, 511 lb/hr disposal rate)	-	-	4,750,000	2,640,000	1,175,000	24.8	1.30	1.83	4.05
Base Case	2,975,000	3,815,000	-	-	-	-	0.95	2.84	-
7. Solvent distribution on spent coolant (15% HB content, 422 lb/hr disposal rate)	-	-	3,210,000	2,030,000	970,000	30.2	1.80	2.60	3.3
Base Case	1,975,000	3,000,000	-	-	-	-	1.38	4.29	-
8. Solvent distribution on spent coolant (22% HB content, 333 lb/hr disposal rate)	-	-	2,010,000	1,525,000	775,000	38.5	2.50	3.75	2.6
Base Case	1,280,000	2,300,000	-	-	-	-	2.06	6.75	-
9. Solvent distribution on spent coolant (30% HB content, 303 lb/hr disposal rate)	-	-	1,500,000	1,302,000	753,000	50	3.20	4.92	2.0
Base Case	950,000	2,055,000	-	-	-	-	2.8	10.1	-
10. Primary distillation and solvent distribution on HB (from 30 wt-% spent coolant), 250 lb/hr disposal rate	-	-	1,350,000	1,314,000	741,000	55	3.49	4.95	1.8
Base Case	950,000	2,055,000	-	-	-	-	2.8	10.1	-

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[a] The base case is processes 5, 5a, 6, 7, 8, 9, and 10 is primary distillation, burning of the HB residue and replacement of HB with fresh terphenyl coolant

Table 42

ECONOMIC EVALUATION OF CHEMICAL RECLAMATION PROCESSES
(300 MW(e) Reactor, Steady State 30% HB Concentration)

Chemical Methods	Fixed Capital $	Operating Cost and Make-up ϕ_2 at 17 cents/lb $	Incremental Profit Over Base Case $	% Return on Fixed Capital	Operating Cost/lb Reclaimed Coolant cent/lb	Operating and Make-up Cost/lb Reclaimed Coolant cent/lb	Payout Time, yr
1. Primary distillation (1000 lb/hr disposal rate) Base Case	950,000	2,055,000	-	-	2.8	10.1	-
11. Primary distillation and HB hydrocracking (200 lb/hr disposal rate)	2,522,000	1,684,000	371,000	15	5.1	6.1	6.7
12. Primary distillation and HB hydrocracking (300 lb/hr disposal rate)	2,522,000	1,833,000	222,000	8.8	5.1	6.9	11.4
13. Primary distillation and partial reduction and hydrocracking (200 lb/hr disposal rate)	2,775,000	1,796,000	259,000	9.3	5.5	6.5	10.7
14. Primary distillation and partial reduction and hydrocracking (300 lb/hr disposal rate)	2,800,000	1,945,000	110,000	3.8	5.5	7.2	26
15. Primary distillation and partial reduction and hydrocracking (400 lb/hr disposal rate)	2,929,000	2,197,000	-142,000	neg.	6.2	8.5	-
16. Primary distillation and partial reduction of HB (150 lb/hr disposal rate)	2,045,000	1,322,000	723,000	35.8	3.9	4.8	2.8

Kontro "Ajust-O-film" still (Process 2). Processes 3 and 4 are good processes but are not supported by experimental data. Process 3, however, has a high probability of being successful based on process 2 results. The partial reduction-hydrocracking process (process 13) follows those mentioned, but again this process is characterized with high operating and fixed capital costs, moderate profits ($259,000) and a low per cent return on investment (9.3%).

Partial reduction of high boiler (process 16) is equally as good as solvent distribution (processes 8 and 9). Product from such a process has been irradiated and indications are that it may have utility for reuse as a reactor coolant.

The economically attractive processes (processes 2, 3, 7, 8, 9, 10 and 16) should be further developed on a pilot plant scale.

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APPENDIX I

VAPOR PHASE CHROMATOGRAMS OF PARTIALLY REDUCED o-, m-, AND p-TERPHENYL

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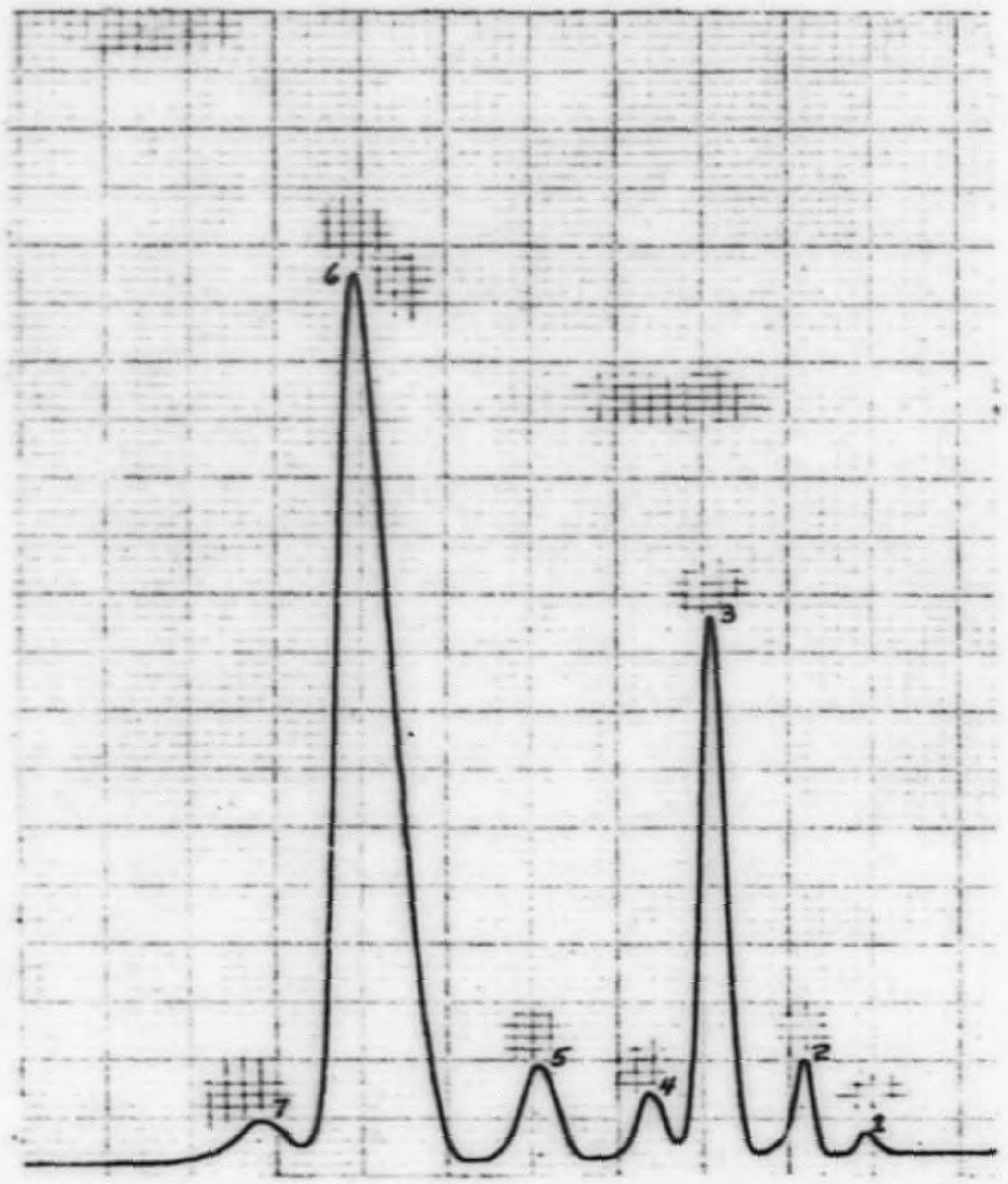


Sample No. 30425

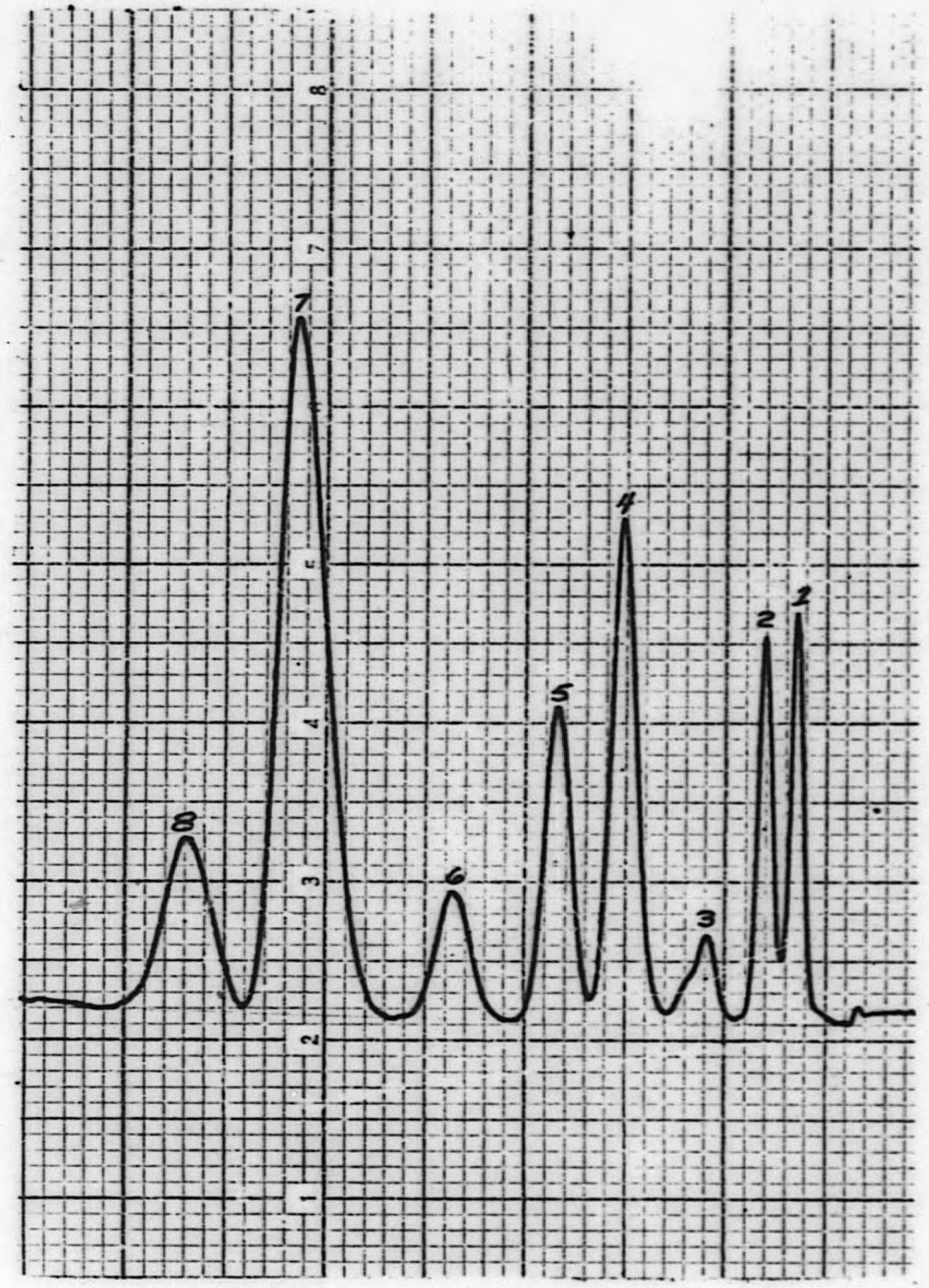
Operating Conditions

1. Solvent: Tetrahydrofuran
2. Sample Size: 5 µl
3. Column: 4 ft. 15% Craig polyester succinate on 30-60 mesh reg. Chromosorb
4. Column temp.: 200°C
5. Helium: 60 psig

Peak Legend:

1. o-tercyclohexyl
2. 1,2-dicyclohexyl benzene
3. 1-cyclohexyl-2-phenylcyclohexane
4. 1-phenyl-2-cyclohexyl benzene
5. Unassigned
6. 1,2-diphenylcyclohexane
7. o-terphenyl

Figure 22. Vapor Phase Chromatogram of o-Terphenyl Reduced with G-13 Copper Chromite Catalyst



Sample No. 30416

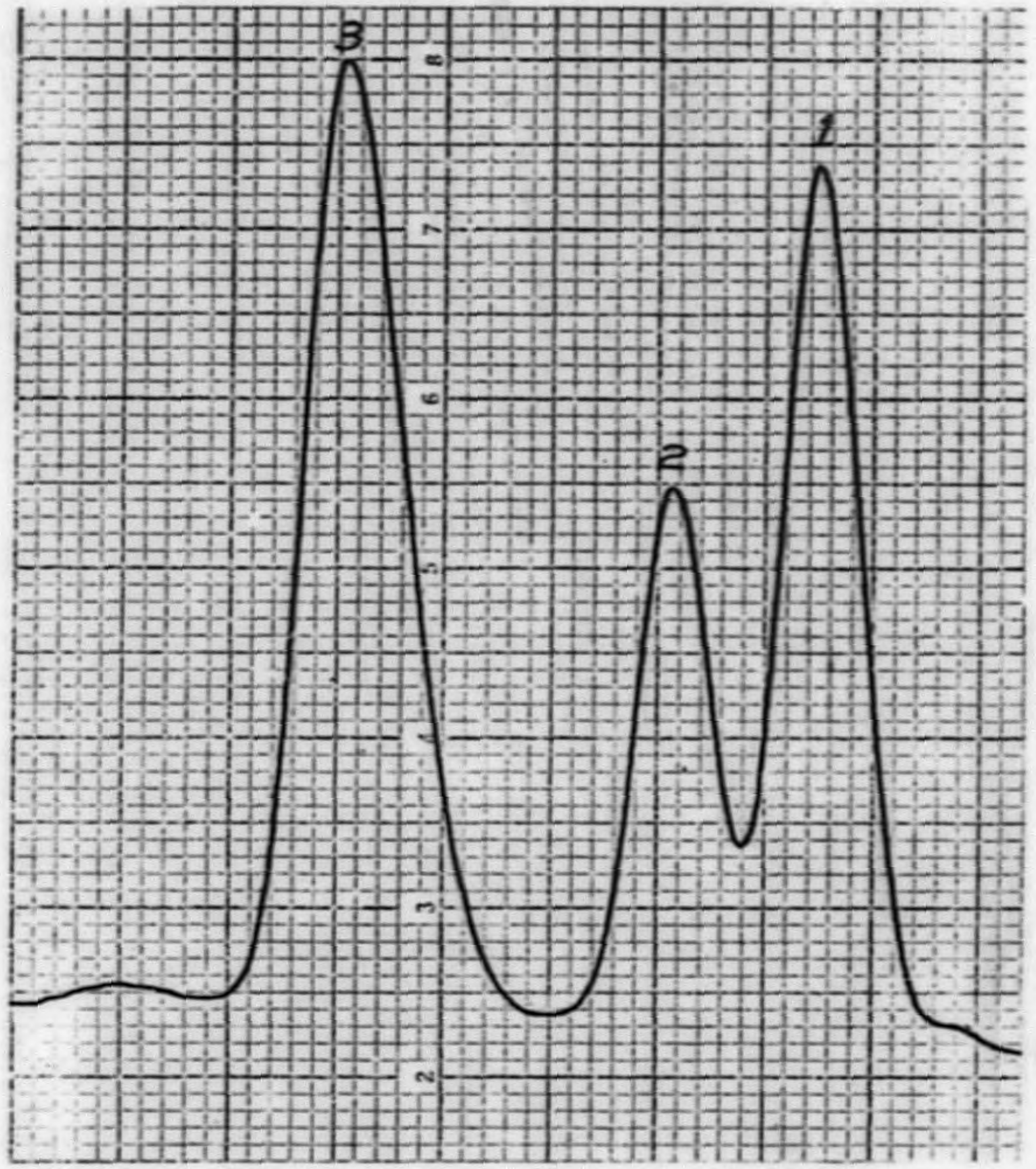
Operating Conditions

1. Solvent: None
2. Sample size: 1 μl
3. Column: 4 ft. 15% Craig polyester succinate on 30-60 mesh reg. Chromosorb
4. Column temp: 200°C
5. Helium: 60 psig

Peak Legend

1. o-tercyclohexyl
2. o-tercyclohexyl
3. 1,2-dicyclohexylbenzene
4. 1-cyclohexyl-2-phenylcyclohexane
5. 1-phenyl-2-cyclohexyl benzene
6. Unassigned
7. 1,2-diphenylcyclohexane
8. o-terphenyl

Figure 23. Vapor Phase Chromatogram of o-Terphenyl Reduced with G-49 Nickel Catalyst



Sample No. 6203-1,2

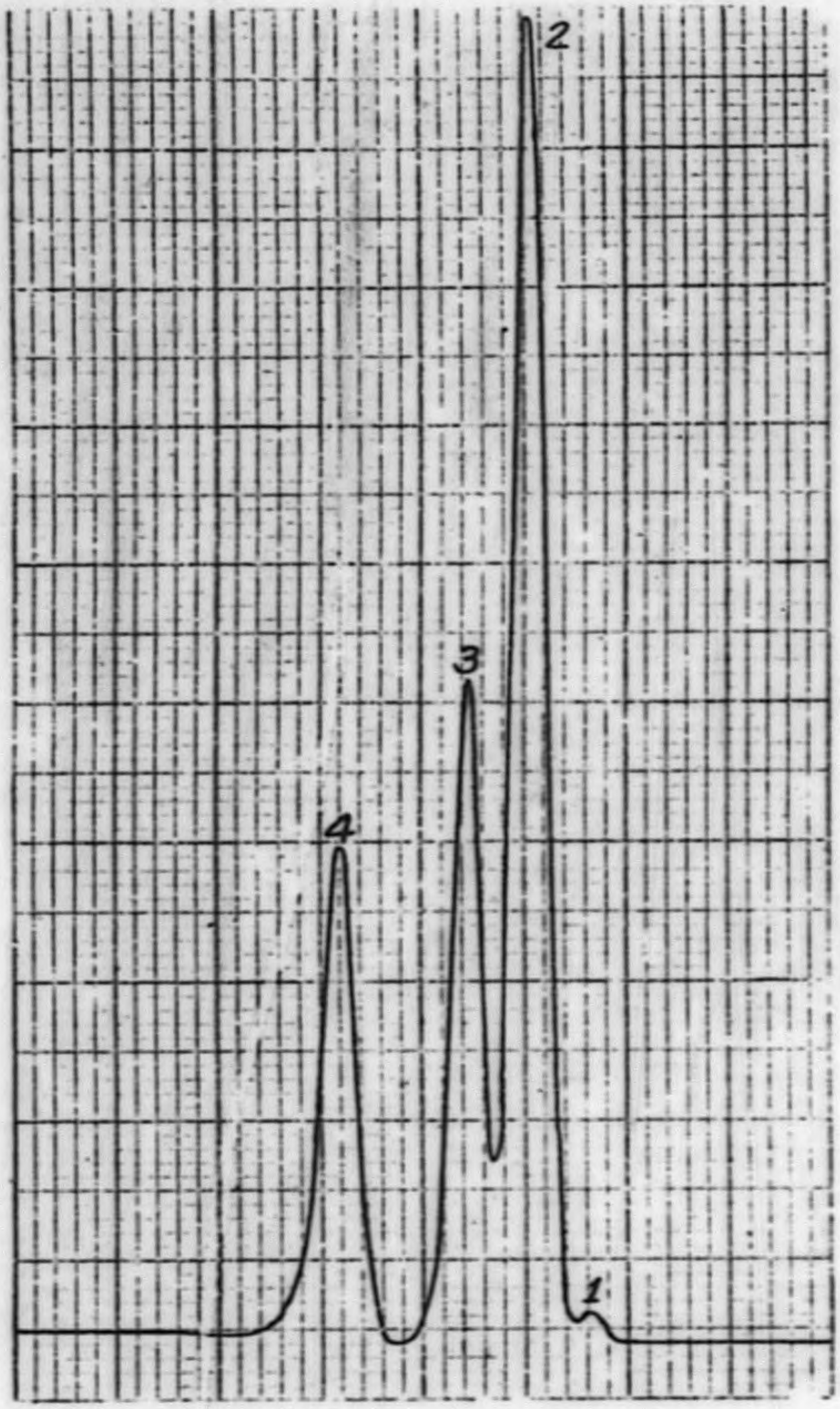
Operating Conditions

Solvent: Tetrahydrofuran
Sample Size: 6 µl
Column: 6 ft. 15% Apiezon L on Chromosorb
Column Temp.: 262°C
Helium: 60 psig

Peak Legend

1. 1,3-Diphenylcyclohexane
2. 1-Phenyl-3-cyclohexylbenzene
3. m-Terphenyl

Figure 24. Vapor Phase Chromatogram of m-Terphenyl Reduced with Copper Chromite Catalyst.



Sample No. 25699

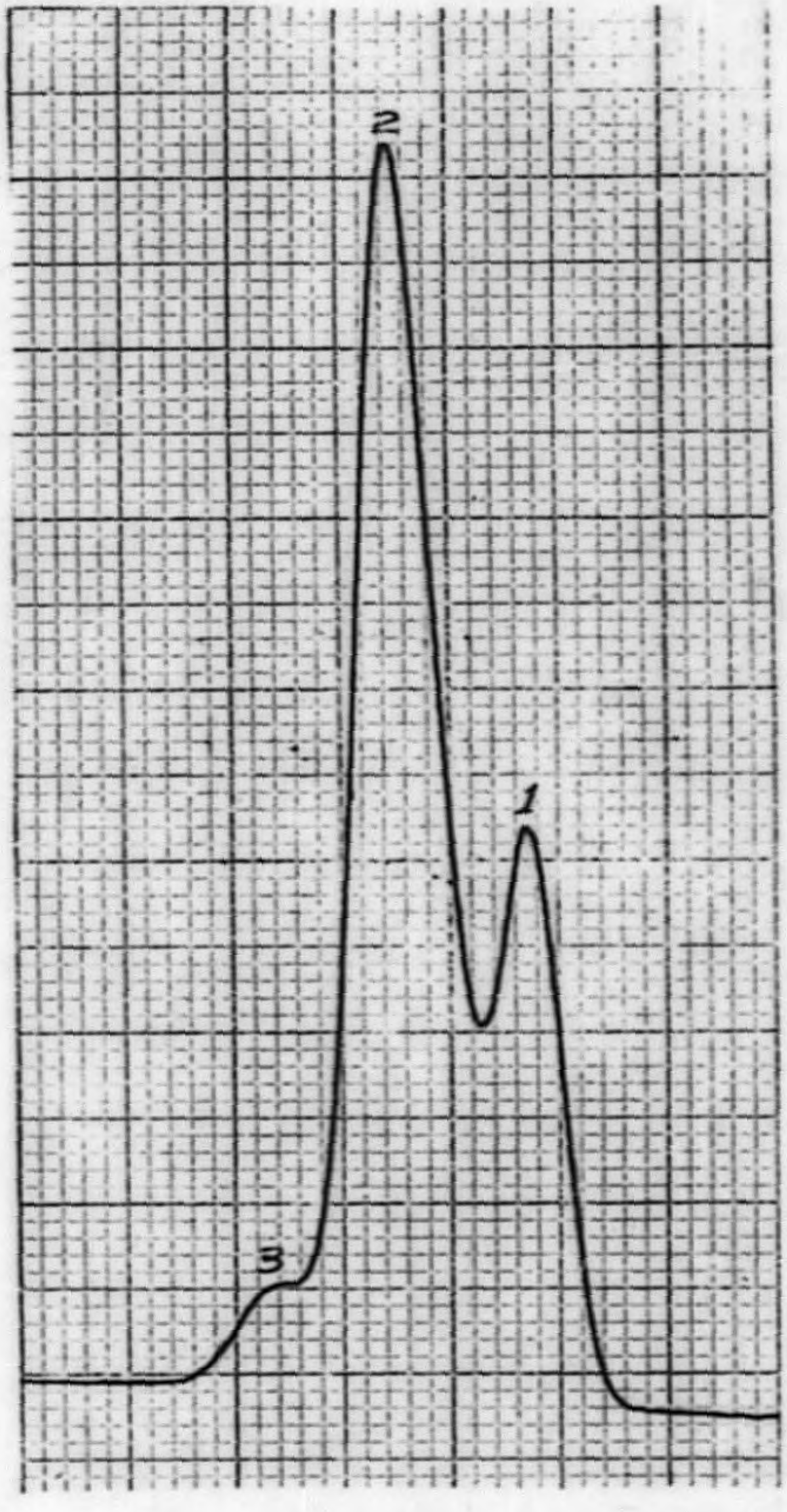
Operating Conditions

1. Solvent: Benzene
2. Sample size: 1 µl
3. Column: 6 ft. Apiezon L
   on Chromosorb W.
4. Column Temp.: 262°C
5. Helium: 60 psig

Peak Legend

1. Trace component
2. 1,3-diphenylcyclohexane
3. 1-phenyl-3-cyclohexyl benzene
4. m-terphenyl

Figure 25. Vapor Phase Chromatogram of m-Terphenyl Reduced With G-13 Copper Chromite Catalyst



Sample No. 1377A

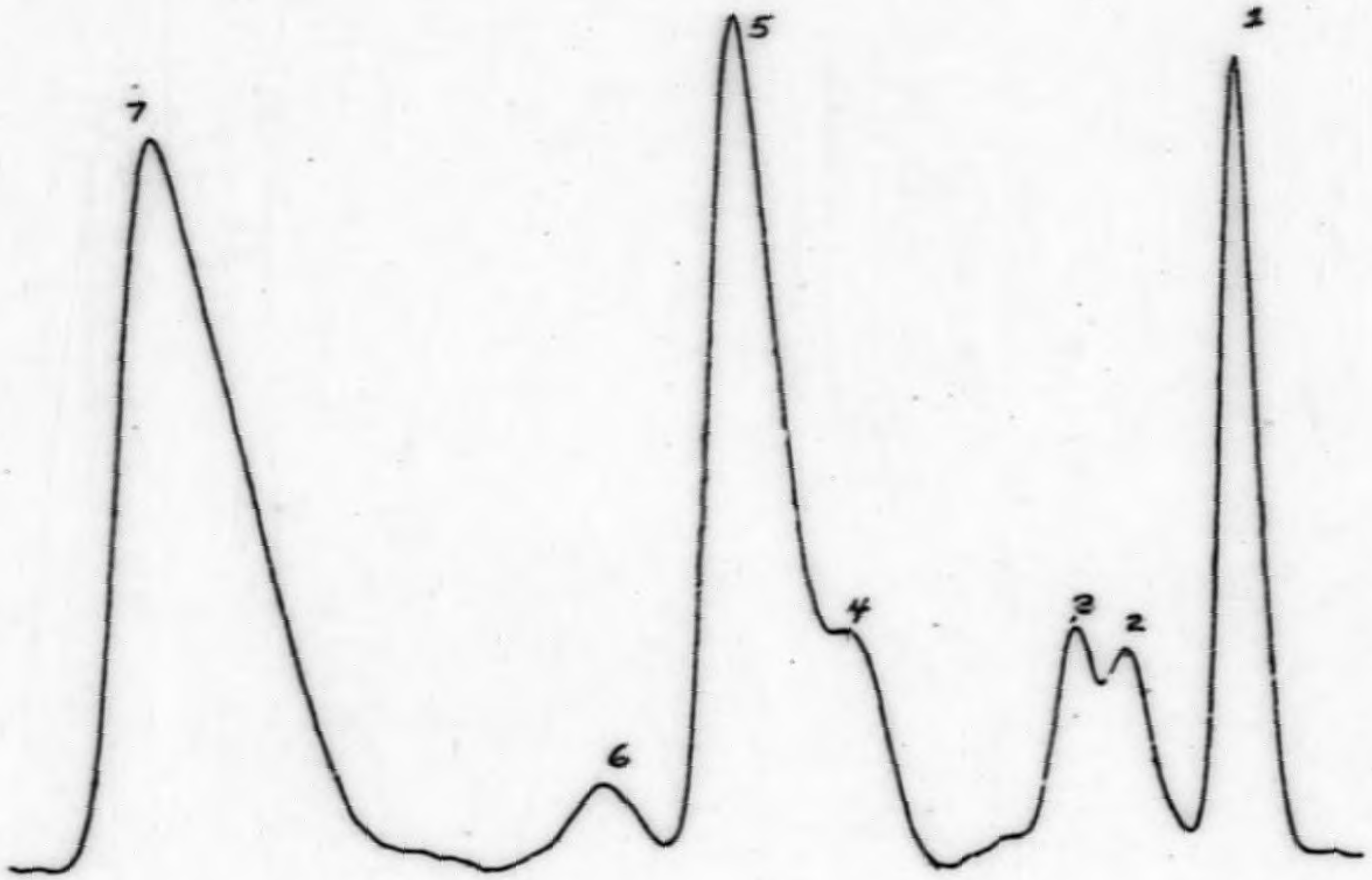
Operating Conditions

Solvent: none
Sample size: 3 µl
Column: 15% 6 ft. Apiezon L
on Chromosorb
Column Temp.: 262°C
Helium: 60 psig

Peak Legend

1. 1,3-Dicyclohexylbenzene
2. 1,3-Diphenylcyclohexane
3. 1-Phenyl-3-cyclohexylcyclohexane

Figure 26. Vapor Phase Chromatogram of m-Terphenyl Reduced with Copper Chromite Catalyst.



Sample No. 6204

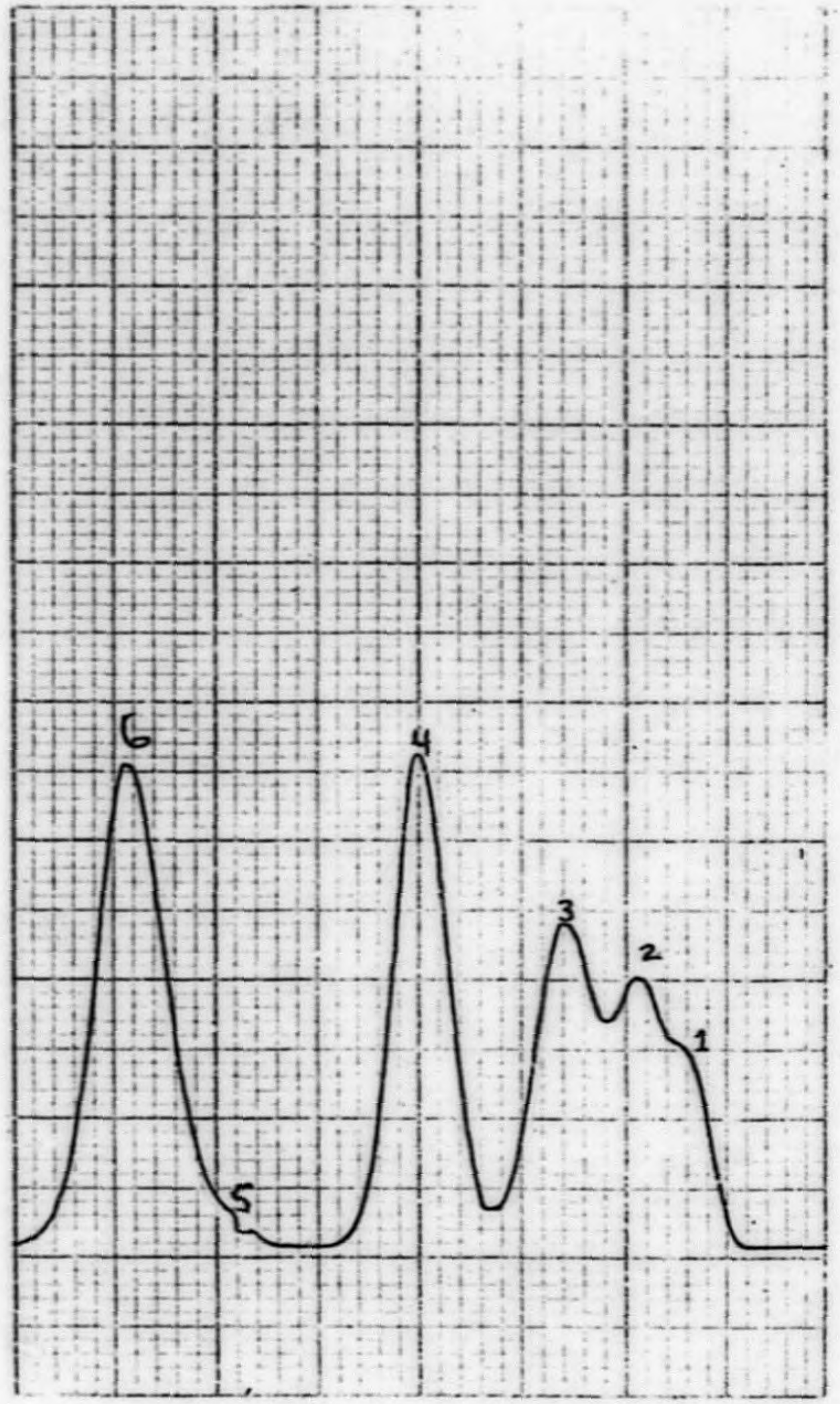
Operating Conditions

Solvent: Tetrahydrofuran
Sample Size: 1½ µl
Column: 6 ft. 5% Polyphenyl ether on Chromosorb P
Column Temp.: 250°C
Helium: 20 psig

Peak Legend

1. m-Tercyclohexyl
2. 1,3-Dicyclohexylbenzene
3. 1-Phenyl-3-cyclohexyl-cyclohexane
4. 1,3-Diphenylcyclohexane
5. 1-Phenyl-3-cyclohexyl benzene
6. 1-Phenyl-3-cyclohexyl benzene
7. m-Terphenyl

Figure 27. Vapor Phase Chromatogram of m-Terphenyl Reduced with Girdler G-49 Nickel Catalyst



Sample No. 30403

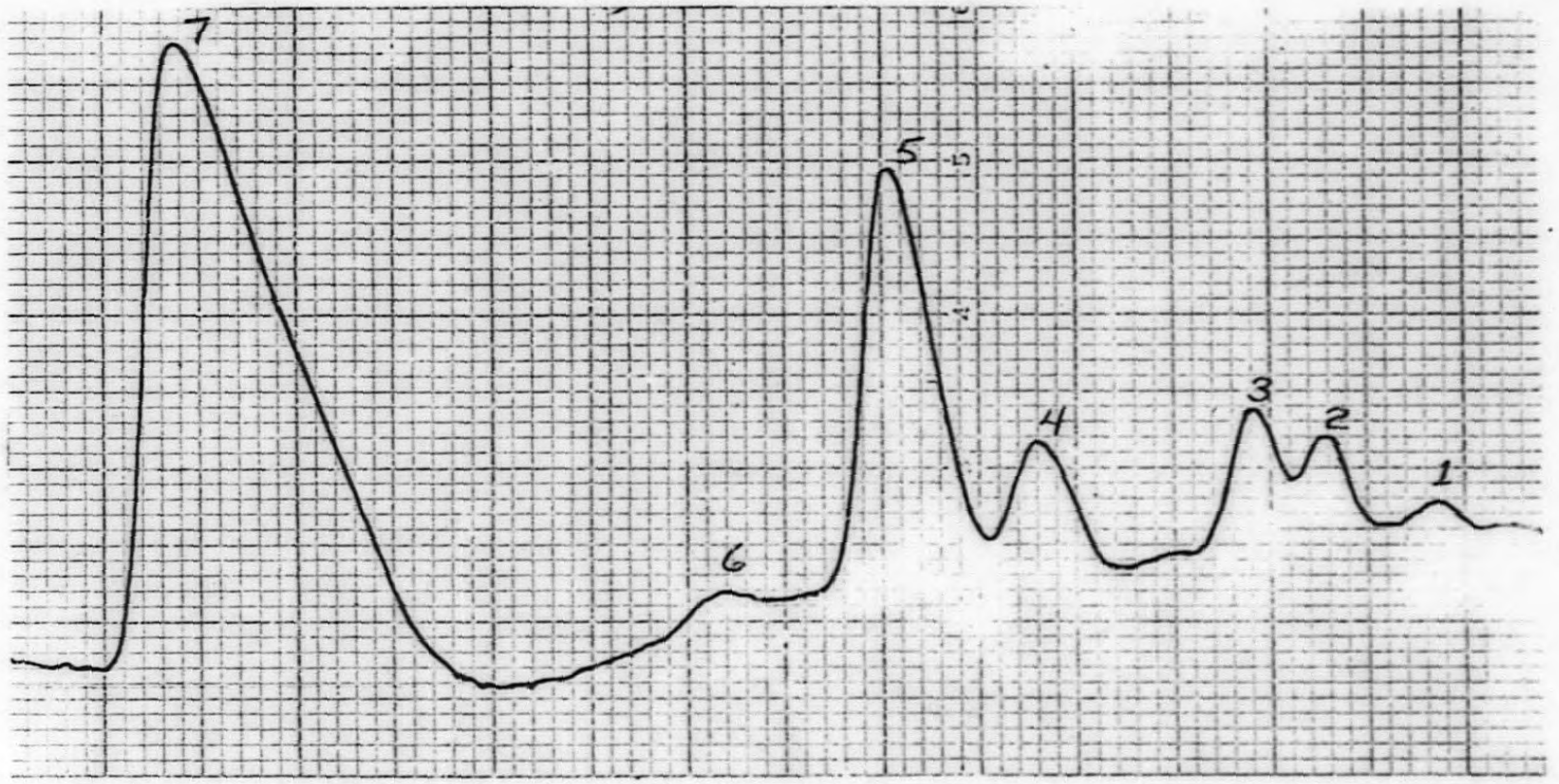
Operating Conditions

1. Solvent: Benzene
2. Sample Size: 2 µl
3. Column: 6 ft. 15% Apiezon L on Chromosorb W.
4. Column Temp: 300 °C
5. Helium: 60 psig.

Peak Legend

1. meta-dicyclohexyl benzene
2. meta-tercyclohexyl
3. 1,3-diphenylcyclohexane
4. 1-phenyl-3-cyclohexyl benzene
5. Trace component
6. meta-terphenyl

Figure 28. Vapor Phase Chromatogram of m-Terphenyl Reduced With G-49 Nickel Catalyst



Sample No. 6207

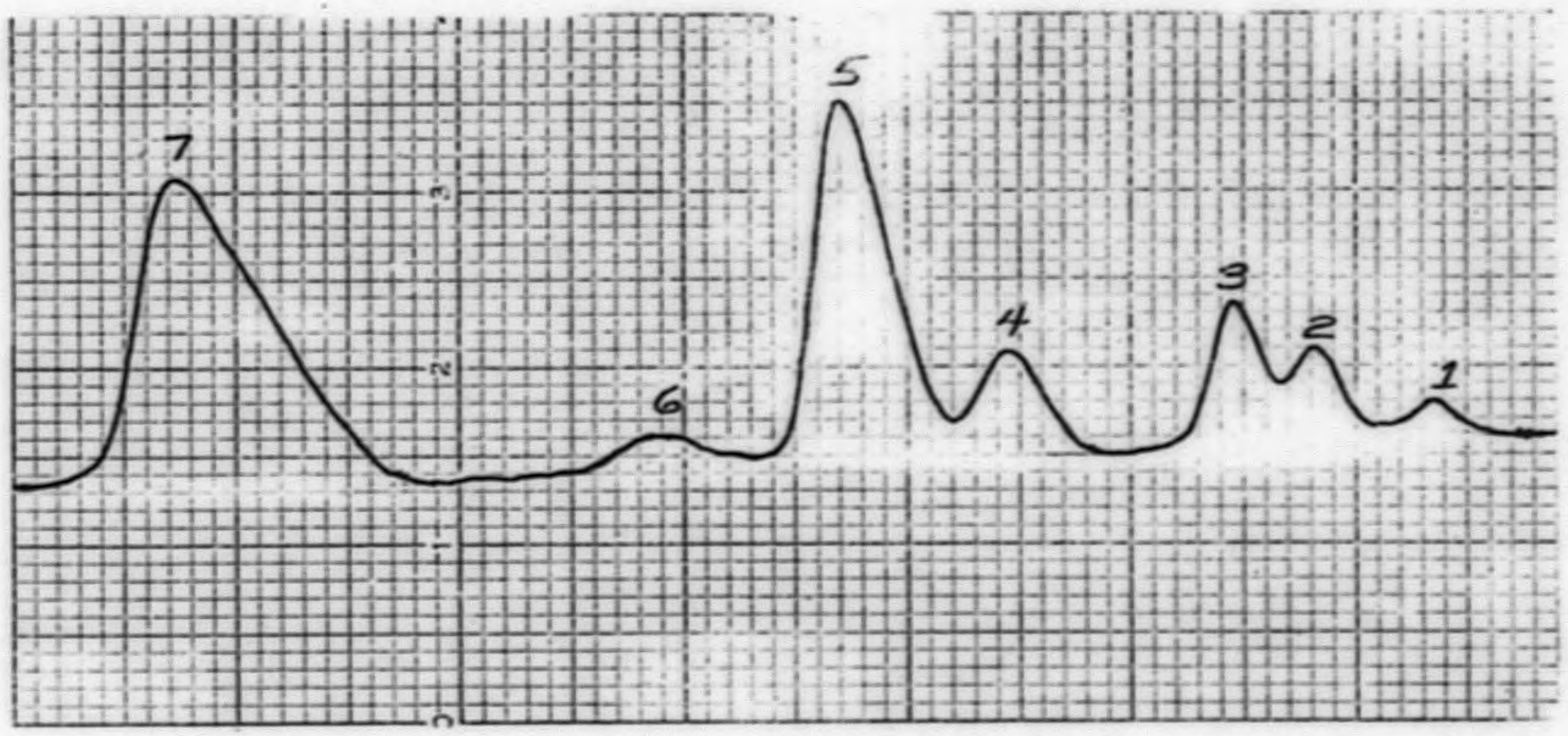
Operating Conditions

Solvent: Tetrahydrofuran
Sample Size: -
Column: 6 ft. 5% Polyphenyl ether
on Chromosorb P
Column Temp.: 250°C
Helium: 26 psig

Peak Legend

1. m-Tercyclohexyl
2. 1,3-Dicyclohexylbenzene
3. 1-Phenyl-3-cyclohexylcyclohexane
4. 1,3-Diphenylcyclohexane
5. 1-Phenyl-3-cyclohexylbenzene
6. Unidentified
7. m-Terphenyl

Figure 29. Vapor Phase Chromatogram of m-Terphenyl Reduced with Harshaw Nickel Catalyst.



Sample No. 6208

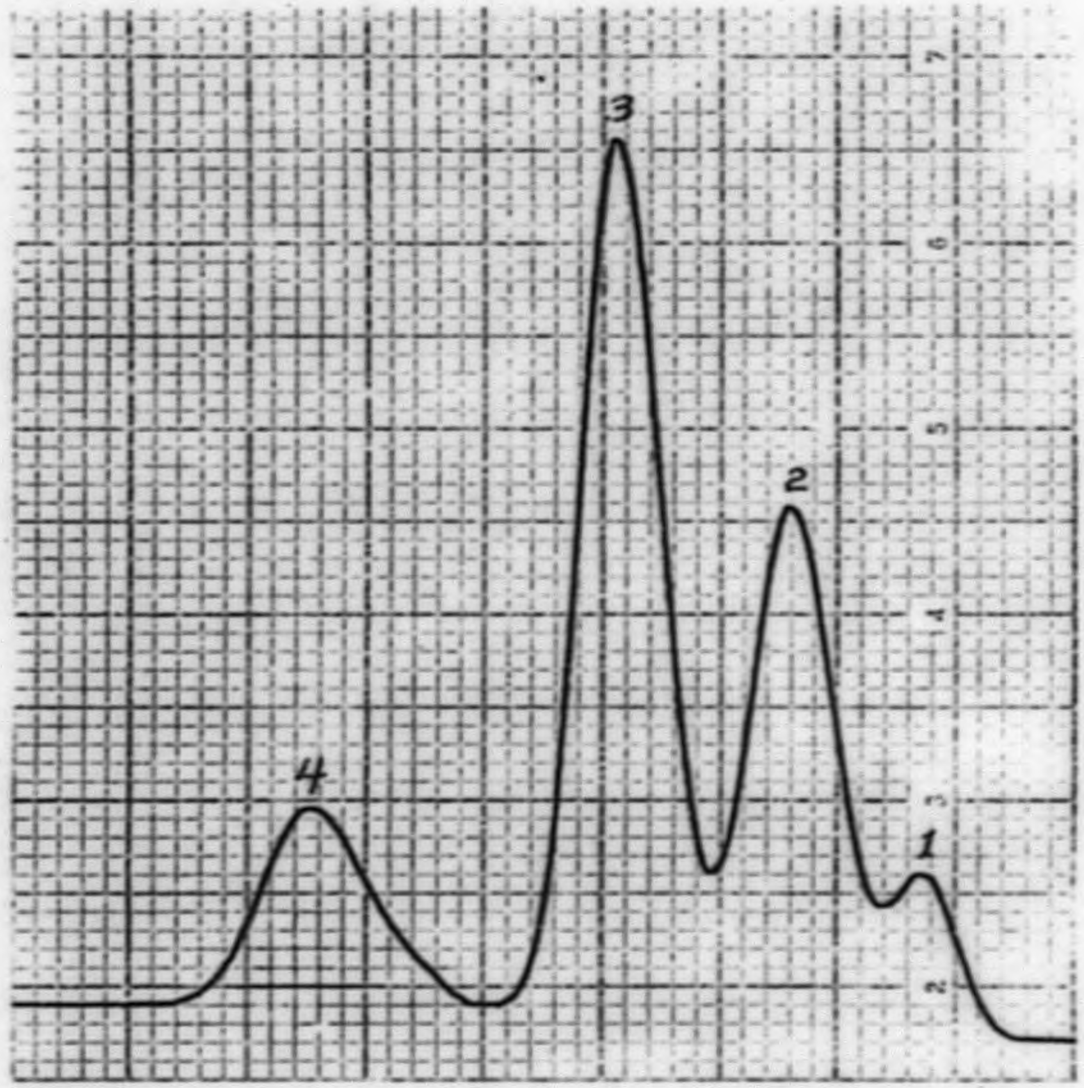
Operating Conditions

Solvent: Tetrahydrofuran
Sample Size: -
Column: 6 ft. 5% Polyphenyl ether
on Chromosorb P
Column Temp.: 250°C
Helium: 26 psig

Peak Legend

1. m-Tercyclohexyl
2. 1,3-Dicyclohexylbenzene
3. 1-Phenyl-3-cyclohexylcyclohexane
4. 1,3-Diphenylcyclohexane
5. 1-Phenyl-3-cyclohexylbenzene
6. Unidentified
7. m-Terphenyl

Figure 30. Vapor Phase Chromatogram of m-Terphenyl Reduced with Harshaw Nickel Catalyst.



Sample No. 4745-1

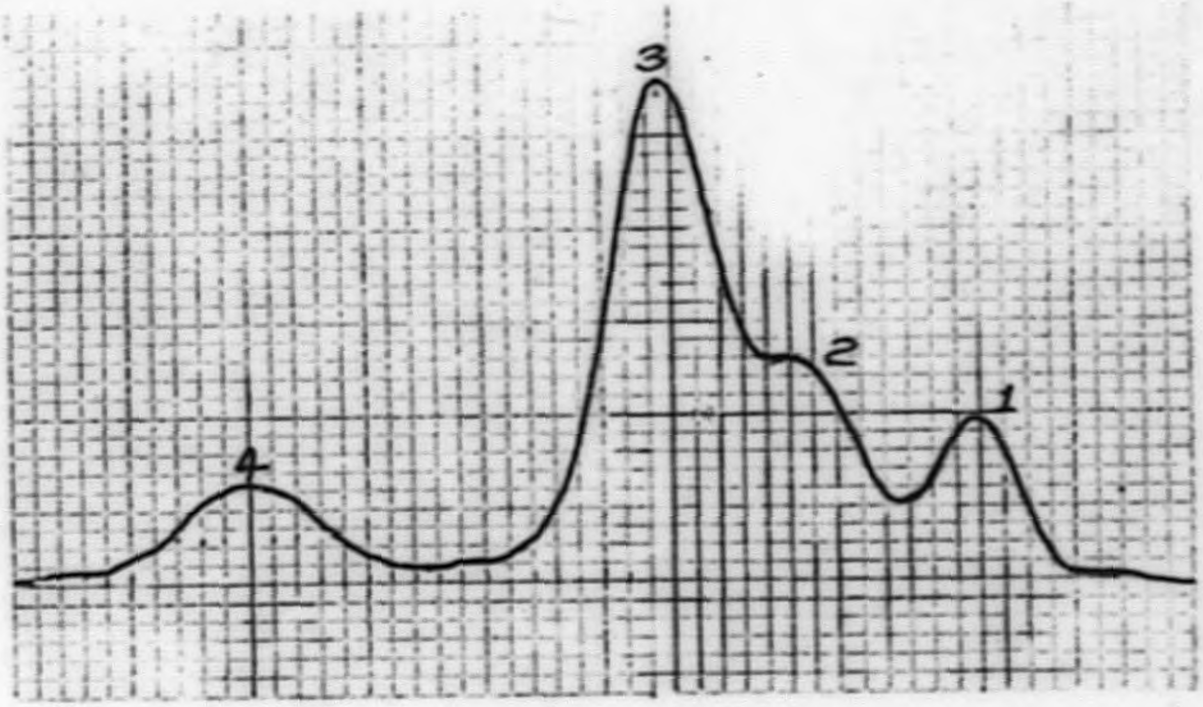
Operating Conditions

Solvent: Tetrahydrofuran
Sample size: 2 µl
Column: 6 ft 15% Apiezon L on Chromosorb P
Column Temp.: 262°C
Helium: 60 psig

Peak Legend

1. m-Tercyclohexyl and 1,3-Dicyclohexylbenzene
2. 1,3-Diphenylcyclohexane and 1-Phenyl-3-cyclohexylcyclohexane
3. 1-Phenyl-3-cyclohexyl benzene
4. m-Terphenyl

Figure 31. Vapor Phase Chromatogram of m-Terphenyl Reduced with Harshaw Nickel Catalyst



Sample No. 4727

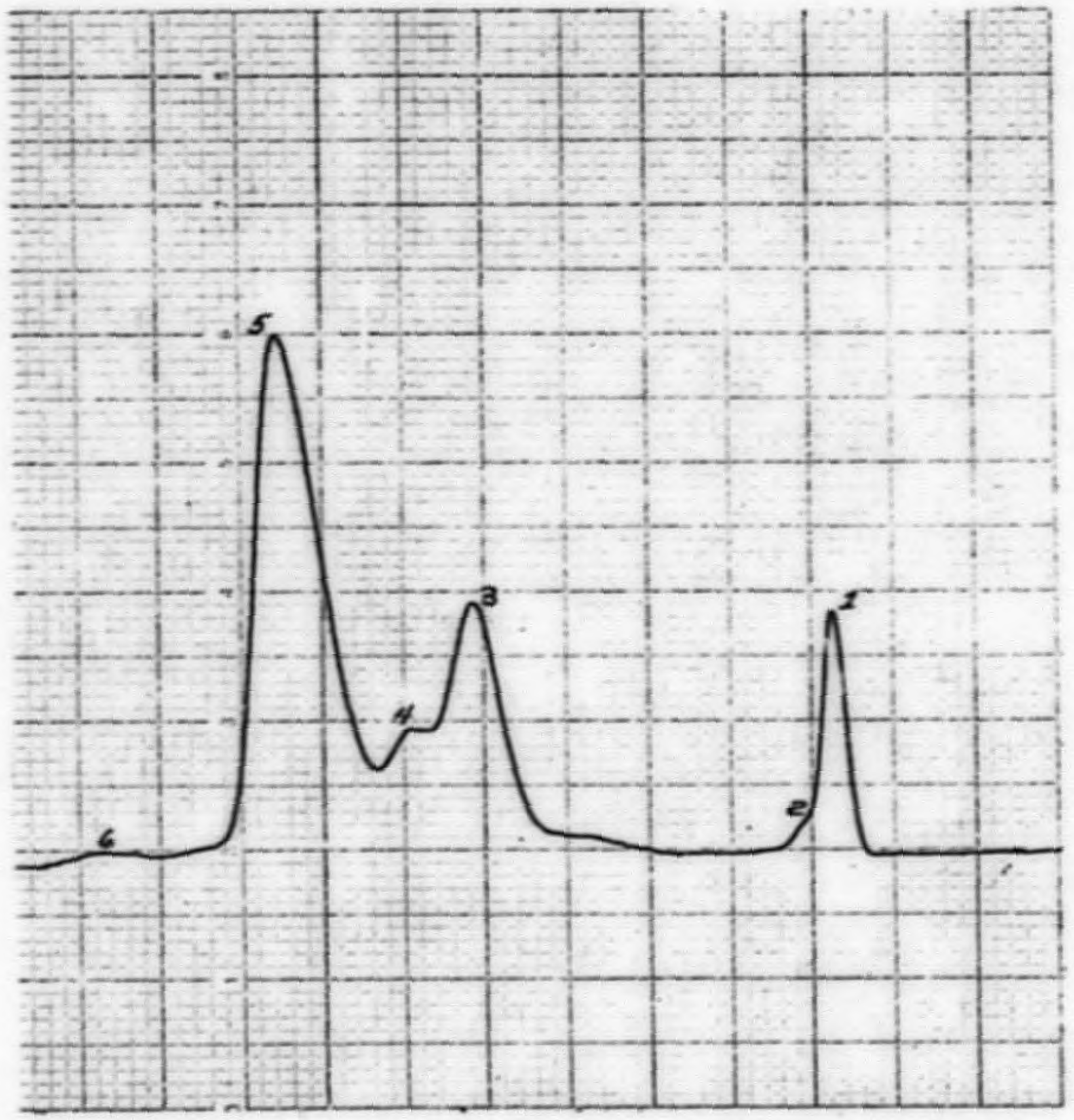
Operating Conditions

Solvent: Nitrobenzene
Sample size: -
Column: 6 ft. 5% Polyphenyl ether
on Chromosorb P
Column Temp.: ~250°C
Helium: 16 psig

Peak Legend

1. 1-Phenyl-4-cyclohexylcyclohexane
2. 1,4-Diphenylcyclohexane
3. 1-Phenyl-4-cyclohexylbenzene
4. p-Terphenyl

Figure 32. Vapor Phase Chromatogram of p-Terphenyl Reduced with Girdler G-13 Copper Chromite Catalyst.



Sample No. 30-28

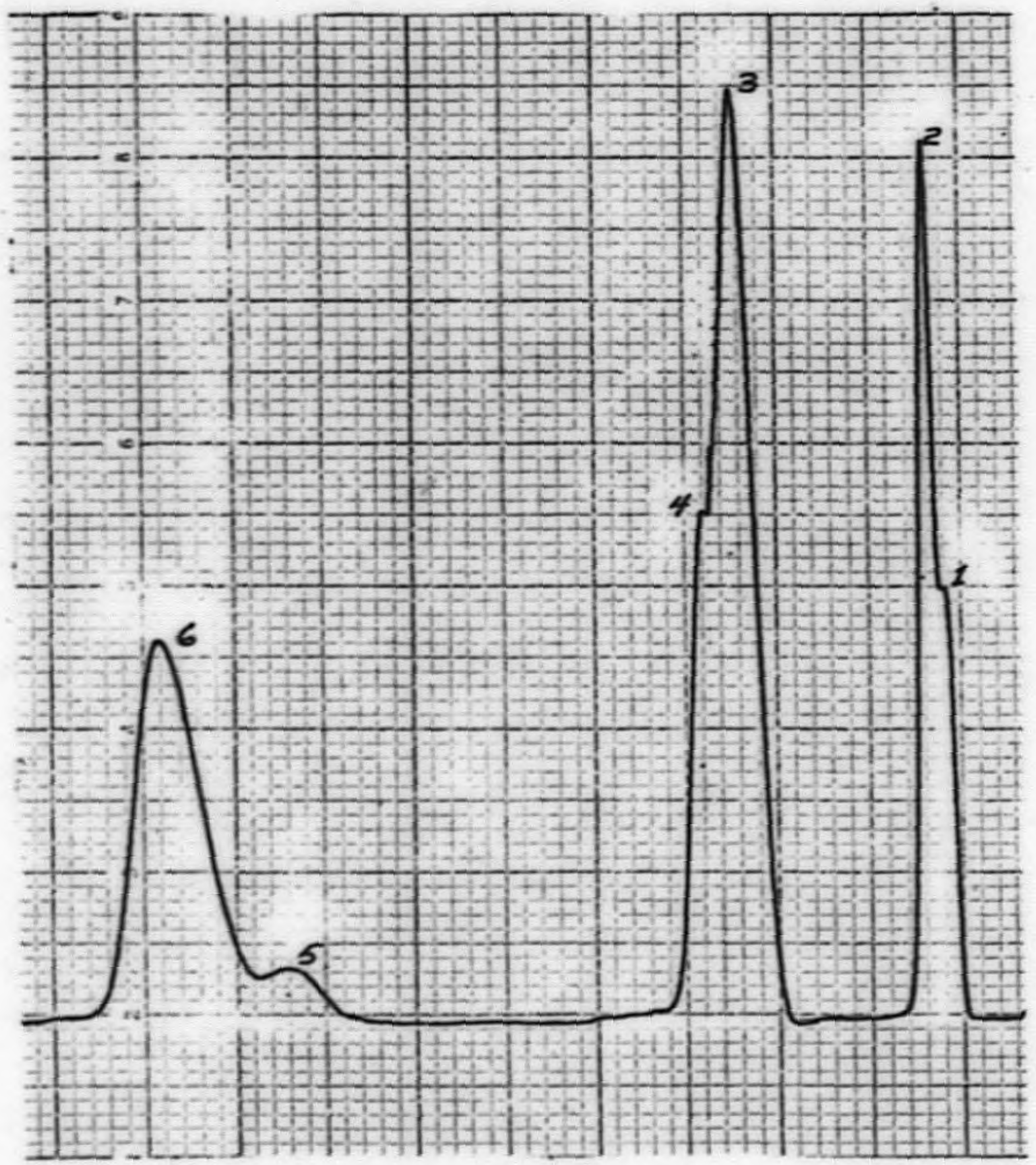
Operating Conditions

1. Solvent: Tetrahydrofuran
2. Sample size: 5 λl
3. Column: 4 ft. 15% Craig polyester succinate on 30-60 mesh Chromosorb
4. Temperature: 210°C
5. Helium: 60 psig

Peak Legend

1. 1,4-dicyclohexyl benzene
2. 1,4-dicyclohexyl benzene
3. 1-phenyl-4-cyclohexylcyclohexane
4. 1,4-diphenylcyclohexane
5. 1-phenyl-4-cyclohexyl benzene
6. Unassigned

Figure 33. Vapor Phase Chromatogram of p-Terphenyl Reduced with Copper Chromite Catalyst



Sample No. 30417

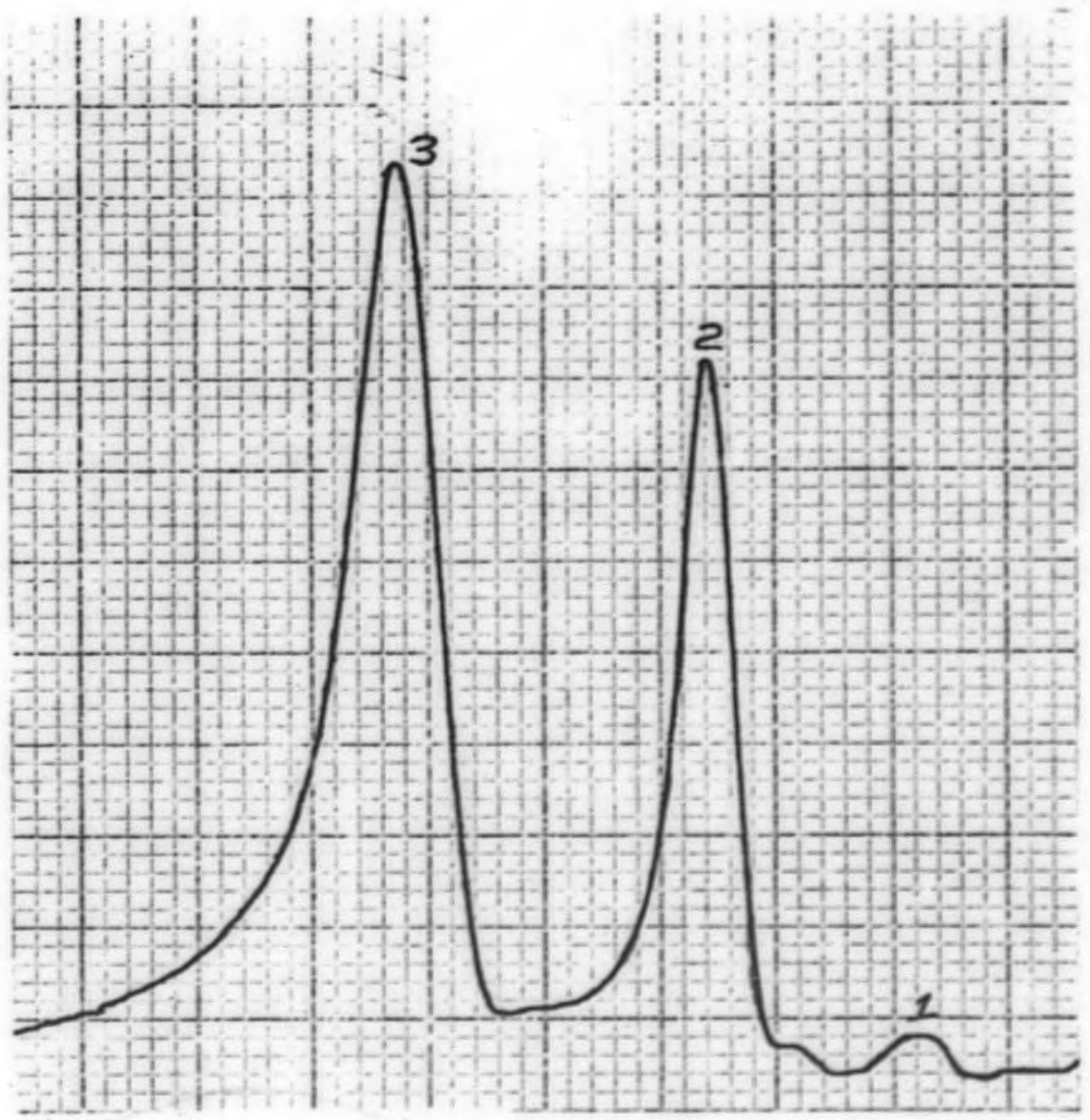
Operating Conditions

1. Solvent: Tetrahydrofuran
2. Sample Size: 5 µl
3. Column: 4 ft. 15% Craig polyester succinate on 30-60 mesh chromosorb
4. Column temp.: 210°C
5. Helium: 60 psig

Peak Legend

1. p-tercyclohexyl
2. p-tercyclohexyl
3. 1,4-dicyclohexyl benzene
4. 1,4-dicyclohexyl benzene
5. 1,4-diphenylcyclohexane
6. 1-phenyl-4-cyclohexyl benzene

Figure 34. Vapor Phase Chromatogram of p-Terphenyl Reduced with G-49 Nickel Catalyst



Sample No. 6206

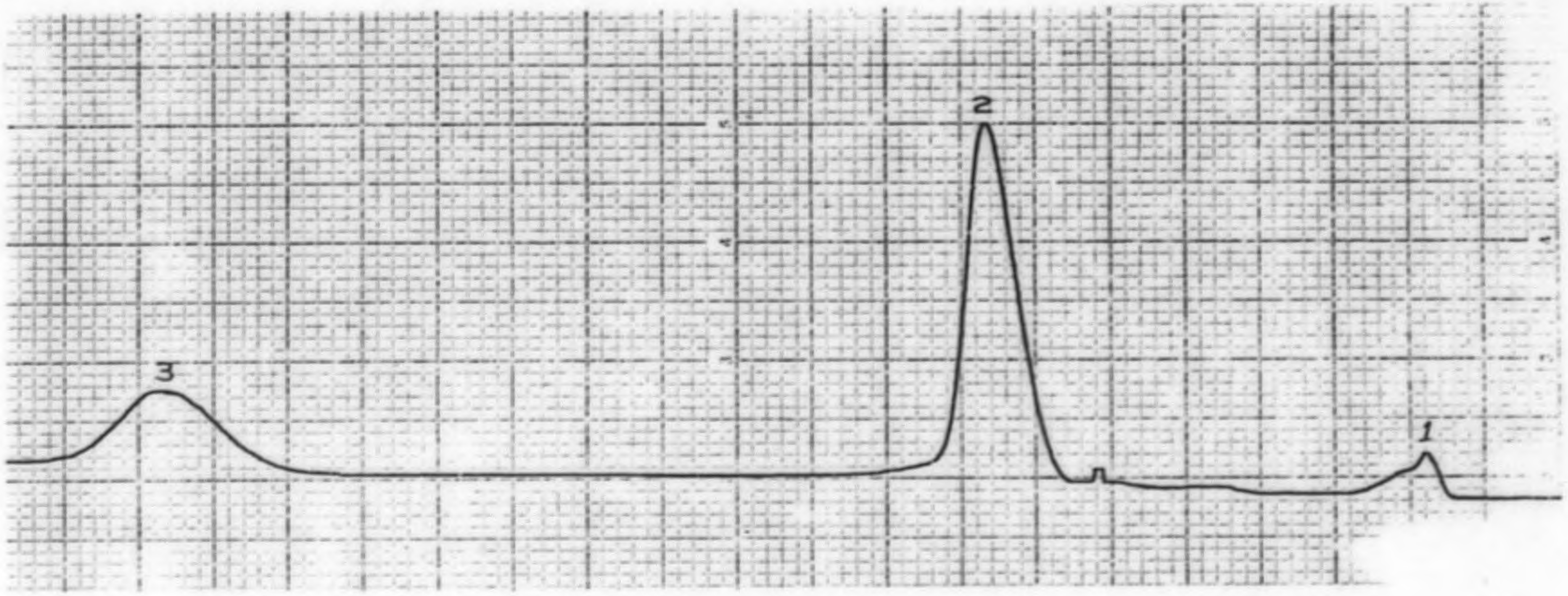
Operating Conditions

Solvent: Tetrahydrofuran
Sample size: -
Column: 6 ft. 10% XE-60 on Diatoport
Column Temp.: 268°C
Helium: 60 psig

Peak Legend

1. Unidentified
2. 1-Phenyl-4-cyclohexylbenzene
3. p-Terphenyl

Figure 35. Vapor Phase Chromatogram of p-Terphenyl Reduced with Harshaw Nickel Catalyst.



Sample No. 6205

Operating Conditions

Solvent: Tetrahydrofuran
Sample Size: 10 µl
Column: 4 ft 10% binary polyester succinate
on Chromosorb
Col. Temp.: 210°C
Helium: 60 psig

Peak Legend

1. Unidentified
2. 1-Phenyl-4-cyclohexylbenzene
3. p-Terphenyl

Figure 36. Vapor Phase Chromatogram of p-Terphenyl Reduced with Girdler G-49 Catalyst.

APPENDIX II

EXPERIMENTAL SYNTHESIS WORK

A. INTERMEDIATES

1. Dihydroresorcinol Ethyl Enol Ether

To a five-liter, three-necked flask equipped with stirring motor and a Dean-Stark trap surmounted by a Fredrichs condenser was added 350 grams of moist dihydroresorcinol (containing 4% sodium chloride as an impurity) and 2315 ml of benzene. The third neck of the flask was equipped with a nitrogen inlet to maintain a nitrogen atmosphere during the drying operation and during the course of the reaction. The dihydroresorcinol-benzene solution was refluxed while stirring to remove water. After 50 ml water was removed (leaving about 286 grams, 2.55 moles of dihydroresorcinol), 535 ml (9.17 moles) of absolute ethanol and 11.7 grams of practical grade p-toluenesulfonic acid were added. Stirring at reflux was continued until 42.5 ml water was collected (10 hours). The reaction mixture was cooled to room temperature and washed with 1080 ml of a cold, saturated solution of sodium bicarbonate. The organic layer was then washed with four 250-ml portions of ice cold 1M potassium carbonate solution followed by washes with ice water until neutral. All aqueous washes were saved and subsequently extracted with ether. Both the benzene and ether solutions were dried over anhydrous magnesium sulfate. These solutions were then concentrated in a rotary evaporator and subsequently distilled through a Vigreux column. The major fraction boiled between 65-67°C at 0.35-0.45 mm Hg yielding 220.2 grams of a nearly colorless liquid, $n_D^{20} = 1.5052$ [(ref. 34), $n_D^{25} = 1.5057$ and 1.5040]. The ether extract yielded an additional 11.1 g boiling at the same temperature and pressure. The yield based on pure dihydroresorcinol was 64.7%. The purity of the product was 98.5 area-% as determined by gas chromatography.

2. 3-Phenylcyclohex-2-enone

To a three-liter, four-necked flask equipped with stirring motor, reflux condenser (protected with a calcium sulfate drying tube), a 500-ml pressure-equalizing dropping funnel with nitrogen inlet adapter and a thermometer was added 54.5 g (2.22 moles) magnesium turnings. The system was heated with a low Bunsen flame to drive off adsorbed moisture. Anhydrous ether (750ml) was added followed by a dropwise addition of 40 ml of bromobenzene (reagent grade). Refluxing for fifteen minutes initiated formation of the Grignard reagent, after which the remaining bromobenzene (2.42 moles total) was added dropwise over a two-hour period. Dihydroresorcinol ethyl enol ether (171.3 g, 1.22 moles) dissolved in 630 ml of anhydrous ether was added dropwise to the reaction flask over a three-hour period, while maintaining temperature of the reaction mixture between 5 and 10°C. At the end of this time, the reaction was allowed to reflux with stirring for one-half hour. The reaction mixture was then cooled and one liter of 1.7 M sulfuric acid was added slowly with stirring and cooling with an ice bath. After hydrolysis the mixture was steam distilled until 3.6 liters of distillate containing the excess bromobenzene and some biphenyl was collected. The distilland, which consisted of a heavy red oil and an aqueous phase, was separated. The water layer was extracted with ether and the ether extract combined with the oily material. This solution was washed three times with 5% sodium bicarbonate solution and then with water and dried over anhydrous magnesium sulfate. The ether solution was concentrated and the residue distilled through a Vigreux column. The major fraction (133.4 g, 71.7% yield) boiling between 121-124°C at 0.6 mm Hg was collected. The distillate was a viscous, pale-yellow oil that crystallized on standing, mp 63-65°C (literature ref. 35, 63-65°C). Vapor phase chromatography showed 97 area-% purity. The infrared spectrum was consistent with the 3-phenylcyclohex-2-enone structure.

3. 3-Bromoethylbenzene

A 300-ml, 3-necked flask was equipped with a reflux condenser and thermometer. To the flask was added 25.2 g (0.127 mole) of 3-bromoacetophenone (reagent grade), 140 ml of diethylene glycol (practical), 12 ml of 85% hydrazine hydrate solution (0.21 mole hydrazine), and 17.5 g (0.3 mole) potassium hydroxide. The reaction mixture was refluxed at a pot temperature of 136°C for 1.5 hours. A Dean-Stark trap was placed between the reaction vessel and condenser, and refluxing was continued with subsequent removal of water and product until the reaction temperature reached 195°C. The reaction mixture was allowed to reflux for an additional three hours. The reaction mixture was then cooled, neutralized with 200 ml of dilute hydrochloric acid, and the heavy oil product separated. The water diethylene glycol layer was then extracted with benzene and these extracts combined with the oil and distillate (collected in the Dean Stark trap). The benzene solution was dried over anhydrous magnesium sulfate, concentrated, and the residue distilled. The major fraction boiled between 78-80°C at 11 mm Hg and amounted to 18 grams (76.5% yield). Vapor phase chromatography showed it to be 99.6 area-% pure with no starting 3-bromoacetophenone present. The infrared spectrum was consistent with 3-bromoethylbenzene structure.

B. MODEL COMPOUNDS

1. 4-Ethylbiphenyl

A 2-liter, 3-necked flask was equipped with a Dean-Stark trap (surmounted by a reflux condenser), stirrer and thermometer. To the flask was added 95.2 g (0.486 mole) of 4-acetylbiphenyl (reagent), 900 ml of reagent grade diethylene glycol, 62.7 g of 85% hydrazine hydrate solution (1.06 moles hydrazine), and 53.2 g (1.33 moles) sodium hydroxide. The reaction mixture was heated slowly with stirring to reflux (~130°C). As copious quantities of hydrazone formed, the stirrer was turned off since the stirring action promoted rapid decomposition of the hydrazone resulting in solid being carried up into the Dean-Stark trap. The hydrazone was then slowly decomposed by removal of water till the reaction temperature reached 200°C. Refluxing was then continued for an additional two hours. After cooling, the reaction mixture was extracted with three 200-ml portions of benzene. The benzene solution was washed with 5% hydrochloric acid followed by several washings with water and then was dried over anhydrous magnesium sulfate. The solution was concentrated and the residue distilled using a Vigreux column. The major fraction boiled between 116-118°C at 2.0 - 2.4 mm Hg and amounted to 74.6 grams (85.5% yield). Vapor phase chromatography showed it to be 99.5 area-% pure with no starting 4-acetylbiphenyl present. The infrared spectrum was consistent with the structure of 4-ethylbiphenyl. The compound is a white solid at room temperature, melting at 33-34°C (lit. mp = 34°C, ref. 36). Analysis: Calc'd for $C_{14}H_{14}$: C, 92.3; H, 7.7. Found: C, 92.4; H, 7.6.

2. <u>1-(4-Xenyl)-4-methylcyclohexanol-1 (Precursor to 4-methyl-p-terphenyl)</u>

To a 500-ml, 3-necked flask equipped with a dropping funnel, nitrogen inlet, stirrer, and reflux condenser was added 3.2 g (0.133 g-atom) magnesium turnings, and 100 ml tetrahydrofuran (previously distilled from calcium hydride). The dropping funnel was charged with 30.0 g (0.129 mole) of 4-bromobiphenyl dissolved in 120 ml tetrahydrofuran. About one-fourth of this charge was added to the reaction flask and the reaction mixture stirred and heated to reflux under a nitrogen atmosphere. After reaction had started (as evidenced by darkening and a mild exotherm), the remaining charge was added dropwise over a period of one-half hour at reflux temperature. The reaction mixture was then refluxed with stirring for an additional 45 minutes. At the end of this time, the Grignard reagent was cooled with an ice bath and a solution of 11.4 g (0.102 mole) 4-methylcyclohexanone in 100 ml tetrahydrofuran was added dropwise over a one-hour period while stirring and maintaining the reaction temperature at 5-10°C. The reaction mixture was then refluxed for one-half hour, cooled to room temperature, and poured into a saturated ammonia chloride-ice mixture (-5°C). After separating the two layers, the cloudy water layer was extracted twice with ethyl ether and the extracts were added to the organic layer. This solution was dried over anhydrous magnesium sulfate and concentrated to yield 25 grams of a yellowish solid. Vapor phase chromatography of this solid showed that it contained 17 grams of the alcohol (64% yield) and 8 grams biphenyl. Trituration of 2 grams of this material with petroleum ether, followed by recrystallization of the triturated material from petroleum ether yielded 1.0 gram white needles, m.p. 119-120°C. Analysis: Calc'd for $C_{19}H_{21}O$: C, 86.1; H, 8.0. Found: C, 86.0; H, 8.4.

3. 1-(4-Xenyl)-4-methylcyclohexene-1 (Precursor to 4-methyl-p-terphenyl)

A solution of 129 grams of crude 1-(4-xenyl)-4-methylcyclohexanol (containing about 25 grams biphenyl) in 150 ml benzene was charged to a one-liter 3-necked flask equipped with a thermometer, stirrer, Dean-Stark trap and condenser. A small crystal of iodine was added and the reaction mixture was stirred and heated to reflux. As benzene was distilled from the reaction vessel to the trap, the temperature of the flask contents gradually rose from 90 to 130°C, at which time dehydration started as evidenced by appearance of water in the trap. After 7.5 ml water was collected (95.5% theoretical), the reaction mixture was allowed to cool and 500 ml of 10% sodium thiosulfate solution was added with vigorous stirring. The organic layer was then separated, dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The resulting oily residue was distilled to remove biphenyl. A 10-gram portion of the residue was dissolved in petroleum ether, decolorized with charcoal and the solution of mono-olefin in petroleum ether cooled to yield 5.5 g of white fluffy plates, mp 128.5 - 130°C. An additional 2.1 g was obtained in second and third crops. Vapor phase chromatography showed the first crop to be 99 area-% pure, and an infrared spectrum was consistent with the structure of the olefin showing an absorption band for the double bond region. The olefin was free of alcohol as was shown by the absence of a hydroxyl band. Analysis: Calc'd for $C_{10}H_{19}$: C, 92.3; H, 7.7. Found: C, 92.0; H, 8.1.

3a. 1-(4-Xenyl)-4-methylcyclohexane

Ten grams (0.0405 mole) of 1-(4-xenyl)-4-methylcyclohexene-1 suspended in 190 ml ethanol-cyclohexane (50:50 by volume) was reduced in the presence of 1.5 g 5% palladium on charcoal using a Parr shaker at an initial hydrogen pressure of 49 psig. The final pressure after two hours was 47 psig (room temperature). The reaction mixture was filtered and the filtrate concentrated on a rotary evaporator to yield 9.7 grams of a nearly colorless oil which crystallized when diluted with a small amount of petroleum ether and allowed to stand in the cold. The resultant solid cake was broken up and dried in a vacuum desiccator to yield 9.5 grams of a white powder, mp = 55-59°C. The vapor phase chromatogram of a sample of this material showed two partially resolved peaks (65 and 35 area-%). The infrared spectrum of the entire sample and the 65 area-% component were consistent with the structure of 1-(4-xenyl)-4-methylcyclohexane. No attempt was made to collect the 35 area-% component. The UV spectrum of the entire sample also was identical with the UV spectrum of the disproportionation product isolated from catalytic dehydrogenation of 1-(4-xenyl)-4-methylcyclohexene-1 (see below). Analysis: Calc'd for $C_{19}H_{21}$: C, 91.5; H, 8.5. Found: C, 91.3; H, 8.8.

From the above data, it was concluded that the sample was a mixture of cis- and trans-stereoisomers of 1-(4-xenyl)-4-methylcyclohexane.

3b. 4-Methyl-p-terphenyl (1-(4-xenyl)-4-methylbenzene) (By catalytic dehydrogenation with palladium on charcoal)

Five grams of crude 1-(4-xenyl)-4-methylcyclohexene-1 (free of biphenyl) was dissolved in 30 ml p-cymene and charged to a 100-ml, 2-necked round-bottom flask containing 2.0 g 5% palladium on charcoal. The flask was fitted with a reflux condenser and nitrogen bleed. The contents were refluxed for four hours, filtered hot, and then allowed to cool with resulting deposition of yellow-white crystals. These were filtered and recrystallized from benzene-petroleum ether to yield gray-white crystals, mp 208-209°C (lit. mp = 207°C, ref. 37). The infrared spectrum was consistent with the structure of 4-methyl-p-terphenyl. Analysis: Calc'd. for $C_{19}H_{16}$: C, 93.4; H, 6.6. Found: C, 93.4; H, 6.6.

This experiment was carried out on a larger scale using 60 grams of 1-(4-xenyl)-4-methylcyclohexene-1 in 200 ml p-cymene and 10 g 5% palladium on charcoal. After refluxing for eight hours, the reaction mixture was filtered and p-cymene was removed by distillation in a simple still at about 90°C head temperature and 45 mm Hg. The solid product remaining was slurried in 200 ml warm benzene, chilled in ice water, and then filtered to yield 26.3 grams of a damp white solid. Further concentration of the benzene solution yielded an additional 3.0 grams of material. These solids were combined and recrystallized from benzene to give 22.3 grams of 4-methyl-p-terphenyl, mp = 209-210°C.

The remaining benzene filtrate was concentrated in the rotary evaporator to yield an orange red oil, which was diluted with an equal amount of petroleum ether. The resulting solution was chilled to yield fluffy plates which were recrystallized from petroleum ether to give 10.6 grams of product, mp = 90.5 - 94°C. This compound was identified by its infrared and ultraviolet spectra as 1-(4-xenyl)-4-methylcyclohexane. The spectra obtained were identical with those obtained from the hydrogenation product of 1-(4-xenyl)-4-methylcyclohexene-1. Vapor phase chromatography showed it to be 97.6 area-% pure with the remaining 2.4% being 4-methyl-p-terphenyl. Only one isomer of the cyclohexane derivative was resolved on the gas chromatogram.

3c. Dehydrogenation with Chloranil

To a solution of 40.1 grams (0.16 moles) of 1-(4-xenyl)-4-methylcyclohexene-1 in 350 ml Eastman reagent p-xylene was added 80.2 grams (0.32 moles) reagent grade chloranil. The wine red solution was refluxed for ten hours. The cooled semisolid was slurried in additional xylene, filtered to remove tetrahydrochloranil and the filtrate diluted with ether. This solution was washed with three 500-ml portions of 5% sodium hydroxide solution, followed by water washes until neutral. The solution was then dried over anhydrous magnesium sulfate, filtered and concentrated to yield a viscous oil. Trituration of this oil with petroleum ether gave 16 grams of white 4-methyl-p-terphenyl. Additional material was obtained by further concentration. One recrystallization of the crude material from benzene-ethanol gave 20 grams of 4-methyl-p-terphenyl, mp 209-210°C.

3d. Attempted Vapor Phase Catalytic Dehydrogenation

A specially adapted dropping funnel, electrically trace heated and surmounting a quartz reaction tube, was charged with 21.7 grams 1-(4-xenyl)-4-methylcyclohexene-1. The reaction tube (18" x 1 1/4") packed with 0.6% platinum-silica catalyst was enclosed in an electric furnace. The reaction tube was held at 500°C while the molten reactant was added dropwise (100 minutes) to the reaction zone in the presence of hydrogen so that the reaction contact time was about 20 sec. A total of 13.9 grams solid product condensed in the first product receiver. About 0.75 ml of a liquid (probably benzene) was noted in the Dry Ice trap following this receiver and about 1 ml liquid in the following liquid nitrogen trap. This latter liquid boiled far below room temperature and was presumably methane. The solid product was shown by vapor phase chromatography to contain 70% p-terphenyl and about 30% 4-methyl-p-terphenyl.

4. 3-Methyldihydro-m-terphenyl, [1-(3-tolyl)-3-phenylcyclohexadiene-1,3]

A four-necked flask equipped with reflux condenser, dropping funnel, stirring motor, and thermometer was charged with 15.8 g (0.66 mole) of magnesium turnings. The system was flamed out, and 450 ml of anhydrous ether was added through the dropping funnel. 3-Bromotoluene (120 g, 0.70 mole) was charged to the dropping funnel and about one-fourth was added to the flask to initiate the Grignard preparation. The reaction was begun only after addition of a small amount of ethyl bromide. After preparation of the Grignard reagent was complete (2 hours), 3-phenylcyclohex-2-enone, 59.5 g (0.346 mole) dissolved in 500 ml of anhydrous ether was added dropwise with stirring (one hour) while maintaining the temperature at 20°C When the addition was complete, the reaction mixture was stirred at reflux for 30 minutes. Upon cooling, 380 ml of 9.5% sulfuric acid solution was slowly added while maintaining the flask contents at 5-10°C with cooling and stirring. The ether layer was separated and washed three times with 250-ml portions of 5% potassium carbonate solution followed by water washes until neutral. After the ether solution was dried over anhydrous magnesium sulfate, it was concentrated in a rotary evaporator, and the residue was then distilled. A forerun containing bromotoluene, biphenyl and 3,3'-dimethylbiphenyl was collected. The major fraction boiled between 160-168°C at 0.3 mm Hg.

A total of 64.5 grams representing a crude yield of 75.8% of 3-methyldihydro-m-terphenyl was collected. (Vapor phase chromatography indicated that part of the dihydroterphenyl derivative had dehydrogenated thermally to 3-methyl-m-terphenyl during distillation.

5. 3-Methyl-m-terphenyl [3-(3-xenyl)-toluene]

a. Dehydrogenation with Palladium on Charcoal

A solution of 215 g of crude 3-methyldihydro-m-terphenyl (prepared as described above) in 500 ml p-cymene was added to a 1-liter, 2-necked flask equipped with a reflux condenser and nitrogen bleed. Twenty-two grams of 5% palladium on charcoal was added to the solution. The reaction mixture was refluxed for three hours while bubbling nitrogen through to sweep out the hydrogen and prevent disproportionation. The reaction mixture was then cooled, filtered, and the filtrate was distilled to remove solvent. The residue was fractionated to yield 35 g of pure 3-methyl-m-terphenyl (98% pure as determined by vapor phase chromatography), bp 169-171°C/0.25 mm Hg. Several fractions (116.5 g) containing varying amounts of 3-methyl-m-terphenyl were collected at the temperature range 100-168°C/0.25 mm Hg. Analysis: Calc'd. for $C_{19}H_{16}$: C, 93.4; H, 6.60. Found: C, 93.3; H, 6.5.

b. Vapor Phase Catalytic Dehydrogenation

Six cuts from the distillation of 3-methyl-m-terphenyl above, totaling 82.4 grams, were combined. These cuts contained two components - 3-methyl-m-terphenyl and 1-(3-tolyl)-3-phenylcyclohexane - in varying proportions. The combined cuts, containing 62.6% 3-methyl-m-terphenyl, were charged to a specially adapted dropping funnel surmounting a Vycor reaction tube (18" x 1 1/4") which in turn was enclosed in an electric furnace. The reaction tube, packed with 1% platinum-alumina catalyst was maintained at 500°C under an atmosphere of hydrogen while the reactant was added over a period of 4 hours and 30 minutes (ca. 20 seconds contact time). A total of 74.1 grams was collected in the first receiver attached to the reaction tube. A small amount (<2 ml) of a colorless liquid (presumably benzene and/or toluene) was collected in a Dry Ice trap connected in series with this receiver. About 0.5 ml of a liquid boiling below room temperature was found in a liquid nitrogen trap which followed the Dry Ice trap. This was not analyzed, but was presumably methane. Distillation of the main product yielded 45.3 grams of material boiling between 150.5 - 152°C/0.10 mm Hg, shown by vapor phase chromatography to contain a 96 area-% component.

It was identified as 3-methyl-m-terphenyl by infrared analysis.

6. 3-Ethyl-m-terphenyl[3-(3-xenyl)-ethylbenzene]

A 500-ml, 4-necked flask was equipped with a stirrer, dropping funnel, nitrogen inlet, thermometer, and Friedrichs condenser, protected with a calcium sulfate drying tube. To the flask was added 100 ml anhydrous ether and 5.0 g (0.206 g-atom) magnesium turnings. About one-fourth of a solution of 3-bromoethylbenzene

(37.2 g, 0.20 mole) in 70 ml anhydrous ether was added to the reaction flask and stirring and heating was started. The Grignard reagent formation began in about ten minutes and the remaining charge in the dropping funnel was added over a one-hour period with stirring at reflux temperature. The reaction mixture was then cooled to 10°C and a solution of 30.0 g (0.174 mole) 3-phenylcyclohex-2-enone in 200 ml anhydrous ether was added dropwise with stirring and cooling over a one-hour period. When addition was complete, the reaction mixture was refluxed with stirring for 30 minutes, and then allowed to stand for one hour. The reaction mixture was then poured with stirring into 200 ml of 10% sulfuric acid solution containing ice. The ether layer was separated and washed three times with 200-ml portions of 5% sodium bicarbonate solution followed by water washes until neutral. After the ether solution was dried over anhydrous magnesium sulfate, it was concentrated on the rotary evaporator to yield a viscous yellow-orange semisolid. This material showed no evidence of a hydroxyl band in the infrared.

Into a 500 ml, 2-necked round-bottom flask (equipped with a reflux condenser and nitrogen inlet) containing a solution of the crude diene in 150 ml p-xylene was added 5.0 g 5% palladium on charcoal. After refluxing for 4 hours in the presence of a stream of nitrogen, the reaction mixture was cooled, filtered, and the filtrate fractionated using a 1-foot glass helices packed column. After p-cymene and low boiler had been removed, several fractions (25.1 g total) were collected boiling between 164-170°C at 0.05 - 0.10 mm Hg. A gas phase chromatogram of the last cut (4.1 gram), bp 167-170°C/0.10 mm Hg, showed a 96 area-% peak identified as 3-ethyl-m-terphenyl by collection and analysis by infrared. The remaining fraction contained varying amounts (up to 86%) of 3-ethyl-m-terphenyl. Analysis of 96% fraction: Calc'd. for $C_{20}H_{18}$: C, 94.1; H, 5.9. Found: C, 93.8; H, 6.1.

7. 1,3-Diphenylcyclohexadiene-1,3

A 2-liter, 4-necked flask was equipped with a dropping funnel, nitrogen inlet, stirrer, reflux condenser, and thermometer. To the flask was added 193 ml of a 3M solution of phenylmagnesium bromide (0.58 mole) in ethyl ether. The Grignard reagent was stirred and cooled with an ice bath and a solution of 3-phenylcyclohex-2-enone (75 g, 0.44 mole) in 300 ml of anhydrous ethyl ether was added dropwise to the reaction mixture, held at 5-10°C, over a 1.5 hour period. After addition was complete, the reaction mixture was refluxed with stirring for one hour, cooled, and poured with stirring into 500ml of saturated ammonium chloride solution containing ice.

The layers were separated and the ethereal solution was washed with 5% sodium bicarbonate solution and water, and was dried over anhydrous magnesium sulfate. This solution was then concentrated on a rotary evaporator, and a small sample of the resultant semisolid recrystallized from absolute ethanol. The slightly yellow plates were dried in a vacuum oven at 40°C and dissolved in carbon tetrachloride. An infrared spectrum of this solution showed the absence of a band in the region 3200-3600 cm^{-1} indicating the absence of a hydroxyl group. The remaining crude diene was recrystallized once from absolute ethanol yielding 60 g of pale yellow plates, mp 97-99°C (lit. mp = 98-99°C, ref. 38). Twenty grams of this material was dissolved in hot absolute ethanol, decolorized with charcoal to yield white platelets, mp 97-99°C Analysis: Calc'd. for $C_{18}H_{16}$: C, 93.1; H, 6.9. Found: C, 92.9; H, 7.0.

8. 1,3-Diphenylcyclohexane

To a 300 ml stainless steel rocking autoclave containing a solution of 1.75 g (0.0077 mole) of 1,3-diphenylcyclohexadiene-1,3 in 100 ml ethanol and 50 ml cyclohexane was added 0.4 g 5% palladium on charcoal catalyst. After the bomb was sealed, the reduction was carried out at room temperature and 150 psig initial hydrogen pressure. When hydrogen uptake had ceased, the bomb was depressurized, opened, and the solution filtered to remove catalyst. Concentration of the solution on the rotary evaporator yielded 1.63 g product which was shown to contain 72% 1,3-diphenylcyclohexane, 21% unidentified component and 7% m-terphenyl by VPC in conjunction with infrared and ultraviolet spectrophotometry.

9. 1-(4-Xenyl)-3-phenylcyclohexadiene-1,3

A 2-liter, 4-necked flask was equipped with a dropping funnel, nitrogen inlet, stirrer, reflux condenser, and thermometer. To the flask was added 11.0 g (0.457 g-atom) of magnesium turnings and 200ml of tetrahydrofuran (previously distilled from calcium hydride). The dropping funnel was charged with 99.1 g (0.423 mole) of 4-bromobiphenyl dissolved in 250 ml of tetrahydrofuran. About one-eighth of this charge was added to the reaction flask, and the reaction mixture was stirred and heated to reflux under a nitrogen atmosphere. After reaction had started, the remaining charge was added dropwise over a period of one hour at reflux temperature. The mixture was then refluxed with stirring for an additional one-half hour. At the end of this time, the Grignard reagent was cooled with an ice bath and a solution (55.7 g, 0.324 mole) of 3-phenylcyclohex-2-enone in 150 ml of tetrahydrofuran was added dropwise over a one-half hour period while stirring and maintaining the reaction temperature at 10-15°C After addition was complete, the reaction mixture was refluxed with stirring for one-half hour, cooled, and allowed to stand overnight. The reaction mixture was then poured with stirring into 600ml of saturated ammonium chloride solution containing ice. The layers were separated, and the ethereal layer was washed with water and dried over anhydrous magnesium sulfate. The dry yellow solution was concentrated on a rotary evaporator and the concentrate, a yellow viscous oil, was extracted with warm petroleum ether to remove biphenyl. The oil was then crystallized from absolute ethanol followed by a recrystallization from petroleum ether to yield 70 grams of crude diene. Recrystallization of 10 grams of this material from benzene-ethanol gave 5 grams white powder, mp 162-164°C (lit mp = 162-163°C, ref. 28).

10. 1-(4-Xenyl)-3-phenylcyclohexane

A 300-ml stainless steel rocking autoclave was charged with 5.0 g (0.016 mole) 1-(4-xenyl)-3-phenylcyclohexadiene-1,3 and 0.4 g 5% palladium on charcoal catalyst slurried in 150 ml absolute ethanol. The reduction was carried out at room temperature and 150 psig initial hydrogen pressure. When the reduction was complete, the bomb contents were washed out with benzene, filtered, and concentrated on the rotary evaporator to yield 4.8 g of gray-white powder. Vapor phase chromatography of the powder showed two peaks comprising 34.5 and 65.5 area-%, respectively. Recrystallization from benzene-ethanol gave 3 crops of white powder. The second and third crop melted at 158.5-165°C and 158.5-161°C, respectively.